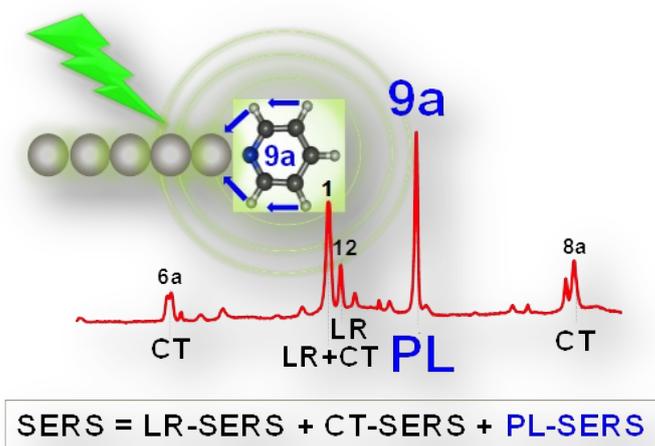


ELECTRONIC SUPPLEMENTARY MATERIAL

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

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CALCULATION DETAILS

RR intensities

Resonance Raman (RR) intensities have been calculated by using the methodology by A. Jarzecki¹ following two different ways:

Single-state approximation:

In this case only a single S_g - S_e resonant excitation involving the ground (S_g) and the selected excited state (S_e) is taking into account. RR intensities are calculated by assuming short-time propagation of the ground state wave function on the single excited state as well as the gradient approximation, i.e., the excited-state displacements with respect to the ground state geometry are proportional to the gradient of the excited state potential energy surface in the Franck-Condon region. The intensities for the k-th mode can be estimated from the equation:

$$I_{k,FC}^{g \rightarrow e} \propto (\nu_o - \nu_k^g)^3 \nu_o \left(\frac{\nu_k^g}{\mu_k} \right) \frac{\partial E_e}{\partial Q_k} \quad (1)$$

where ν_o is the excitation energy, ν_k^g is the vibrational wavenumber of the k-th mode in the electronic ground state S_g , μ_k is the corresponding effective mass and $\left(\frac{\partial E_e}{\partial Q_k} \right)$ is the gradient with respect to the respective normal mode Q_k :

$$\left(\frac{\partial E_e}{\partial Q_k} \right) = \mathbf{f} \mathbf{M}^{-1/2} \mathbf{L}_k \quad (2)$$

which is obtained^{2,3} from the Cartesian molecular forces \mathbf{f} in the excited state evaluated at the Franck-Condon geometry, \mathbf{M} is the diagonal matrix of atomic masses and \mathbf{L}_k is the eigenvector of the Hessian matrix associated with the k-th normal mode.

Multi-states approximation:

The limitation of the single-state gradient formulation described above is extended to several states by introducing the weighted-gradient approximation,¹ where each computed excited-state gradient is weighted by the appropriate $W_{\Gamma,e}$ factor at the amplitude level as shown in Eq. 3:

$$I_{k,FC}^{g \rightarrow e} \propto (\nu_o - \nu_k^g)^3 \nu_o \left(\frac{\nu_k^g}{\mu_k} \right) \sum_e \left| \left(\frac{\partial E_e}{\partial Q_k} \right) W_{\Gamma,e} \right|^2 \quad (3)$$

with

$$W_{\Gamma,e} = \frac{|\mu_e^g|^2}{N} \left[\frac{\Gamma_e^2}{\Gamma_e^2 + (\nu_o - (\nu^{e,k} - \nu^{g,i}))^2} \right] \quad (4)$$

where $|\mu_e^g|$ is the dipole moment integral, Γ_e the empirically determined energy offset (damping parameter) and $(\nu^{e,k} - \nu^{g,i})$ is the energy of the electronic transition.

