# SPECIFIC AND SELECTIVE SERS ACTIVE SITES GENERATION ON SILVER NANOPARTICLES BY CATIONIC AND ANIONIC ADATOMS

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*Abstract*. The here proposed specific adatom approach for surface-enhanced Raman scattering (SERS) highlights the fact that the Raman enhancement originates from the electronic coupling of the analyte with the metal surface, mediated by specific ions that form SERS active sites on the surface of the nanoparticles. The spectra of anionic and cationic analytes can be recorded specifically by generating specific SERS active sites, obtained by adsorbed ions (adions) such as $Ca^{2+}$ and $Cl^-$, respectively. Thus, the SERS spectrum of anionic and cationic species is turned on by the electronic coupling of the analyte with the metal surface at such SERS active sites. Moreover, the selective SERS turn on of anions, like citrate and $Cl^-$ from their mixture is determined by their competitive adsorption to the metal surface. Furthermore, a proportional dependence of the SERS intensity with the number of SERS active sites was observed. The sequential detection of the three analytes, citrate, chloride and Nile Blue in the same solution can't be explained by a model based on the aggregation of the nanoparticles. In the adatom approach, the aggregation of the nanoparticles is an unnecessary step that rather contributes to the low reproducibility of SERS spectra. We strongly believe that the proposed specific adatom approach will lead to a better understanding and control in SERS spectroscopy, thus improving the predictability of the method.

*Keywords*: adatom, electronic coupling, Raman, silver nanoparticles, SERS active sites, SERS turn on.

## 1. INTRODUCTION

Despite of an increasing number of SERS studies in a wide range of research areas, some aspects of the SERS phenomenon [1, 2] remain misunderstood. Many publications explain the SERS effect by the formation of electromagnetic hot-spots – sites with highly increased field strengths, generated by aggregated nanoparticles [3]. In line with this model, the analytes are trapped in the gaps between adjacent nanoparticles and in consequence their Raman signal is enhanced by the strong electromagnetic field. However, Otto stated some inconsistencies of this model [4]. For example, why is it so difficult to obtain SERS signal from anions such as

citrate? Or why the Raman signal from water is not enhanced? Are these molecules not trapped into the hot-spots, too?

In the electronic enhancement mechanism, proposed by Otto and coworkers [4-7], atomic scale roughnesses (e.g. adsorbed atoms - adatoms) play an important role by providing pathways for metal–molecule electronic transitions. Therefore, considering the electronic mechanism, the strong Raman enhancement of an adsorbate on a silver surface is possible only when the adsorbate is bound to an adatom which facilitates electronic transfer between the metallic nanoparticle and the molecule.

In a recent experimental study [8], we highlighted the role of chloride ions in SERS and demonstrated generally that the Raman enhancement originates from the electronic coupling of the analyte with the metal surface, mediated by specific adions such as $Cl^-$, $I^-$, $Ag^+$, $Ca^{2+}$ or $Mg^{2+}$ which form SERS active sites on the metal nanoparticle surface.

In this study we show that, besides the specificity of SERS for anionic and cationic species, determined by the type of adion that activates the nanoparticle surface, SERS spectra can also be obtained in a selective manner. The competitive chemisorption of citrate and $Cl^-$ anionic species at SERS active sites enables the selective SERS detection of chloride in the presence of citrate. The selective SERS experiments demonstrate that the aggregation of the nanoparticles is not necessary for the turn on of the SERS effect, instead, the intensity of the SERS spectra varies proportionally with the number of SERS active sites.


## 2. EXPERIMENTAL SECTION


For the silver colloid obtained by citrate reduction (cit-AgNPs), 0.017 g $AgNO_3$ (Sigma Aldrich) were dissolved in 98 ml ultrapure water (resistivity higher than 18 MΩ) under magnetic stirring and the solution was brought to boil. Afterwards, 2 ml of sodium citrate (Sigma Aldrich) solution 1% was added and the solution was left to boil for another 30 minutes.

For the acquisition of the SERS spectra, a Renishaw InVia Raman spectrometer, equipped with a NdYAG frequency-doubled laser emitting at 532 nm and a laser power of ~80 mW on the sample was used.

For each measurement, 10 μl of the sample was placed on a microscope slide that was covered with aluminum foil. The laser light was focused on the drop using a 5x objective (NA=0.12). The spectra were recorded by averaging 4 acquisitions of 4 seconds each.

