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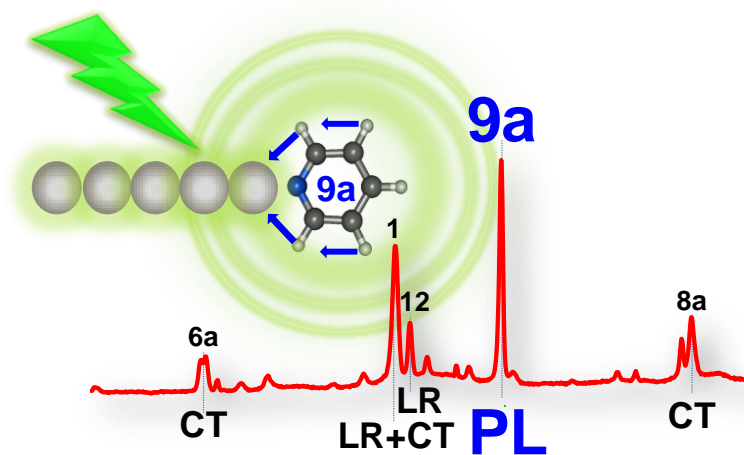


**SERS = LR-SERS + CT-SERS + PL-SERS**

A new kind of SERS selection rules
derived from plasmon-like resonances in
metal-molecule hybrids

# Journal Name

## COMMUNICATION

# The electronic structure of metal-molecule hybrids in charged interfaces: Surface-enhanced Raman selection rules derived from plasmon-like resonances

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**DFT calculations predict plasmon-like excitations in small metal clusters able to selectively modify the relative intensities of specific SERS bands of adsorbed molecules. These electronic resonances provide a new kind of SERS selection rules which allow to explain the huge enhancement of mode 9a of pyridine in the spectra recorded at negative electrode potentials.**

Localized surface plasmons (LSP) are recognized as the main and universal contribution to the enormous enhancement of the Raman signal of molecules adsorbed on, or close to, large curvature sites of coinage metal surfaces.[1] The metal is the main responsible for this physical mechanism and in principle, a uniform enhancement of the Raman spectrum should be expected without modifying the relative intensities of the bands. This could be the case of the SERS of Py recorded on silver at 0 or -0.25 V (514.5 nm excitation) where vibrational modes 1 and 12 dominate the SERS as occurs in the Raman spectrum of its aqueous solution (Fig. 1a).[2] These SERS whose relative intensities are not significantly modified with respect to the Raman spectrum will be named as "long range" (LR-SERS).

But both the Raman and the SERS of a molecule show very often quite different relative intensities. This is the case of the SERS of Py recorded in the range -0.5 to -1.40 V (Fig. 1a).[2] Therefore, the analysis of a particular SERS requires operative selection rules for recognizing the presence of the particular enhancement mechanism from which they have been derived. This is a key issue in SERS given that it determines which kind of information can be obtained from the analysis of the spectrum.

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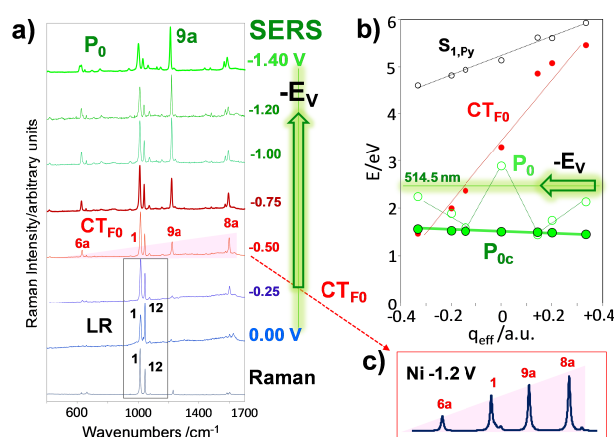
**Figure 1.** a) Raman of an 1 M aqueous solution and SERS spectra of pyridine (0.1 M) adsorbed on silver at different electrode potentials measured vs. Ag/AgCl/KCl(sat.) (514.5 nm exciting line). b) TD-M06-HF/LanL2DZ vertical energies (E) of the plasmon-like states (size-corrected ($P_{0c}$) and uncorrected ($P_0$)), the first forward charge transfer state ($CT_{F0}$) and the first excited singlet of pyridine ($S_{1,Py}$) of linear $[Ag_n\text{-}Py]^q$ complexes versus the effective charge $q_{eff}=q/n$. c) Redrawn of the SERS reported by Tian et al. of pyridine adsorbed on nickel at -1.2 V (632.8 nm exciting line, ref. 9).