The normalization constant N is obtained so a full spectrum of computed weighting factors sum up to unity:

$$N = \left[\sum_e \left\{ \left| \mu_e^g \right|^2 \left[\frac{\Gamma_e^2}{\Gamma_e^2 + (\nu_o - (\nu^{e,k} - \nu^{g,i}))^2} \right]^2 \right\} \right]^{1/2} \quad (5)$$

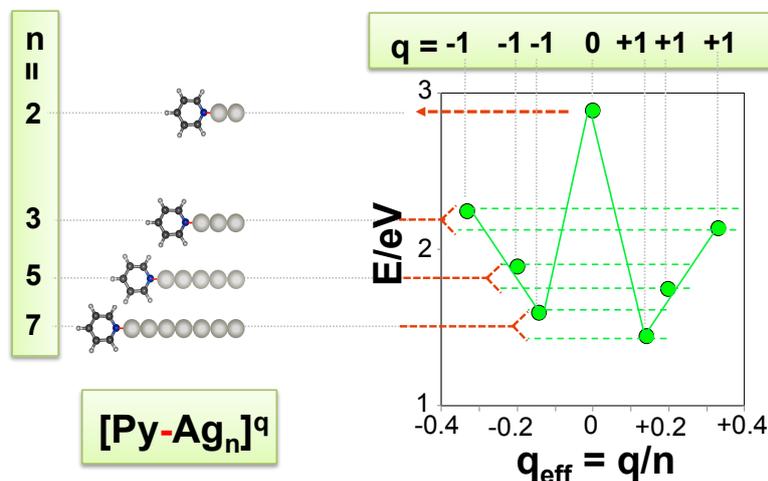
Electronic structure calculations:

(TD)-DFT calculations provide all the required numerical values for estimating the RR intensities: the force field in the ground electronic state and the energies and dipole moment integrals for the resonant electronic transitions.

All the density functional theory (DFT) calculations have been carried out by using the Gaussian 09 suite of programs.⁴ The geometry of the ground state (S_0) of each M-A system has been fully optimized with the only constrain of keeping the linear structure with C_{2v} symmetry (see Scheme S1). Then, the vertical energies of the singlet excited states have been obtained by means of time dependent DFT (TDDFT) calculations. Vertical excitation energies correspond to the difference between the respective energies of the ground S_0 and the excited states calculated without any structural rearrangement, i.e., by keeping unaltered the nuclear positions of the optimized S_0 geometry.

The effect of the electrode potential on the properties of pyridine bonded through its aromatic nitrogen to a charged silver atom of a nanometer size surface has been modelled by means of linear stick-like Ag_n^q clusters with different sizes ($n=2,3,5$ and

7) and charges ($q=0,\pm 1$ a.u.) (Scheme S1), giving the corresponding metal-adsorbate $[\text{Ag}_n\text{-Py}]^q$ complexes. These closed-shell Ag_n^q clusters allow to account smoothly for the effect of a fractionary charge excess on the properties of the M-A complex.



Scheme S1. TD-M06-HF/LanL2DZ vertical energies (E) of the plasmon-like state P_0 in linear $[\text{Ag}_n\text{-Py}]^q$ complexes versus the effective charge $q_{\text{eff}}=q/n$.

We have shown that the time-dependent density functional theory (TDDFT) energies of the singlet electronic states of the M-A hybrid with a relevant participation of the adsorbate show a linear dependence on $q_{\text{eff}}=q/n$. q_{eff} is a combined variable that quantifies the atomic charge excess averaged amongst the metallic atoms (a.u./atom of surface) and can be envisaged as a microscopic analogue to the macroscopic surface excess of charge ($q'=\text{C}/\text{cm}^2$). Therefore, the role of the cluster size is just to modulate the effective charge of the metal surface atom to which the molecule is bonded like the electrode potential does.

Specifically, these states with important participation of the adsorbate are: the forward and reverse metal-to-molecule charge transfer states (CT), the $S_0\text{-}S_1$ transition of the adsorbate ($S_{1,\text{PY}}$ in the case of pyridine) and the bonding energies of the M-A complex in its ground electronic state S_0 .