## 3. RESULTS AND DISCUSSION

The cit-AgNPs, introduced by Lee and Meisel in 1982 [9], are the most common SERS substrate. The colloidal nanoparticles are capped with citrate molecules, which stabilize the colloid and provide a negative charge to the nanoparticles.

According to the hot-spot approach, the SERS spectra of analytes can be obtained after the aggregation of the nanoparticles (usually done by adding salts such as NaCl) and the subsequent hot-spots formation. However, as stated in the introduction, this model can't provide an answer for why the capping agent of cit-AgNPs, i.e. citrate molecule, is not trapped inside the hot-spots and why the SERS signal of citrate is not observed, even at mM concentration.

Our studies suggest instead that the Raman enhancement is turned on only after the electronic coupling of the analyte with the metal surface, mediated by specific adions that form SERS active sites on the nanoparticle surface.[8] According to the proposed specific adatom approach [8], ions like $Ca^{2+}$, $Mg^{2+}$ or $Ag^+$ form SERS active sites that mediate the chemisorption of anionic species, while ions like $Cl^-$ or $I^-$ form SERS active sites that facilitate the chemisorption of cationic species.

For simplicity, we show firstly the selectivity of SERS detection, the specificity of SERS being highlighted subsequently.

## 3.1. SELECTIVE SERS ACTIVE SITES FOR ANIONIC ANALYTES

Fig.1 shows the SERS turn on effect determined by $Ca^{2+}$ adions, which form SERS active sites on the silver surface, and the competitive chemisorption of citrate and $Cl^-$ anionic species at these SERS active sites. Each of the two spectra series were recorded sequentially, by modifying the same colloidal solution.
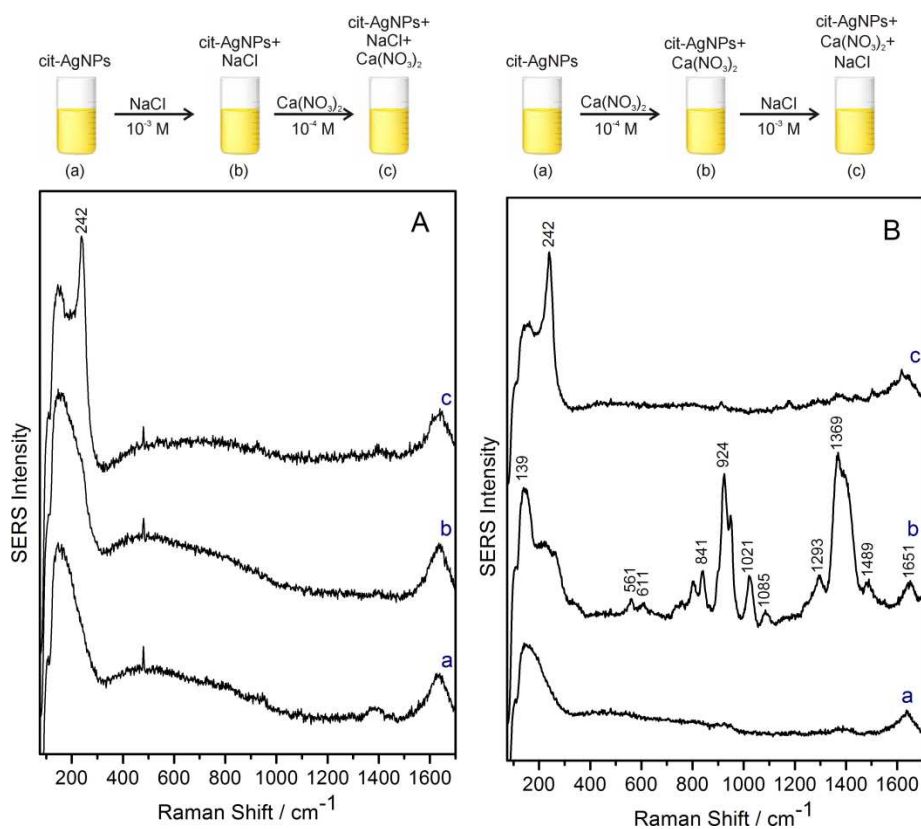
Fig. 1 – A. SERS active sites generation by $Ca^{2+}$ adions and chemisorption of $Cl^-$ anions: (a) Raman blank spectrum of cit-AgNPs, (b) Raman blank spectrum of the cit-AgNPs/NaCl mixture, (c) intense Ag-$Cl^-$ SERS band, obtained after the activation of the nanoparticles with $Ca^{2+}$. The spectra were recorded by modifying the same colloidal solution, as shown by the top picture; B. SERS active sites generation by $Ca^{2+}$ adions and competitive chemisorption of citrate and $Cl^-$ anions: (a) Raman blank spectrum of cit-AgNPs, (b) SERS spectrum of citrate obtained after activation of cit-AgNPs with $Ca^{2+}$, (c) intense Ag-$Cl^-$ SERS band, obtained after the replacement of citrate molecules by $Cl^-$ ions at the $Ca^{2+}$ SERS active sites. The spectra were recorded by modifying the same colloidal solution, as shown by the top picture.

