

Using Surface-enhanced Raman Scattering to Probe the Capacitance of Metallic Nanostructures

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Though it is generally accepted that the electromagnetic mechanism related to the excitation of localized plasmons of the metal surface is the most important contribution in SERS, the chemical interaction between molecule and metal plays also a crucial role. [1] This is especially relevant in SERS electrochemical experiments where adsorbates can undergo photoinduced charge transfer processes (CT) with the metal. In some of these experiences huge energy gains (G) of up to 5 eV/V have been reported, which are in conflict with the classical picture of the metal-adsorbate CT mechanism ($G=1$). [2] Supported on electronic structure calculations of metal-molecule nanoclusters, we are able to elucidate that this "anomalous" gain is mainly due to two different contributions, firstly, the sensitivity of the CT electronic states of the metal-molecule system on the effective charge excess of the metal, and, secondly, to an increased electric capacitance of the metallic nanocluster with respect to the macroscopic values. We are able to semiquantitatively estimate this capacitance enhancement and explain it by assuming that the strongest SERS signal comes from those surface nanostructures where a higher charge excess is stored. Therefore, we believe that SERS can become a useful tool for capacitance measurements at nanometer scale.

- [1] E.C. Le Ru,; P.G. Etchegoin, Principles of Surface-Enhanced Raman Spectroscopy and related plasmonic effects. *Elsevier*, Amsterdam, 2009.
- [2] L. Cui, D-Y Wu, A. Wang, B. Ren, Z-Q Tian, *J. Phys. Chem. C*, **2010**, *114*, 16588-16595.

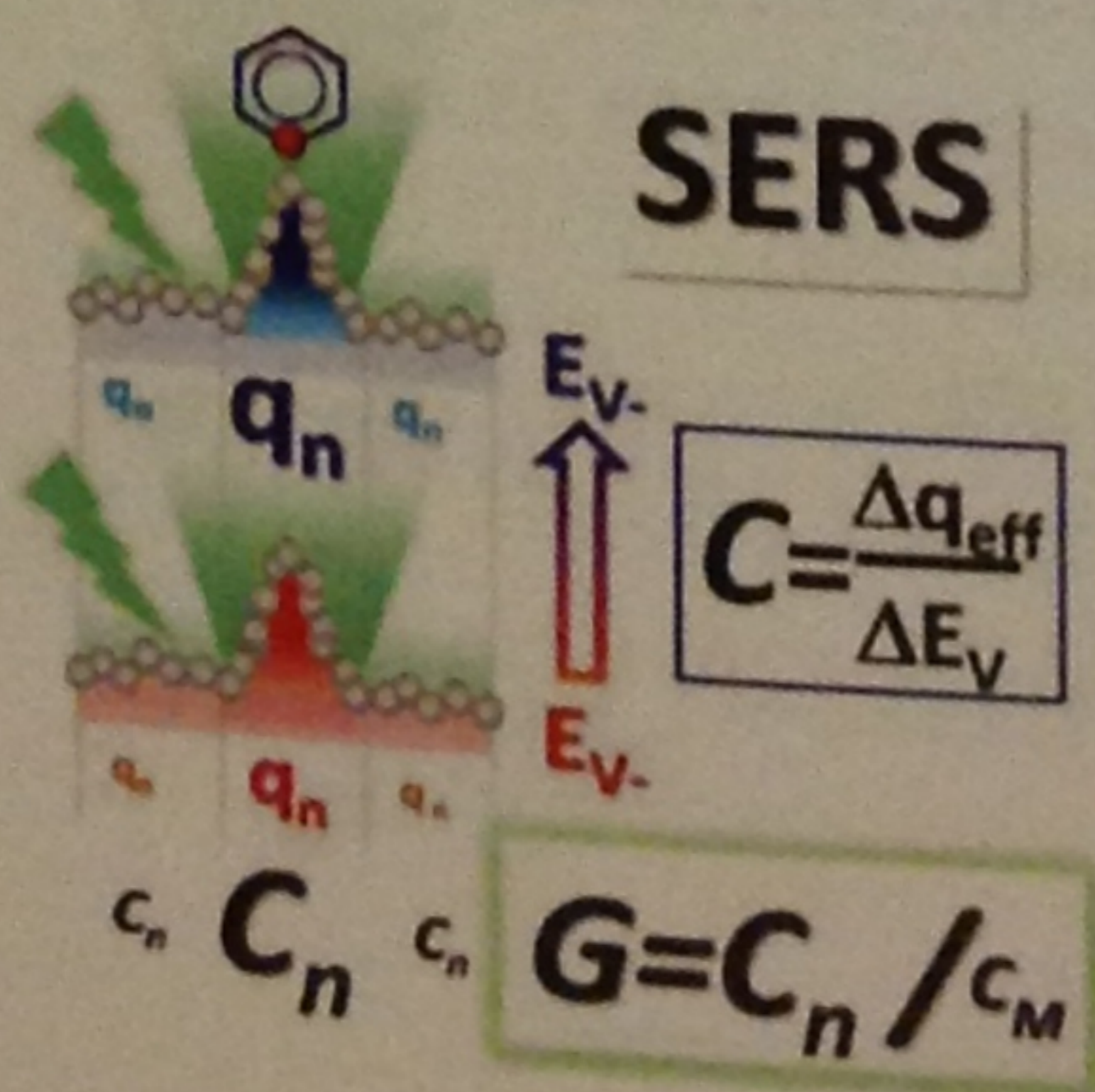


Figure 1: Postulated model for the enhancement of the metallic capacitance at the SERS active sites