The very especial surface sites where the spectra undergo huge SERS enhancement are usually named "hot spots"[3] and correspond to a rather unspecified nanometer-size metal cluster or surface roughness where surface plasmons are localized and the electromagnetic field is very efficiently strengthened. In addition, the unknown excess of charge of the metal atoms on these special locations and the presence of water or the electrolyte gives a view of the intrinsic complexity of SERS. This might explain the persistent controversy about the mechanisms acting in a particular experiment and the difficulty to develop a set of operative selection rules for quantifying, or at least recognizing, the presence of any of them.

The effect of the electrode potential ($E_V$) is to modify the macroscopic excess of charge of the surface i.e., to modify in a continuous way the effective charge of the silver atom to which pyridine is directly bonded. This fractionary atomic charge is

modeled in our calculations through the combined variable $q_{eff}$. Each $q_{eff}$ value defines a new Ag-Py chemical system and changes smoothly its electronic structure as discussed in previous works.[6,7] Fig. 1b shows the energy (E) vs. effective charge ($q_{eff}=n/q$) diagrams of the time-dependent M06-HF/lanL2DZ[5] energies of selected singlet electronic states of silver-pyridine $[Ag_n-Py]^q$ stick-like complexes (Scheme S1) with different sizes (n=2,3,5 and 7) and charges (q=0,±1 a.u.) discussed in the previous communication of this issue.[6] Only the first dipole allowed metal-to-molecule forward charge transfer state ($CT_{F0}$;$^1B_1$), the first excited singlet of pyridine ($S_{1,Py}$;$^1B_1$) and the size-corrected ($P_{0c}$;$^1A_1$) and uncorrected ($P_0$;$^1A_1$) energies of the plasmon-like states of the metal discussed in ref. 6 are drawn. Fig. 1b shows how the averaged atomic charge $q_{eff}$ tunes smoothly the energies of these electronic states and accounts for the effect of the electrode potential on the fulfillment of the electronic resonance condition under 514.4 nm laser excitation. Calculation and methodological details are given in refs. 4-8 and are summarized also in ESI.

Our aim is to correlate the enhancement of specific SERS bands with resonant processes involving the ground and excited states of $[Ag_n-Py]^q$, but theoretical prediction of the relative Raman intensities remains a challenge given that is quite sensitive to the level of theory and the molecular model assumed for the Ag-Py complex. Reliable results can be obtained when the Raman spectrum is dominated by Franck-Condon (FC) factors in resonance (resonance Raman, RR) with a single excited state as is the case for $S_0$-$CT_F$ transitions in silver/benzene-like systems characterized by the enhancement of vibration 8a.[7,8] Resonance SERS intensities in Fig. 2a have been estimated from the forces acting in the molecule at the FC point of the excited state as detailed in ESI. The characteristic triangle-shaped enhancement of the totally symmetric Wilson´s modes 6a, 1, 9a, and especially 8a, recorded in SERS at ca. 605, 990, 1215 and 1580 cm$^{-1}$, respectively, in the range -0.25/-0.75 V (Fig. 1a) and in that reported by Tian et al.[9] on nickel (Fig. 1c), correlates very well with the calculated intensities from FC factors related to changes in the electronic structures of the ground ($S_0$) and the forward charge transfer ($CT_{F0}$) states (Fig. 2a, bottom).[8] All the $S_0$-$CT_{F0}$ transitions of the seven $[Ag_n-Py]^q$ complexes predict results similar to those of the neutral $[Ag_2-Py]^0$ hybrid,[8] what allows for confirming the presence of a resonant photoinduced $CT_F$ process (CT-SERS) in the spectrum at -0.5 V and competing with the strong LR enhancement mechanism which dominates at positive electrode potentials.