The Raman spectrum of as synthesized cit-AgNPs (Fig.1A) shows a blank spectrum, since the concentration of the reagents (in the mM range) is too low for normal Raman spectroscopy. After adding NaCl $10^{-3}$ M to the cit-AgNPs, the Raman spectrum of cit-AgNPs/NaCl mixture shows only a slight change, characterized by a weak shoulder at 242 cm$^{-1}$, assigned to metallic Ag-Cl vibration (Fig.1A, spectrum b). This indicates that a few chloride ions are chemisorbed to the metallic surface. However, after the addition of $Ca(NO_3)_2$ $10^{-4}$ M to the cit-AgNPs/NaCl mixture, an intense peak appears at 242 cm$^{-1}$, indicating that a high

number of Cl$^-$ ions have been chemisorbed to the metallic silver surface. Thus, we conclude that Ca$^{2+}$ adions turn on the SERS effect, by mediating the chemisorption of Cl$^-$ to the metallic silver surface and facilitating the electronic transfer between the Cl$^-$ ions and the silver metal surface.

Fig.1B highlights the selectivity of SERS due to the competitive chemisorption of citrate and Cl$^-$ anionic species at SERS active sites, generated by Ca$^{2+}$ adions. By adding Ca$^{2+}$ $10^{-4}$ M to the cit-AgNPs, the SERS spectrum of the citrate capping agent is turned on (Fig.1B, spectrum b). However, after the addition of NaCl $10^{-3}$ M to the same colloidal solution, the SERS spectrum of citrate is completely replaced by the SERS band at 240 cm$^{-1}$, attributed to metallic Ag-Cl$^-$ (Fig.1B, spectrum c). The selective adsorption of citrate and chloride can be explained by their different affinities for the nanoparticle silver surface. Particularly, Cl$^-$ has a stronger affinity for the surface of the nanoparticles, as reported in other studies as well [10], and therefore it can replace citrate molecules from Ca$^{2+}$ specific sites on the activated cit-AgNPs.

The appearance of the citrate and chloride SERS spectrum due to the aggregation of the nanoparticles was excluded because the concentration of the added salt was too low to induce the aggregation of the nanoparticles, the cit-AgNPs colloidal solution containing Ca(NO$_3$)$_2$ and NaCl $10^{-4}$ M and $10^{-3}$ M, respectively, were found to be stable for weeks.

Fig.2 shows schematically a model for the competitive adsorption of citrate and Cl$^-$ anionic species at SERS active sites generated by Ca$^{2+}$.
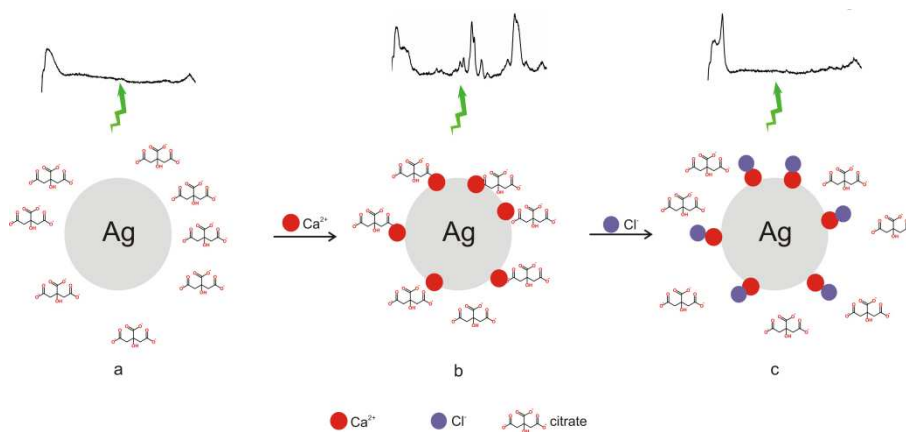


Fig. 2 – Schematic representation for specific SERS active sites generation and selective chemisorption of citrate and chloride: (a) cit-AgNPs, (b) specific SERS active sites generation by Ca$^{2+}$ and electronic coupling of the citrate molecules with the silver surface, (c) displacement of the citrate molecules and chemisorption of Cl$^-$ at the specific SERS active sites, due to the higher affinity of Cl$^-$ for the silver surface.

