

# Using SERS to probe electrical capacitive enhancement in nanometer-size hot spots

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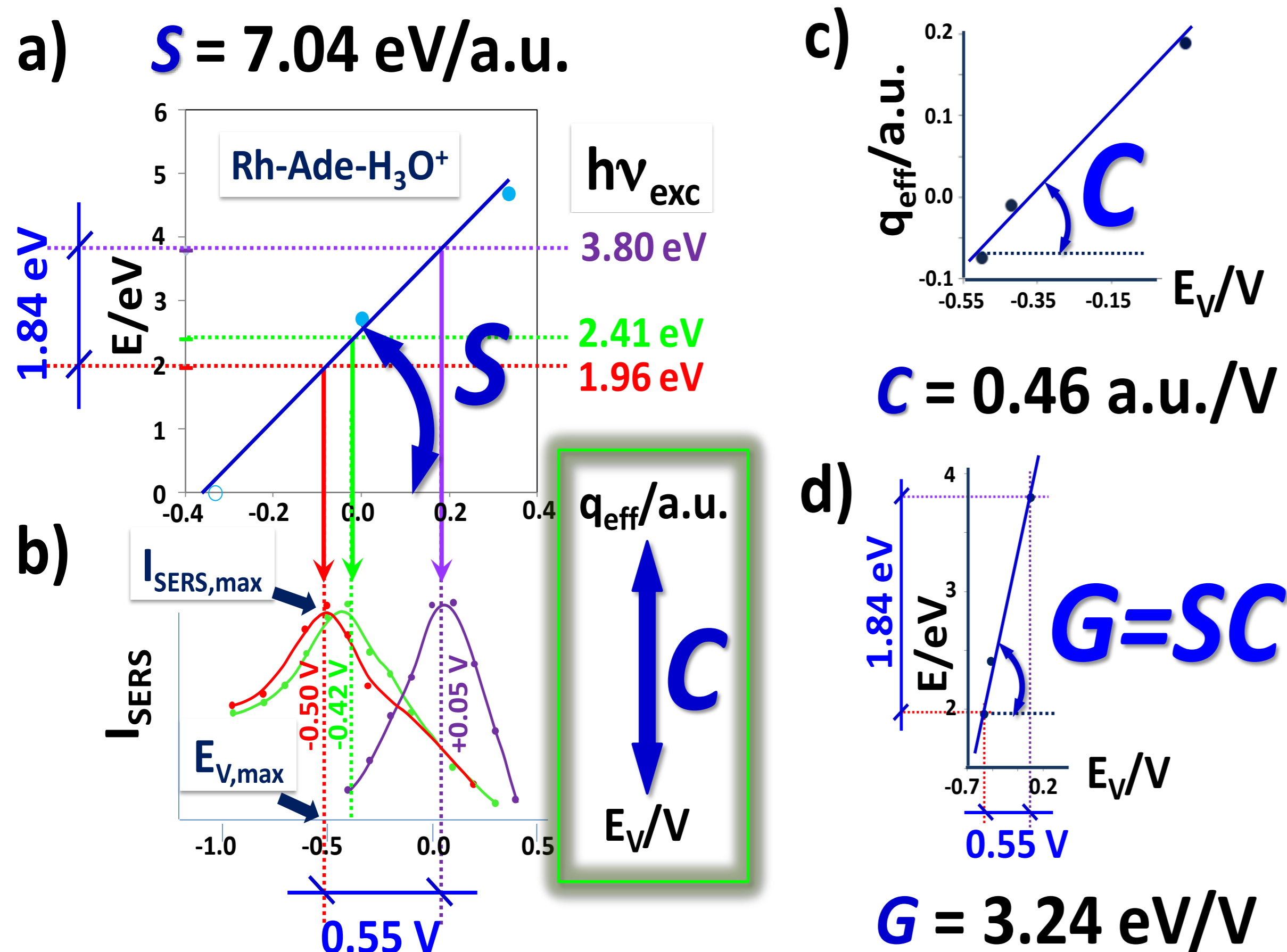
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## INTRODUCTION

The chemical interaction between molecule and metal plays a crucial role<sup>1</sup> in SERS electrochemical experiments where adsorbates (A) can undergo photoinduced charge transfer processes (CT) with the metal (M).

Huge energy gain  $G$  has been observed when the electrode potential ( $E_V$ ) tunes the energy of the charge transfer states ( $E_{CT}$ ) of metal-adsorbate surface complexes in electrochemical SERS experiences.<sup>2,3</sup>

Supported on electronic structure calculations of metal-molecule nanoclusters,<sup>5,6</sup> it has been demonstrated that this “anomalous” gain  $G$  is due to two different contributions:  $G = \Delta E / \Delta E_V = SC$ . The first one is responsible for the effect of a fractional charge ( $q_{eff} = q/n$ ) on the electronic structure of  $[Mn-A]^q$  complexes which tunes the CT states through the slopes  $S$  of the  $E$  vs  $q_{eff}$  diagrams. The second contribution ( $C = \Delta q_{eff} / \Delta E_V$ ) is a kind of capacitance that quantifies the ability of the metal to convert the electrode potential  $E_V$  into the atomic excess of charge  $q_{eff}$ .



