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Does the excitation of a plasmon resonance induce a strong chemical enhancement in SERS? On the relation between chemical interface damping and chemical enhancement in SERS

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Abstract In this contribution, a fundamental new approach is made to explain high enhancement factors in surface-enhanced Raman spectroscopy (SERS) on the basis of chemical enhancement. Usually, high SERS enhancement factors are explained by electromagnetic enhancements due to the excitation of localized surface plasmon resonances and strong near field dipole–dipole coupling. However, very often the corresponding SERS spectra show clear signatures of a chemical enhancement. I propose that this contradiction is easily solved by taking chemical interface damping of the plasmon resonance into account. Chemical interface damping is caused by an electron transfer from the metallic structure into an adsorbate. However, this mechanism is also the basis for chemical enhancement in SERS, i.e., an electron transfers in the lowest unoccupied molecular orbital of the molecule and back to the metal. Hence, if a molecule causes a strong chemical interface damping, the excitation of plasmons is still the key factor for the SERS enhancement. But the reason for this enhancement might be not solely due to electromagnetic fields rather than by a chemical enhancement due to electron transfers from the metal to the molecules.

1 Introduction

Raman spectroscopy is a powerful technique for molecule specific detection. Its drawback, the low Raman cross sections, has been overcome by the discovery of surface-enhanced Raman spectroscopy (SERS) that allows under certain circumstances the detection of single molecules [1–3]. Nowadays, SERS is a standard analytic tool in laboratories and on its way to real-life applications [4–6]. SERS has two contributions, a chemical and a electromagnetic contribution. The surface-enhanced Raman-Stokes signal $P^{\mathrm{SERS}}(\nu_{\mathrm{s}})$ can be expressed by [7]:

$$P^{\mathrm{SERS}}(\nu_{\mathrm{s}}) = N\sigma^{R}_{\mathrm{ads}}|A(\nu_{\mathrm{L}})|^{2}|A(\nu_{\mathrm{S}})|^{2}I(\nu_{\mathrm{L}}). \tag{1}$$

N is the number of molecules involved in the process, $\sigma^{R}_{\mathrm{ads}}$ describes an increased Raman cross section of the adsorbed molecules, $A(\nu_{\mathrm{L}})$ and $A(\nu_{\mathrm{S}})$ are the enhancement factors for the laser and for the Raman scattered field, respectively, and $I(\nu_L)$ is the laser intensity. While the electromagnetic contribution is explicitly given in Eq. (1), the chemical contribution is implicitly given by a different Raman cross section.

To express the electromagnetic enhancement, lets consider a molecule in a distance d from a small spherical noble metal nanoparticle that falls into the quasistatic regime. In this case, the electromagnetic enhancement for the laser field is expressed by [8]:

$$A(\nu_{\mathrm{L}}) = \frac{\varepsilon(\nu_{\mathrm{L}}) - \varepsilon_{\mathrm{m}}}{\varepsilon(\nu_{\mathrm{L}}) + 2\varepsilon_{\mathrm{m}}}\frac{r^{3}\sqrt{[1 + 3\cos^{2}\theta]}}{(r + d)^{3}}, \tag{2}$$

or if the angular dependence is neglected [7, 8]:

$$A(\nu_{\mathrm{L}}) = \frac{\varepsilon(\nu_{\mathrm{L}}) - \varepsilon_{\mathrm{m}}}{\varepsilon(\nu_{\mathrm{L}}) + 2\varepsilon_{\mathrm{m}}}\frac{r^{3}}{(r + d)^{3}}. \tag{3}$$

Neglecting the angular dependence in Eq. (3) is justified since the physical relevant square of the modulus of the electric field falls off rapidly ($|E|^{2} \propto 1/(r + d)^{6}$).

Assuming that the scattered Stokes field is in resonance with the localized surface plasmon resonance (LSPR) of

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the noble metal sphere, the contribution to the SERS effect is the same as for $A(\nu)$ and the Stokes signal power G_{em} can be written as [7]:

$$G_{\mathrm{em}}(\nu) = |A(\nu_{\mathrm{L}})|^2 |A(\nu_{\mathrm{S}})|^2 \sim \left| \frac{\varepsilon(\nu_{\mathrm{L}}) - \varepsilon_{\mathrm{m}}}{\varepsilon(\nu_{\mathrm{L}}) + 2\varepsilon_{\mathrm{m}}} \right|^2 \left| \frac{\varepsilon(\nu_{\mathrm{S}}) - \varepsilon_{\mathrm{m}}}{\varepsilon(\nu_{\mathrm{S}}) + 2\varepsilon_{\mathrm{m}}} \right|^2 \left(\frac{r}{r+d} \right)^{12}. \tag{4}$$

$G_{\mathrm{em}}(\nu)$ is particularly strong when the real parts of $\varepsilon(\nu_{\mathrm{L}})$ and $\varepsilon(\nu_{\mathrm{S}})$ are equal to $-2\varepsilon_{\mathrm{m}}$. As already mentioned, the chemical effect is implicitly expressed by using the Raman cross section for an adsorbed molecule $\sigma^{R}ads$ instead of the conventional Raman cross section σ^{R}. This might reflect why for a long time more attention has been paid to the electromagnetic enhancement rather than to chemical enhancement. However, there is still an ongoing discussion about the origins of SERS.