Fig.2a presents schematically the cit-AgNPs without an electronic interaction between the capping agent and the silver surface. Thus, no SERS signal can be observed as shown in Fig.1, spectra a.

After the chemisorbtion of the $Ca^{2+}$ ions (Fig.2b), the citrate anionic molecules chemisorb to the silver surface at the $Ca^{2+}$ SERS active sites, which facilitate the electronic transfer between the metallic silver surface and the citrate molecules (Fig.1B, spectrum b). After the addition of NaCl $10^{-3}$ M, the $Cl^-$ ions replace citrate molecules at $Ca^{2+}$ specific sites (Fig.2c) and thus only the SERS band due to Ag-$Cl^-$ vibration (Fig.1B, spectrum c) is observed.

### 3.2. SPECIFIC SERS ACTIVE SITES FOR ANIONIC AND CATIONIC ANALYTES

Controlling the formation of SERS active sites at the surface of the nanoparticles opens up the possibility to control the adsorption of analytes to nanoparticles and hence to increase the predictability of the SERS phenomenon.

As we show in this section, in a solution containing both anionic and cationic molecules, we can choose which molecule species chemisorbs to the nanoparticles, by using specific types of adions.

Fig.3 presents the specific SERS detection of citrate molecules and Nile Blue (NB) cationic dye, recorded from the same solution, using the cit-AgNPs as SERS substrate.
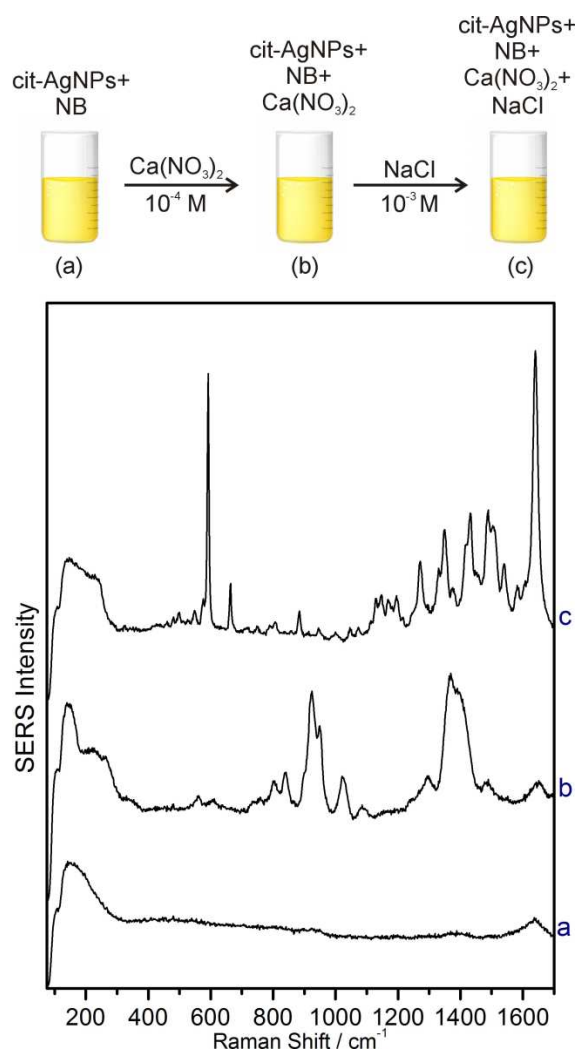
Fig. 3 – Specific SERS turn on of citrate and NB after activation of cit-AgNPs with $Ca^{2+}$ and $Cl^-$, respectively: (a) Raman blank spectrum of the cit-AgNPs/NB $10^{-8}$ M mixture, (b) SERS spectrum of citrate obtained by the addition of $Ca^{2+}$ to the cit-AgNPs/NB mixture, (c) SERS spectrum of NB obtained after addition of $Cl^-$ to the cit-AgNPs/NB/$Ca(NO_3)_2$ mixture. The spectra were recorded by modifying the same colloidal solution, as shown by the top picture.