Plasmon-like states (PL-SERS: P_0)

The remaining electronic states of M-A correspond to excitations inside the metal cluster. Amongst them, the most characteristic excitation corresponds to a totally symmetric excited state P_0 present in any cluster showing low energy (usually is the

first excited singlet) and very high oscillator strength (f). Whereas the CT transitions have characteristic f values in the order of 10^{-3} , TDDFT calculations predict that these quite particular excitations should be three orders of magnitude stronger ($f=0.5-2.4$). This is the reason why we have named them as plasmon-like states as an analogy to the surface plasmons localized in nanometer-size metal clusters, which are widely recognized to be the main contribution to the SERS enhancement.

Charge transfer states (CT-SERS: CT_{F0})

Although in all the ground and excited states some amount of charge is donated from M to A or vice versa, the excited states with net transferred charges are easily recognized by comparing the Mulliken's charges of both moieties in the S_0 and the excited S_i states ($\Delta q_i = q_{A,S_i} - q_{A,S_0}$). Moreover, the corresponding single excitations of the CI expansion are checked in order to confirm the assignment. These CT states are characterized by significant Δq_i usually in the range 0.35-0.9 u.a., while the remaining non-CT excitations shows $\Delta q_i > 0.1$ a.u.

Concerning the theoretical description of the CT excited states, it is well established that DFT requires full Hartree-Fock exchange, what means that, for instance, widespread used functionals like the hybrid B3LYP⁵ are not adequate given that systematically underestimate the energies of the CT transitions. This is the reason why we have used the long-range corrected M06-HF⁶ and wB97X-D⁷ functionals which have been proposed to specifically solve this problem. Anyway, quantitative theoretical prediction of the energies of CT states remains a challenge. Finally, DFT calculations have been carried out by using the LanL2DZ⁸ standard effective core pseudopotential, very often used as basis set in organometallic calculations, and the mixed LanL2DZ(Ag)/6-31G*⁹(Py) basis sets.

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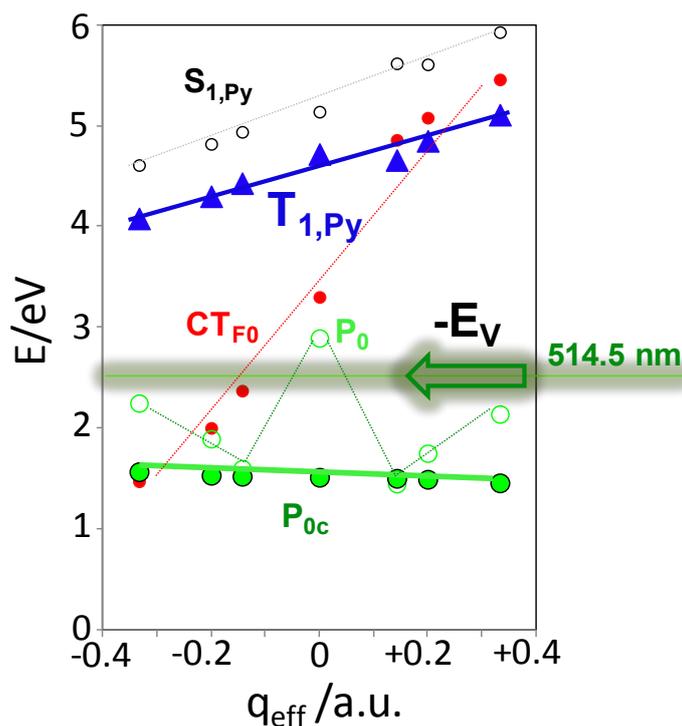


Figure S1. TD-M06-HF/LanL2DZ vertical energies (E) of the plasmon-like states (size-corrected (P_{0c}) and uncorrected (P_0)), the first forward charge transfer state (CT_{F0}), the first excited singlet ($S_{1,\text{Py}}$) and triplet ($T_{1,\text{Py}}$) of pyridine, in $[\text{Ag}_n\text{-Py}]^q$ complexes versus the effective charge $q_{\text{eff}}=q/n$.