But the most striking feature of the SERS in Fig. 1a is the progressive enhancement of the totally symmetric in-plane CH bending mode 9a when the potential is going more negative. Its intensity duplicates that of the strong 1 fundamental at -1.4 V. This behaviour of mode 9a has been already observed but, to our knowledge, no comprehensive explanation has yet been proposed.[4,10] Vibration 9a is the strongest one in the theoretical RR spectrum calculated for the dipole allowed $S_0$-$S_{1,Py}$ transition of the $[Ag_2-Py]^0$ complex (Fig. 2a). We have also checked a more *exotic* electronic resonance with the triplet excited state of Py given that silver atom/cluster could play the role of an external heavy atom, a well known effect which increases the probability of radiative singlet-triplet transitions. Even the ground state of the metal-adsorbate (M-A) system could be a triplet. Although the triplet lies at lower energies than its singlet counterpart, both excitations ($S_0$-$S_{1,Py}$ or $T_{1,PY}$)

should be discarded to explain the enhancement of mode 9a given that their energies are expected to be in the UV (ca. 4-5 eV) and show little dependence on $q_{eff}$ (Fig. S1). Furthermore, we have also checked the effect of the chemical adsorption on the non-resonant Raman intensities in the $S_0$ ground state of the complex.
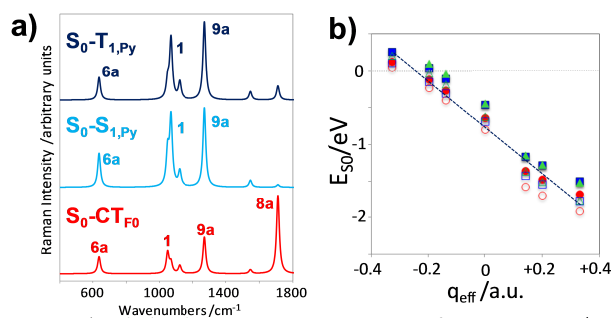


**Figure 2.** a) Calculated resonance Raman spectra from TD-M06-HF/*Lan*L2DZ Franck-Condon forces for $S_0$-$CT_{F0}$, $S_0$-$S_{1,Py}$, and $S_0$-$T_{1,Py}$ transitions of the $[Ag_2-Py]^0$ complex. b) M06-HF (squares), *w*B97X-D (circles) and B3LYP (triangles) metal-molecule bond energy in the ground electronic state ($E_{S0}$) of $[Ag_n-Py]^q$ complexes versus $q_{eff}$ calculated with LanL2DZ (empty) and LanL2DZ(Ag)/6-31g*(Py) (full) basis sets. See ESI for calculation details.

None of the M06-HF, *w*B97X-D or B3LYP[5] calculated Raman spectra of any of the $[Ag_n-Py]^q$ complexes in the ground state is able to account for the selective enhancement of mode 9a.

As we shall show, there exists a clear correlation between the enhancement of mode 9a at negative potentials and the electronic excitations up to the $P_0$ plasmon-like states. RR relative intensities are here calculated from the forces acting in the molecule at the FC point which are ca. 10-20 times smaller in $S_0$-$P_0$ than in $S_0$-CT transitions, what could imply a larger uncertainty in the prediction of the relative SERS intensities.