## COMPUTATIONAL METHODS

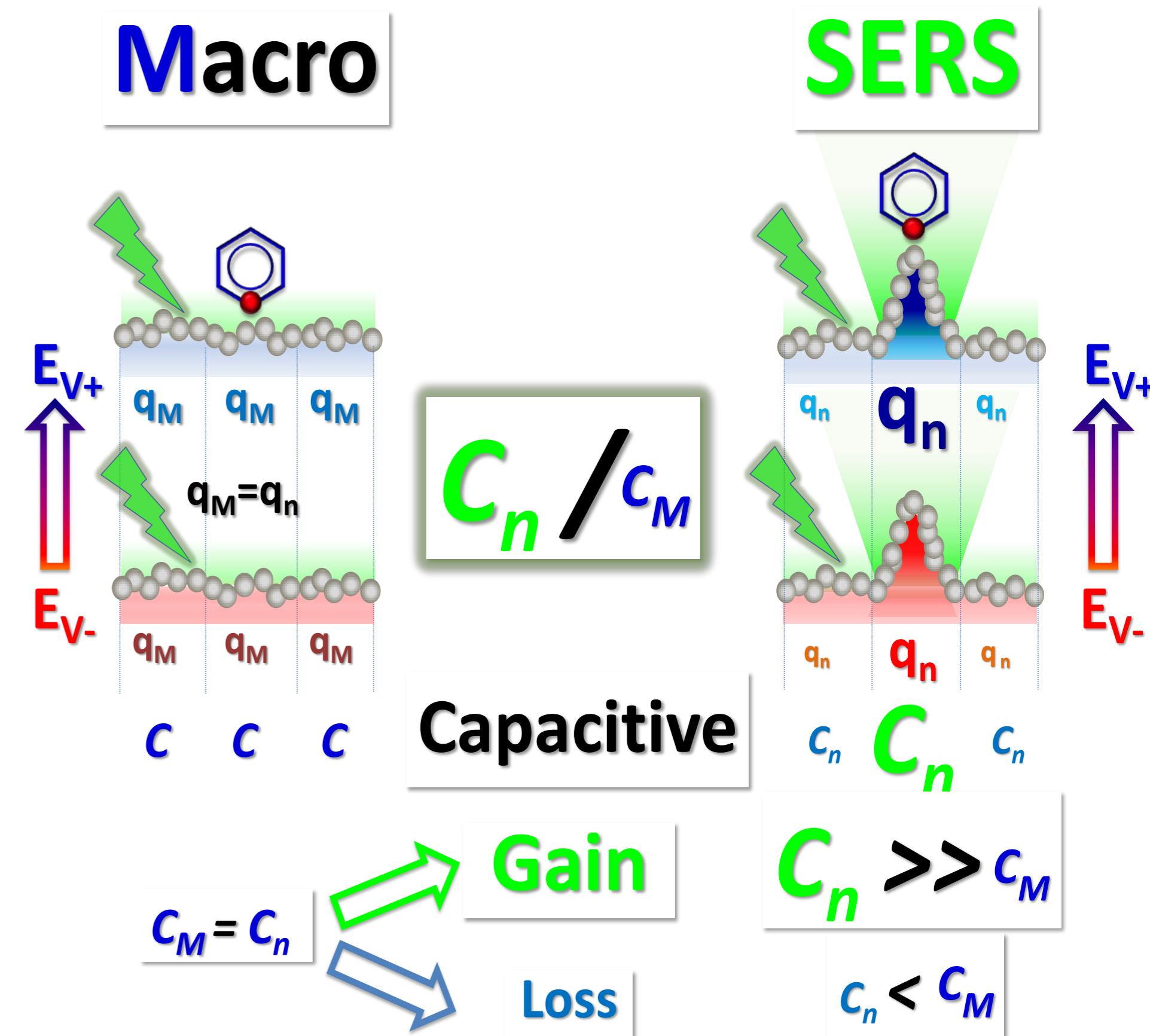
In order to obtain the energies of the studied  $[Mn-A]^q$  systems ( $n=2$  with  $q=0$  and  $n=3$  with  $q=\pm 1$ ), we have used time-dependent density functional theory (TDDFT) calculations with the M06-HF functional as implemented in G09,<sup>7</sup> which contains the full Hartree-Fock exchange and is designed for an accurate treatment of CT states, with the LanL2DZ basis set. The only constraint for geometry optimizations has been to keep linear the  $[Mn]^q$  clusters.