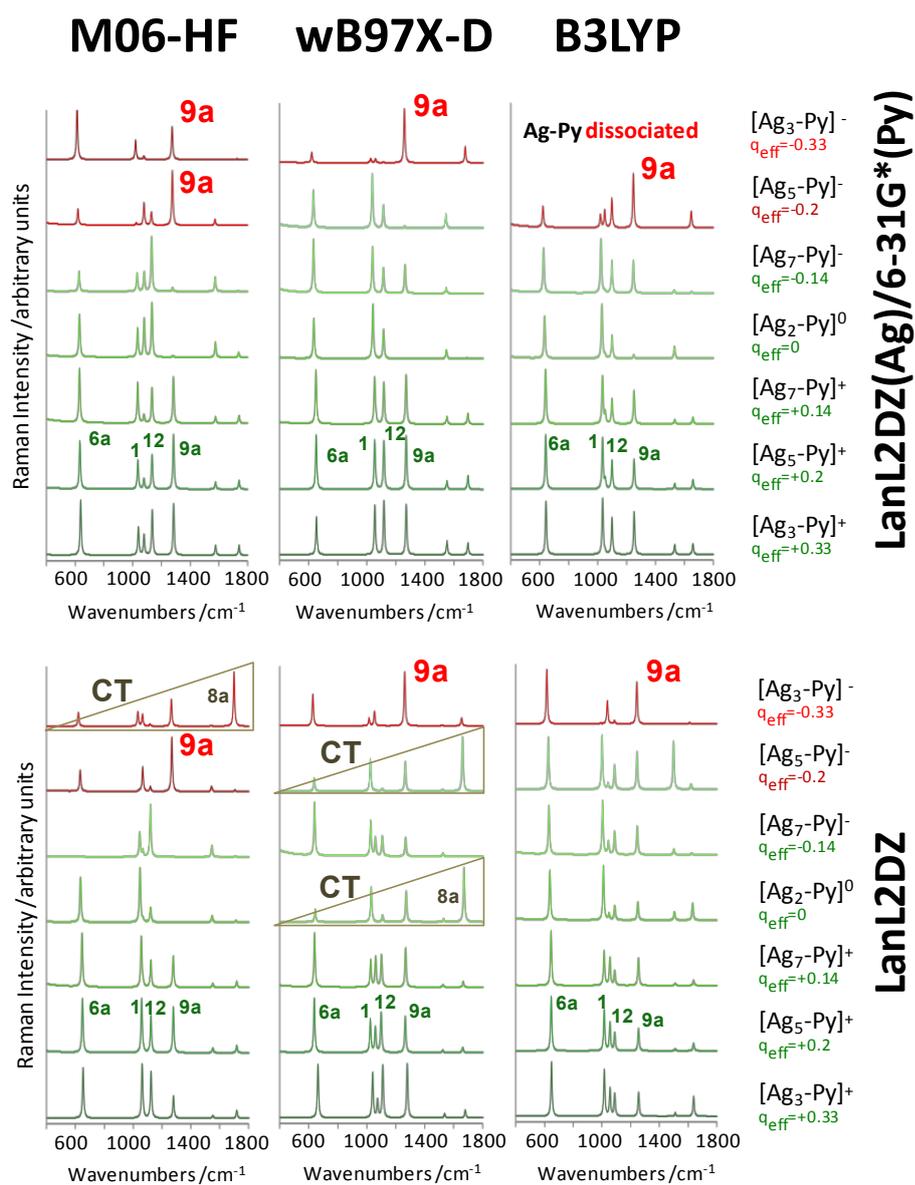


Figure S2. Effect of the effective charge q_{eff} on the single-state Raman intensities in resonance with the S_0 - P_0 plasmon-like transitions of $[\text{Ag}_n\text{-Py}]^q$ complexes calculated at different levels of theory.