Figs. 3a and S2 show the RR intensities calculated for the $S_0$-$P_0$ transitions of the seven complexes by using different functionals with the LanL2DZ and the extended LanL2DZ(Ag)/6-31g*(Py)[5] basis sets, respectively. The effective charge modifies more or less slightly the relative intensities of the calculated spectra of pyridine as expected for excited $P_0$ states of the metal cluster. In almost all cases vibrations 6a, 1, 12 and 9a show strong and similar intensities, irrespective of the level of calculation. This behaviour is found for all the $P_0$ series of results except when $q_{eff}$ is close to -0.33 a.u. Then, mode 9a dominates the calculated SERS. This very especial state at $q_{eff}$=-0.33 will be differentiated by naming it hereafter as $P_0^*$ or $P_{0c}^*$. The cause of the different behaviour of $S_0$-$P_0^*$ intensities is that this complex is the limit of the negatively charged Ag-Py systems. We have shown that $q_{eff}$=-0.33 corresponds to the macroscopic surface excess of charge reached at the negative limit of the electrode potentials usually applied in SERS electrochemical experiments.[4] On the other hand, this complex is almost dissociative. Fig. 2b summarizes the calculated bond energies ($E_{S0}$) of the $[Ag_n-Py]^q$ complexes in the $S_0$ ground electronic state with the three functionals and both basis sets. It can be seen that the M06HF/LanL2DZ energies stabilize ca. -45 Kcal/mol (-2 eV) when going from $q_{eff}$=-0.33 to +0.33 a.u. But all the calculations give a slightly positive bond energy for $[Ag_3-Py]^{-1}$, so indicating that this complex is very weakly bonded and almost dissociated, as it happens in the geometry optimization of the more

charged $[Ag-Py]^{-1}$ system ($q_{eff}=-1$) where each moiety is gradually getting apart from each other. B3LYP/LanL2DZ gives the most unstable species with positive bond energy of +4.8 Kcal/mol. When the basis set size for Py is extended up to 6-31G*, the orbitals are more
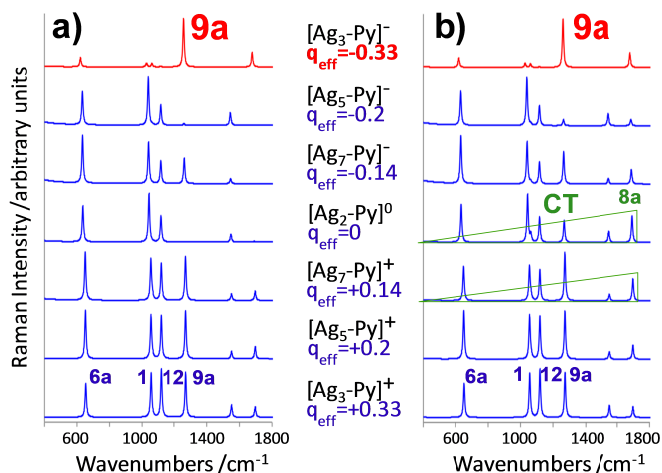


**Figure 3.** a) Effect of the effective charge $q_{eff}$ on the single-state Raman intensities in resonance with the $S_0-P_0$ transition of $[Ag_n-Py]^q$ complexes. b) Effect of the effective charge $q_{eff}$ on the multi-states Raman intensities estimated from the weighted contributions of the first fifty electronic transitions of $[Ag_n-Py]^q$ complexes under 514.5 nm excitation. The intensities have been obtained from TD-wB97X-D/LanL2DZ(Ag)/6-31g*(Py) calculations as explained in ESI.

widespread and B3LYP predicts that $[Ag_3-Py]^{-1}$ also dissociates. The results obtained using the small LanL2DZ basis set are similar although a lesser repulsion can be appreciated (Fig. S2).