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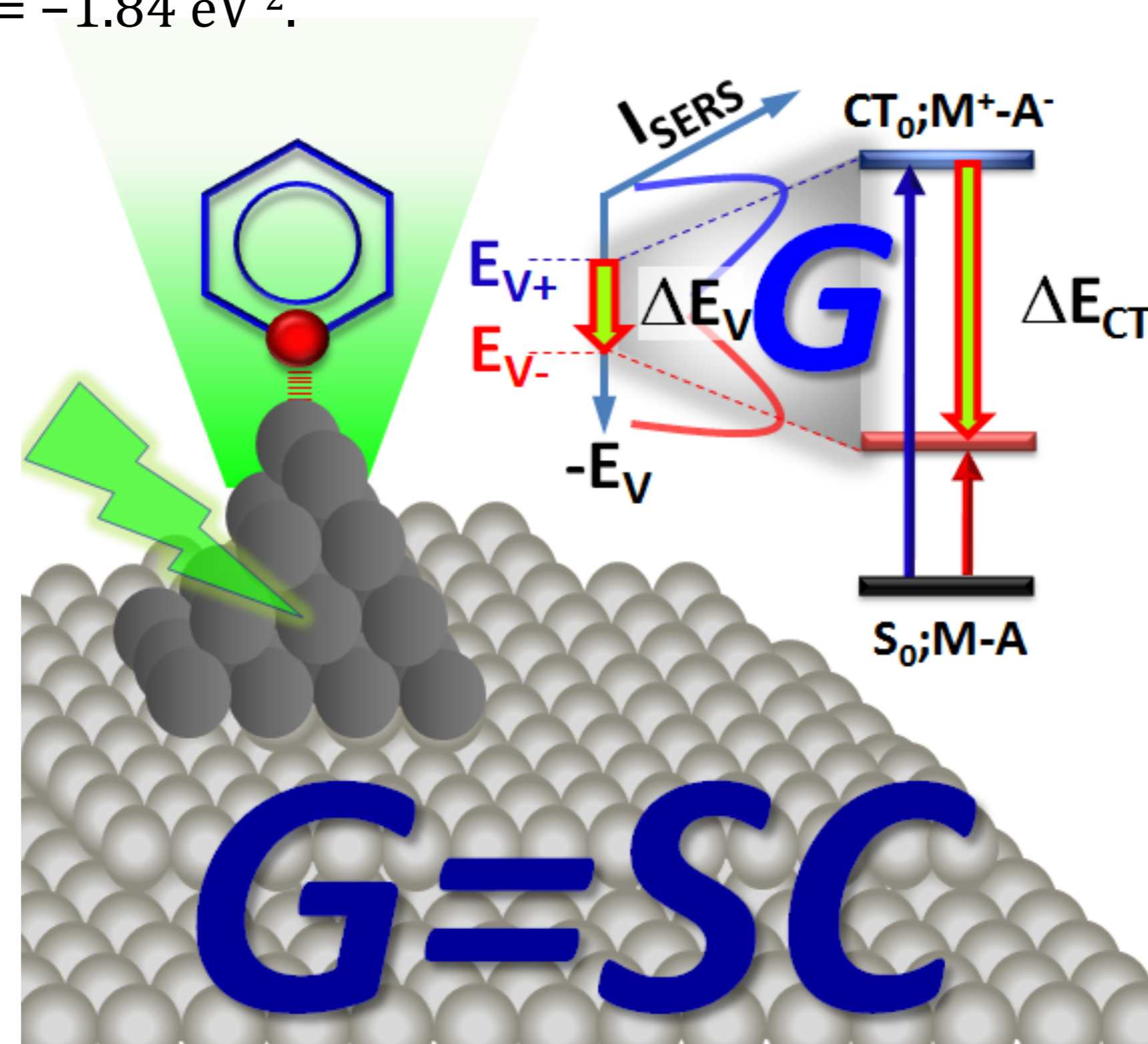
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A positive shift of the electrode potential ( $E_V \rightarrow E_{V+}$ ) on the excess charge ( $q$ ) of a nanostructured metallic surface originates capacitive gains ( $C_n \gg C_M$ ) located on large curvature nanostructures and capacitive losses on flat domains.

- In some of these experiences huge energy gain ( $G$ ) of up to **5 eV/V** have been reported when the electrode potential ( $E_V$ ) tunes the energy of charge transfer ( $E_{CT}$ ) states of hybrid systems:  $E_{CT} = G \cdot E_V + E^0$ . This is in conflict with the classical picture of the metal-adsorbate electron transfer mechanism where  $G=1$ .<sup>2-4</sup>
- A  $G$  value of 3.24 eV/V would imply that a high CT state reachable at 0.05 V when exciting with the 325 nm UV line (3.8 eV) needs only the 632.8 nm red line (1.96 eV) when the electrode potential is raised up to -0.5 V; in other words, a shift of  $\Delta E_V = -0.55$  V produces  $\Delta E_{CT} = -1.84$  eV<sup>2</sup>.



## CONCLUSIONS

- SERS is characterized by the enormous enhancement of the Raman signal molecules adsorbed on very specific surface sites called “hot spots” located in gaps, kinks, edges or sharp features of nanoparticles. Therefore, all the properties derived from SERS spectra, like capacitance, should be restricted to this scale of size, which allows to consider them as nanometric measurements.
- The huge efficiency of the electrode potential in tuning the CT states involves two different contributions ( $G=SC$ ) arising from the subtle electronic structure of the M-A hybrids ( $S$ ) together with an electrical capacitive enhancement ( $C$ ) of metal nanostructures