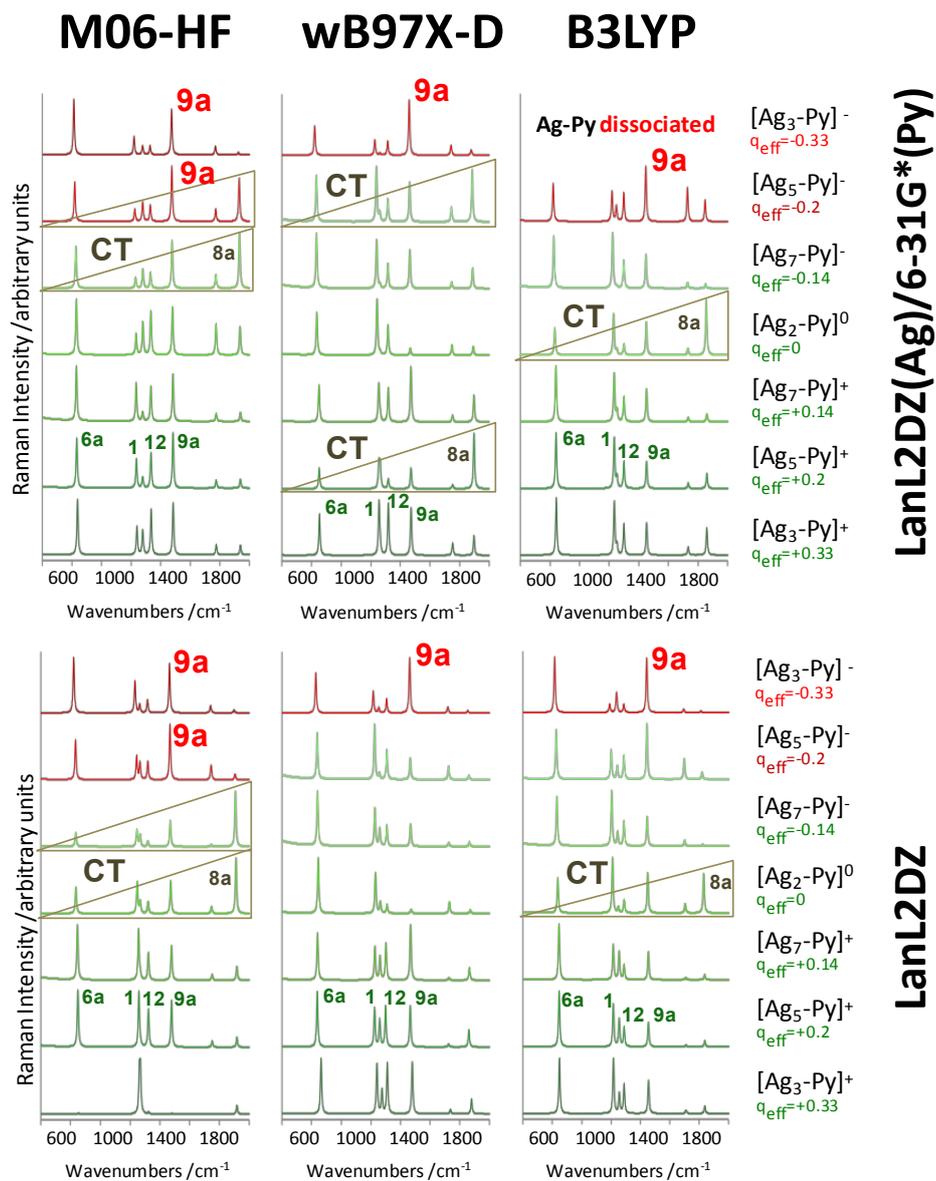


Figure S4. Effect of the effective charge q_{eff} on the Raman intensities calculated at different levels of theory under 514.5 nm excitation from the weighted contributions of the first fifty electronic transitions of $[\text{Ag}_n\text{-Py}]^q$ complexes. The energies of the plasmon-like states correspond to the size-corrected corrected values (P_{0c}).