All this indicates that when $q_{eff}=-0.33$, the complex is in a very particular state where the high chemical affinity of the nitrogen of Py towards the silver atom is in the limit to compensating the Coulombic repulsion between the negative charge of the silver cluster and the dipole of Py. This is a very favourable case to record hugely enhanced SERS. It is assumed very often that strong SERS signals require a direct, physical or chemical bonding, interaction between metal and adsorbate. However this is not always true. For instance, we have shown that it is possible to detect water insoluble polyaromatic hydrocarbons (PAH's) even down to $10^{-8}$ M when the SERS is recorded in a modified metallic surface by building hydrophobic cages of lucigenine where PAH's can be adequately accommodated.[11] This non-touching M....A scenario favours the drastic reduction of the very effective non-radiative (NR) channels acting when M and A are directly bonded, what is the cause of the damping of the fluorescence in SERS. This is also a key factor related to the effectiveness of the ultrathin silica or alumina shell isolated gold nanoparticles called SHINERS in the efficiency of enhancing SERS.[12]

On this basis, it is possible to explain why the plasmon-like excitations dominates only the SERS at negative electrode potentials but not at neutral or positive surface charges i.e., why vibration 6a, for instance, does not reach so strong intensity at positive potentials as mode 9a does at negative ones. In bonded M-A hybrids at either positive or neutral charges the chemical link between the metal and the pyridine is very efficient and the NR processes are very effective

giving a much weaker contribution to SERS than the LR-SERS mechanism, which is characterized by the strong intensity of modes 1 and 12 in the range 0.0/-0.5 V. We postulate that LR-SERS recorded at positive potentials are originated by Py close to the metal but without direct contact with him. The resonant contributions from bonded Py should be damped given that the metal and the adsorbate are strongly bonded (Fig. 2b).

Another interesting question is to jointly compare the enhancements originated by the different RR processes here discussed, namely the $S_0-CT_0$, $S_0-P_0$, $S_0-S_{1,Py}$ or any other excitation of the M-A hybrid at a particular excitation energy $h\nu$. Figs. 3b and S3 show a series of spectra modeling, for the first time, the effect of the electrode potential in the calculated SERS relative intensities at fixed laser excitation (514.5 nm green line Fig. 1b). While Figs. 3a and S2 show the SERS calculated in resonance with a single excited state (single-state), Figs. 3b and S3 summarize the SERS of $[Ag_n-Py]^q$ hybrids obtained by adding the weighted contributions of the respective first fifty electronic excited states (multi-states) under 514.5 nm excitation. The contribution of each transition $S_0-S_i$ to the overall intensity depends on the respective transition moment integral and on the difference between the energies of the particular $S_0-S_{i=1-50}$ electronic transition and the laser excitation as detailed in ESI.[13]

Multi-states intensities predict correctly that vibration 8a (CT-SERS) should become stronger at neutral or slightly negative $q_{eff}$ (Figs. 3b and S3 labeled as CT), in agreement with the SERS recorded at -0.5 and -0.75 V (Fig. 1a). Besides this CT-SERS contribution, it is immediately appreciated that the calculated SERS under either single $S_0-P_0$ or multi-state $S_0-S_i$ approximations are quite similar. Calculated RR intensities under 514.5 nm excitation predict that plasmon-like excitations (PL-SERS) will dominate the overall spectra: $P_0^*$ at very negative $q_{eff}$ and $P_0$ at the remaining negative, neutral or positive $q_{eff}$ values. Given that the experimental SERS intensities do not agree with the theoretical calculations at neutral or positive $q_{eff}$ we again postulate that this is due to the very effective non-radiative processes acting when Py is bonded to silver. In this case, the SERS is dominated by the LR-SERS mechanism whose relative contribution diminishes at negative potentials due to the repulsion between the negative surface charge and the dipole of Py what reduces the amount of molecules in the interface. The LR-SERS spectrum becomes comparatively weaker, while the resonant mechanisms like $S_0-CT_F$ or $S_0-P_0^*$ are relatively intensified. LR-SERS seems to be very dependent on the nature and morphology of the metal and the experimental conditions. This could explain why vibrations 1 and 12 of Py appear very weakly enhanced in the SERS of Py recorded by Tian et al. on nickel (Fig. 1c).[9] On the contrary, our electrode surfaces seem to be very effective on enhancing LR contribution. The cause of the different effectiveness shown by the surfaces in enhancing LR contribution is unknown.