SERS has been discovered in 1974 by Fleischmann et al. [9] and the first sound explanation has been made by van Duyne et al. in 1977 [10]. They have explained the SERS enhancement by high local fields in the vicinity of noble metal nanostructures due to the excitation of LSPRs. Later, in the groups of Stockman and Schatz [11–14] calculations have been made that revealed under certain circumstances local electromagnetic fields that could explain the high enhancement factors necessary for single-molecule SERS. For example, Li et al. [11] calculated for a self-similar chain of spherical silver nanoparticles a field enhancement of approximately 3×10^3. This field enhancement would result in a Raman enhancement of 10^{12} to 10^{13}. Similar high enhancements factors have been calculated, for example, by the group of Schatz and others [13, 15–17]. In contrast, the chemical enhancement in SERS has been usually assumed to be in the order of 10–100 [7, 18, 19]. Note, these factors have been concluded from the fact that the measured SERS enhancements factors are approximately two orders of magnitude larger than the maximal calculated electromagnetic SERS enhancements.

Although electromagnetic enhancement was widely accepted as the main contribution to SERS [7, 13], part of the Raman community still propose chemical enhancement as a strong contribution. The chemical enhancement, sometimes called first layer effect, is assumed to be an averaged contribution of adsorbates at SERS active sites on the surface of rough metal supports [20, 21]. In particular Andreas Otto, one of the SERS pioneers, always highlighted that chemical effects must be a significant contribution to the SERS enhancement. The reasons for this statement are as follows:

- The calculated high SERS enhancements have been obtained for conditions that are experimentally hardly to realize.
- The certainly underestimated difference of two orders of magnitude between the experimentally observed SERS enhancements and corresponding calculations.
- Highest fields are calculated for areas between nanoparticles to small for large molecules to fit in.
- Sometimes non-totally symmetric modes dominate the strongly enhanced SERS spectra, which is a clear indication for a strong chemical enhancement.
- Some molecules show higher enhancement factors than others, although both are on the same substrate, e.g., pyridine (high SERS enhancement) - benzene (low SERS enhancement). In fact, a survey of the molecules with larger enhancement shows that most of them possess either an N- atom, an O- atom, or an S- atom. Hence, the chemical structure plays a role.
- For large molecules, for example adenosine monophosphate, the electromagnetic enhancement should yield also Raman lines from parts of the molecule not directly in contact with the plasmonic nanostructure. However, for the nucleotide adenosine monophosphate, no signal from the phosphate moiety is observed [22, 23].

The explanation of high SERS enhancements mainly by electromagnetic effects becomes even more doubtful since the group of Nordlander has shown that classically calculated local fields at the nanoparticle surface are clearly overestimated [24, 25]. The reason is that classical calculations assume a step function for the electron density, while in reality a spill out of the electrons occurs. Nordlanders group could show with quantum mechanical calculations, for example, that in interacting nanoparticle systems the local field might be reduced by one order of magnitude [26]. Hence, a sound explanation of the origin of the measured SERS enhancement factors that show clear signatures of a chemical enhancement is still lacking. In this contribution, I propose a scheme of chemical enhancement based on the chemical interface damping of LSPRs. This scheme explains high SERS enhancements that show clear signatures of a chemical contribution.

2 Damping of the LSPR

The optical properties of noble metal nanoparticles are dominated by LSPRs, i.e., by coherent oscillations of the conduction band electrons against the ion cores. Recently, the mechanisms which contribute to the damping of the LSPRs have gained interest. The decay of an LSPR, which takes place on the femtosecond time scale, can be caused by different processes widely discussed in the literature [8, 27–33]. These damping mechanisms are radiating damping [34, 35], surface scattering [36–38],

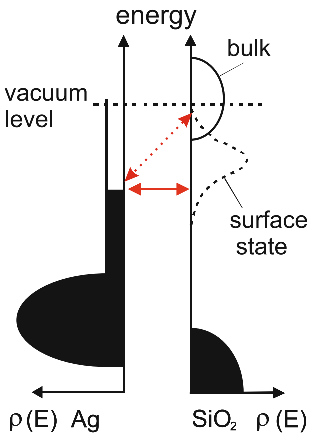

Fig. 1 Schematic of chemical interface damping. Scheme adapted from Persson [36]