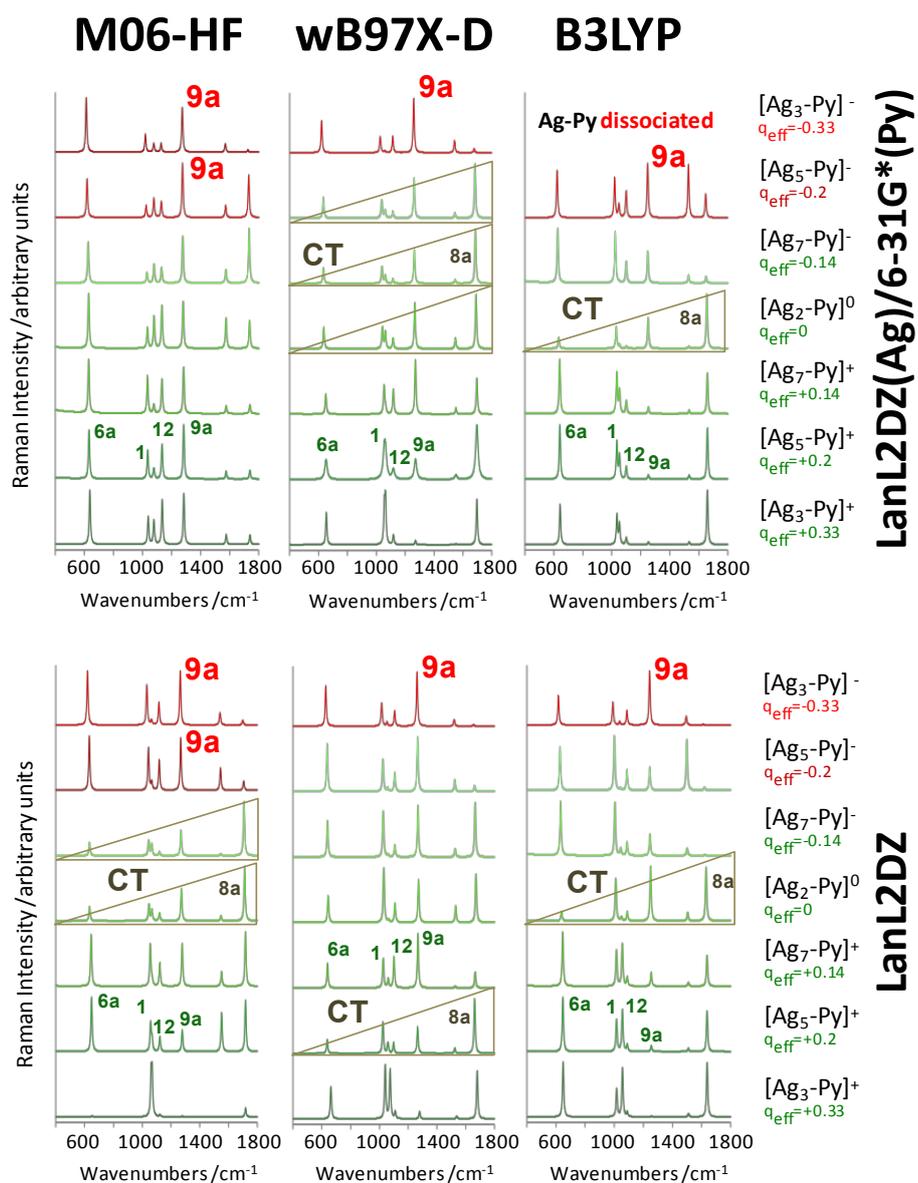


Figure S5. Effect of the effective charge q_{eff} on the Raman intensities calculated at different levels of theory under 514.5 nm excitation from the weighted contributions of the first fifty electronic transitions excluding plasmon-like states of $[\text{Ag}_n\text{-Py}]^q$ complexes.