By adding NB $10^{-8}$ M to the as synthesized cit-AgNPs colloidal solution, no SERS signal can be observed, since the Lee-Meisel colloid does not contain any chloride ions that could form SERS active sites for the cationic dye (Fig.3, spectrum a).

After adding $Ca(NO_3)_2$ $10^{-4}$ M to the cit-AgNPs/NB mixture, the SERS

spectrum of NB is still absent, but the SERS spectrum of citrate is turned on because of the $Ca^{2+}$ adions that form SERS active sites at the surface of the cit-AgNPs and thus allow the chemisorption of the anionic species to the surface of the nanoparticles, similarly to the processes shown in Fig.1B.

Next, NaCl $10^{-3}$ M was added to the cit-AgNPs/NB/Ca(NO$_3$)$_2$ mixture, which leads to the appearance of an intense SERS spectrum, characteristic to NB (Fig.3, spectrum c). Because of the competitive chemisorption at the SERS active sites, the citrate anions have been replaced by chloride anions, which now form specific SERS active sites for cationic molecules such as NB. Thus, Cl$^-$ adions specifically mediate the chemisorption of NB molecules from the cit-AgNPs/NB/Ca(NO$_3$)$_2$ mixture.

The specific chemisorption of citrate and NB molecules to the surface of the silver nanoparticles, determined by $Ca^{2+}$ and Cl$^-$ adions, respectivelly, is schematically shown in Fig.4.
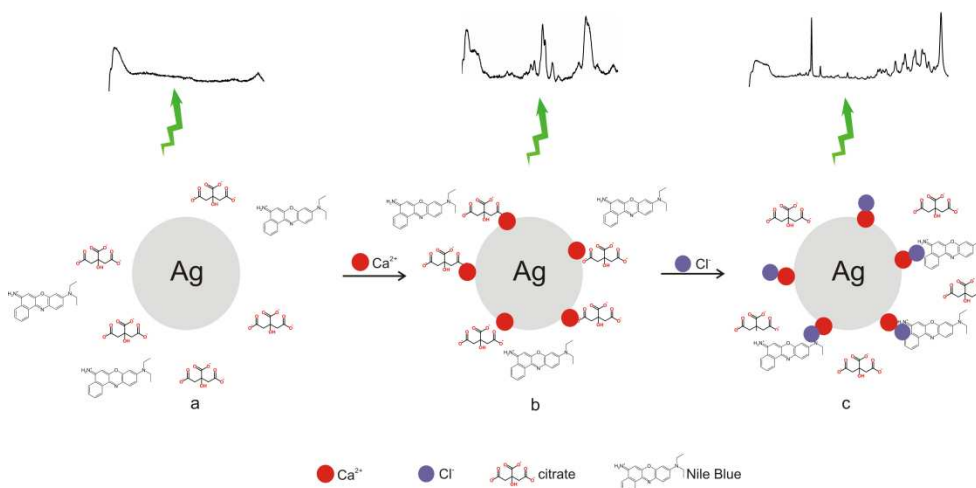


Fig. 4 – Schematic representation of the specific chemisorption of NB and citrate: (a) cit-AgNPs/NB, (b) Chemisorption of citrate after the formation of $Ca^{2+}$ SERS specific sites, (c) Formation of Cl$^-$ specific SERS sites and the chemisorption of NB.

Fig.4 is in fact a continuation of Fig.2. After the chemisorption of Cl$^-$ on $Ca^{2+}$ specific sites, the chemisorption of cationic analytes such as NB is facilitated by the Cl$^-$ adions.

As we previously mentioned, Cl$^-$ has a stronger affinity for the silver surface than citrate, therefore it will replace the citrate molecules at the SERS specific sites (Fig.4c). The chemisorbed Cl$^-$ ions form themselves specific SERS active sites for cationic molecules. Thus, the SERS specific sites generated by Cl$^-$, facilitate the metal-NB molecule electronic transition and lead to the intense SERS spectrum

shown in Fig.3c.

Our experiments highlight that the Raman surface-enhancement is conditioned by the presence of SERS active sites on the surface of the nanoparticles, and that aggregation is just a side effect of the negatively charged species present in the colloidal solution, that are not adsorbed to the nanoparticles. The enhancement of the Raman signal due to the aggregation of cit-AgNPs and formation of hot-spots completely disregards the adions specificity and can't account for the SERS selectivity showed in our experiments.