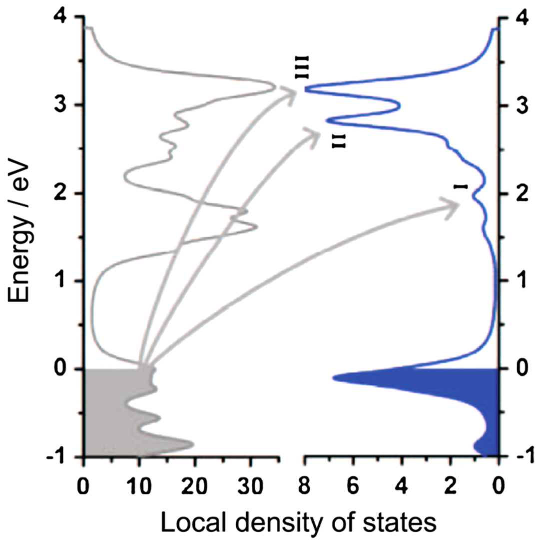

Fig. 2 DFT calculations of the local density of states of a small silver nanoparticle with a chemisorbed PVP monomer. The zero energy corresponds to the Fermi level of the metal. The *gray arrows* pointing from the cluster to the molecules states indicate possible tunneling of electrons that are near the Fermi level to empty adsorbate-induced states with an energy difference close or below the LSPR energy. Reprinted with permission from Almeida et al. [42]

band structure changes [27, 39–41], chemical interface damping (CID) [29, 30, 32, 33, 36, 42–44], and direct emission of electrons [27, 45]. For the proposed scheme, only CID is relevant and should be discussed in more detail. CID is caused by dynamic charge transfer of electrons into and out of adsorbate or surface states. Due to the statistical nature of this process, the electrons lose their phase coherence, which results in a damping of the LSPR. A microscopic understanding of damping mechanism has been given by Persson [36].

The initial CID scheme (see Fig. 1) is based on electron tunneling from the metal, here silver, into surface states of an bulk adsorbate, here SiO_2. Persson proposed that an adsorbate may develop a surface state if in contact with a metal. The surface state might be energetically located in the vicinity of the Fermi level of the metal. Thus, electrons can easily tunnel into and out of adsorbate states, which causes a strong damping of the SPR. This scheme has been adopted by several researchers [30, 46, 47]. However, also a tunneling into bulk states is possible, as already mentioned by Persson [36] and as indicated by the dotted arrow in Fig. 1. For a tunneling in an energetically higher lying bulk state a correlated effect is taken into account, in which the energy of the LSPR is transferred to a single electron [41]. This electron tunnels in the bulk state of the adsorbate and causes the damping of the LSPR [8, 37, 42]. The latter scheme has been adopted, e.g., by Almeida et al. who did ab initio calculations for the interaction of a chemisorbate and a metallic nanostructure. Figure 2 shows the calculated local density of states of the system poly(vinylpyrrolidone) (PVP) chemisorbed on a silver nanostructure. It demonstrates that an electron transfer in higher lying LUMO (lowest unoccupied molecular orbital) states is possible, if an electron takes up the energy of the LSPR. Regardless of the exact mechanism of CID, both previously described processes involve an electron transfer from the metal to the adsorbate. Another important point in the work of Almeida et al. [42] is that they assumed monomers in their calculations and show that for single molecules CID may occur.

3 The proposed scheme

At this point, I recall the mechanisms of chemical enhancement. In general, three different charge transfer mechanism exist [7], a resonant electron transfer, an electron transfer from the molecule to the metal, and an electron transfer from the metal to the molecule. For my purpose, only the latter mechanism is relevant and will be discussed in more detail.

The chemical enhancement by an electron transfer from the metal to the molecule has been explained as follows [7, 18, 19, 48–50]. For a typical adsorbate molecule-metal nanoparticle system, the LUMO and HOMO (highest occupied molecular orbital) of the molecule are situated such that the Fermi level of the metal is between both orbitals, as schematically displayed in Fig. 3. If an LSPR is excited, its photon energy can be used to induce an electron transfer from the metal to the LUMO of the molecule. The molecule acts on this transfer by a relaxation in a new configurational equilibrium, which differs from the equilibrium of its ground state. Thus, the back transfer of the electron in the initial state in the metal might leave the