Summarizing, the SERS of pyridine on silver has been discussed on the basis of two different mechanisms whose relative contributions are very dependent on the electrode potential. The non-resonant long-range mechanism (LR-SERS) dominates at positive surface charges where pyridine is strongly bonded to silver. In this case, non-radiative channels are very effective and compete favourably with any resonant Raman scattering. The other

mechanism is a resonant Raman process involving electronic resonances which give rise to strict SERS selection rules. A photoinduced metal-to-molecule charge-transfer process (CT-SERS) is responsible for the selective enhancement of mode 8a at neutral surface charges. At negative electrode potentials, SERS records are dominated by the enhancement of mode 9a due to a resonant Raman process involving plasmon-like excitation inside the silver cluster (PL-SERS). The effectiveness of non-radiative channels is therefore modulated by the electrode potential and determines the overall SERS enhancement. NR processes play a key role in SERS given that they reduce the efficiency of resonant mechanisms but unfortunately, it is not yet possible to quantify it. NR channels are less operative as the surface charge is made more negative because the electronic repulsion between the charged metal and the dipole of the adsorbate decouples both moieties. In that situation, the resonant Raman scattering becomes stronger and the selection rules derived from each $S_0$-$CT_{F0}$ and $S_0$-$P_{0c}^*$ transitions dominate the relative enhancements. As a conclusion, it should be very difficult to quantify SERS enhancement factors from a single spectrum given that different bands can be related to different mechanisms and even a single band can contain different kinds of contributions.

All the theoretical calculations carried out predict the selective enhancement of mode 9a at negative charges, irrespective of the functional, the basis set, the single or multi-state approximations with the uncorrected or size-corrected energies of plasmon-like states, $P_0$ and $P_{0c}$ respectively (Figs. S2-S4). Even similar results are obtained if the plasmon-like states are not taken into account in multi-state calculations (Fig. S5). This means that the enhancement of mode 9a is due to the overall electronic structure of the $[Ag_3$-$Py]^{-1}$ hybrid and is not exclusively caused by the particular $P_0^*$ state.

One of the most interesting features of SERS is its ability to perform single-molecule experiments (SM-SERS). Until quite recently, it has been assumed that the enormous enhancement needed to record SM-SERS was exclusively due to the excitation of surface plasmons localized in hot spots. The calculated electromagnetic field in the gap between two metal clusters was sufficient to account for the needed enhancement, i.e., no additional resonant processes (chemical mechanisms) were required. However, it has been recently reported that quantum effects in such small metallic gaps could reduce significantly the plasmonic enhancement,[14] what would make necessary to resort to chemical contributions like the here discussed ones in order to account for these experiments. Some of the reported SM-SERS correspond to non-absorbing molecules under VIS excitation like adenine. Therefore, it is possible that electronic resonances involving charge transfer excited states of the metal-molecule hybrid or plasmon-like states of the metal could be involved in these experiments. These resonances are very poorly known but standard electronic structure calculations could be very useful in order to characterize them.

If the close relationship between the SERS spectra and the electronic structure of M-A hybrids is confirmed in future works the SERS will become a very powerful tool to get insight into the electronic structure of interfaces at a molecular level. This would allow for improving the control of adsorption or electrochemistry processes as well as the design of heterogeneous catalysts or circuits based on molecular electronics.

It is to be stressed that some of these conclusions are only valid for the silver-pyridine system given that any chemical interaction is very dependent on the nature of the M-A system and the experimental conditions.

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