### 3.3. SERS INTENSITY DEPENDENCE BY THE NUMBER OF SERS ACTIVE SITES

In Fig.5 we show that the intensity of the SERS spectra of NB is proportional to the number of SERS active sites generated by $Cl^-$ adions on the surface of metallic silver surface.
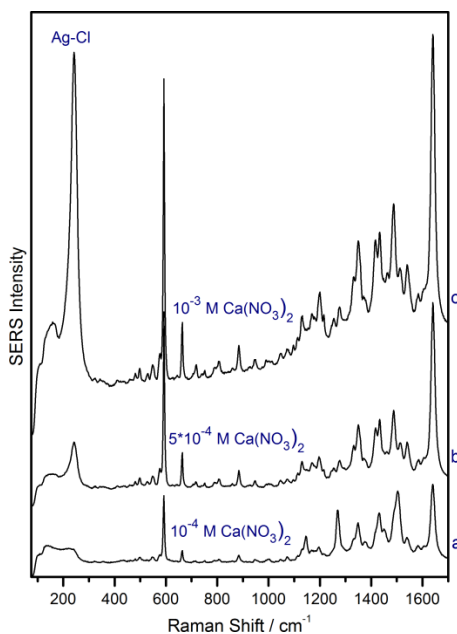


Fig. 5 – The dependence of NB $10^{-8}$ M SERS intensity on the number of SERS active sites generated by: (a) $Cl^-$ $10^{-3}$ M and $Ca^{2+}$ $10^{-4}$ M (b) $Cl^-$ $10^{-3}$ M and $Ca^{2+}$ $5 \times 10^{-4}$ M, (c) $Cl^-$ $10^{-3}$ M and $Ca^{2+}$ $10^{-3}$ M.

By increasing the concentration of $Ca(NO_3)_2$ in the cit-AgNPs/NaCl/$Ca(NO_3)_2$/NB mixture from $10^{-4}$ to $10^{-3}$ M, the number of SERS active sites increases, because $Ca^{2+}$ ions determine the chemisorption of $Cl^-$ ions.

Thus, increasingly more NB molecules are chemisorbed at Cl⁻ specific sites, resulting in a higher intensity of the SERS spectra of NB, as can be observed in Fig.5. Likewise, an intensity increase of the Ag-Cl SERS band is observed, which highlights an increase in the number of SERS active sites on the nanoparticles surface.

At concentrations of $10^{-3}$ M $Ca(NO_3)_2$, the aggregation of the colloidal solution is observed after ~10 minutes. However, the aggregation of the nanoparticles is not the cause for the SERS spectra observed, since the SERS spectra of NB can be observed at lower concentrations, as well, when the colloidal solution is not aggregated. The aggregation of the colloidal solution takes place probably due to the $NO_3^-$ groups that have been added at the same time with $Ca^{2+}$ and which screen the surface charge of the nanoparticles, determining their aggregation.

## 4. CONCLUSIONS

Our results indicate that the SERS effect is turned on by the presence of SERS active sites on the silver nanoparticle surface, which mediate the electronic coupling of the analyte with the silver surface. Moreover, the SERS effect is, in essence, a specific and selective phenomenon, as shown by us in this study. Cationic adions form specific SERS active sites for anionic species, whereas anionic adions such as Cl⁻ form specific SERS active sites for cationic molecules. Furthermore, we show that the intensity of the SERS spectra varies proportionally with the number of SERS active sites.

The selective SERS turn on of anions, like citrate and Cl⁻ from their mixture is done in a competitive manner, as determined by the affinity of these species to the metal surface and not due to the aggregation of silver nanoparticles. The recording of three different SERS spectra such as of citrate, Ag-Cl and Nile Blue, from the same solution, can't be explained by the aggregation of the nanoparticles, because the placement of the molecules in hot-spots is not a selective process. In the adatom approach, the aggregation of the nanoparticles is an unnecessary step that rather contributes to the low reproducibility of SERS spectra.

In summary, to fully exploit the Raman enhancing property of colloidal silver nanoparticles, for cationic molecules, the silver colloid should contain Cl⁻ anions in a concentration range between $10^{-3}$-$10^{-2}$ M and cations such as $Ca^{2+}$ or $Mg^{2+}$ in concentrations between $10^{-4}$ -$10^{-3}$ M. For the SERS detection of anionic analytes, the colloidal solution should contain cations such as $Ca^{2+}$ or $Mg^{2+}$, and should not contain any anionic species with a stronger affinity to the metal surface than the analyte of interest.

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