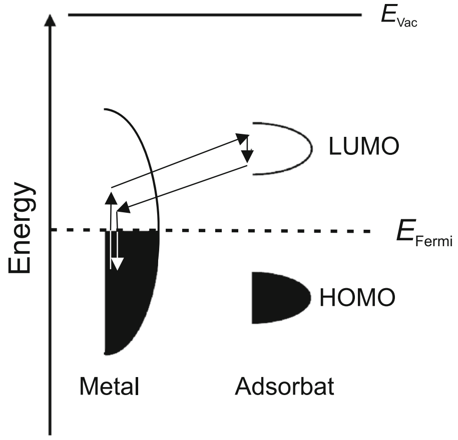

Fig. 3 Schematic of the chemical effect in SERS by an electron transfer from the metal to the molecule. Scheme adapted from Kneipp et al. [7]

molecule in an excited vibrational state. Due to energy conservation, the electron hole pair in the metal is annihilated by emission of a Raman scattered photon.

The mechanism is absolutely the same as for CID, in particular, since Almeide et al. [42] have shown that CID can occur for single molecules. The consequence is that a strong chemical interface damping must significantly increase the chemical enhancement for SERS. Taking into account that for SERS measurements usually continuous Laser light is applied, the LSPR of a nanoparticle is permanently driven. Thus, in 1 s, numerous electrons can transfer (tunnel) in the molecule (adsorbate)[1], which significantly enhance the chemical contribution to SERS. This enhancement might be by far larger than the usually assumed factors of 10–100 [7, 18, 19], which are used to explain the difference between the electromagnetic calculated enhancement and the experimentally observed enhancement. But this points to a critical issue: In all electromagnetic calculations, a possible CID has not been taken into account. On the other hand, it has been demonstrated that CID easily increases the damping factor[2] by a factor of 2 and more [30, 33, 42, 52–56], which dramatically reduces the local field enhancement [8, 34] but, in turn, enhance the chemical effect in SERS. Thus, without an exact knowledge of the CID contribution to the damping factor, exact calculations of the local fields and of the electromagnetic SERS enhancement might fail.

For the future, I suggest that calculations should be performed, which include CID, for example by taking into account a damping parameter two or three times larger compared to nanoparticles in vacuum. Such calculations will show, how much the electromagnetic field is reduced by a possible CID. In addition, experiments should be accomplished that focus not only on the damping via CID or only on SERS. Experiments must be performed, which investigate both effects simultaneously. For example, by combining persistent spectral hole burning [57] with Raman spectroscopy or by performing sophisticated experiments in a photo electron emission microscope. Such a microscope allows, in principle, to measure the difference of the dephasing time of the LSPR and to observe qualitatively a local field reduction upon molecule adsorption. It would be ideal to combine a photo electron emission microscope with a Raman set up to measure the Raman spectra and the dephasing time of the LSPRs simultaneously. To proof the proposed scheme, one has to find molecules that exhibit a high SERS enhancement and cause a strong chemical interface damping of the LSPR. Certainly, a good start would be to use molecules from which are known that they show strong SERS enhancements with clear chemical signatures in their spectra, for example, fluoranthene [6].

On the other hand, for molecules which does not induce a CID, I predict that the SERS enhancement is mainly due to electromagnetic fields. In this case, the SERS spectra should show no significant signatures of a chemical enhancement, although a chemical contribution might still be effective due to a resonant electron transfer or due to an electron transfer from the molecule to the metal. Finally, I emphasize again that the excitation of LSPRs is the key factor for the electromagnetic as well as for the chemical enhancement mechanisms.

4 Summary

A new scheme has been proposed to explain high SERS enhancements via the chemical effect. Along these lines, it has been shown that the mechanisms of chemical interface damping (CID) of localized surface plasmon resonances (LSPR) and the chemical enhancement in SERS via electron transfer in the LUMO of a molecule are essentially the same processes. It has been sound explained how a strong chemical damping would increase the chemical effect in SERS. It has been pointed out that the calculated extraordinary high local fields of nanoparticle aggregates have been performed without taking CID into account. Hence, for all molecules that do not induce CID, the high SERS enhancements are mainly of electromagnetic nature, but for molecules that cause a strong CID, the chemical

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[1] The damping via CID takes place on the sub 10 fs timescale. Hence, in 1 s an LSPR decays 10^{14} times.

[2] The damping factor is an essential parameter that characterizes the size dependence of the dephasing time. Thus, for a precise description of the optical properties of metal nanoparticles the damping factor has to be included in the Drude part of the dielectric function [8, 29, 51].

enhancement might overcome the electromagnetic one. With the presented scheme SERS spectra that show strong enhancement factors but also clear signatures of a chemical enhancement are easily explained. However, both scenarios require a strong excitation of the LSPR of a metallic nanostructure.

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