Brownian motion of gold nanostructures made visible using SERS fluctuations due to single molecules

Surface-Enhanced Raman Spectroscopy (SERS) a surface-sensitive effect which produces a dramatic enhancement of the Raman signature of molecules adsorbed on some nanostructures such as gold nanoparticles. In practical terms, SERS allows the fast acquisition of spectral datasets on one hand and in favorable cases, can even detect single molecules on the other hand.

In spite of the great interest aroused by the huge promises of SERS, general theoretical principles are still under debate. Moreover, the need for dedicated SERS-active nanostructures shaped as convenient analytical substrates orients the to-date research towards the preparation of effective SERS-active materials. This results in a partial exploitation of this most exciting phenomenon.

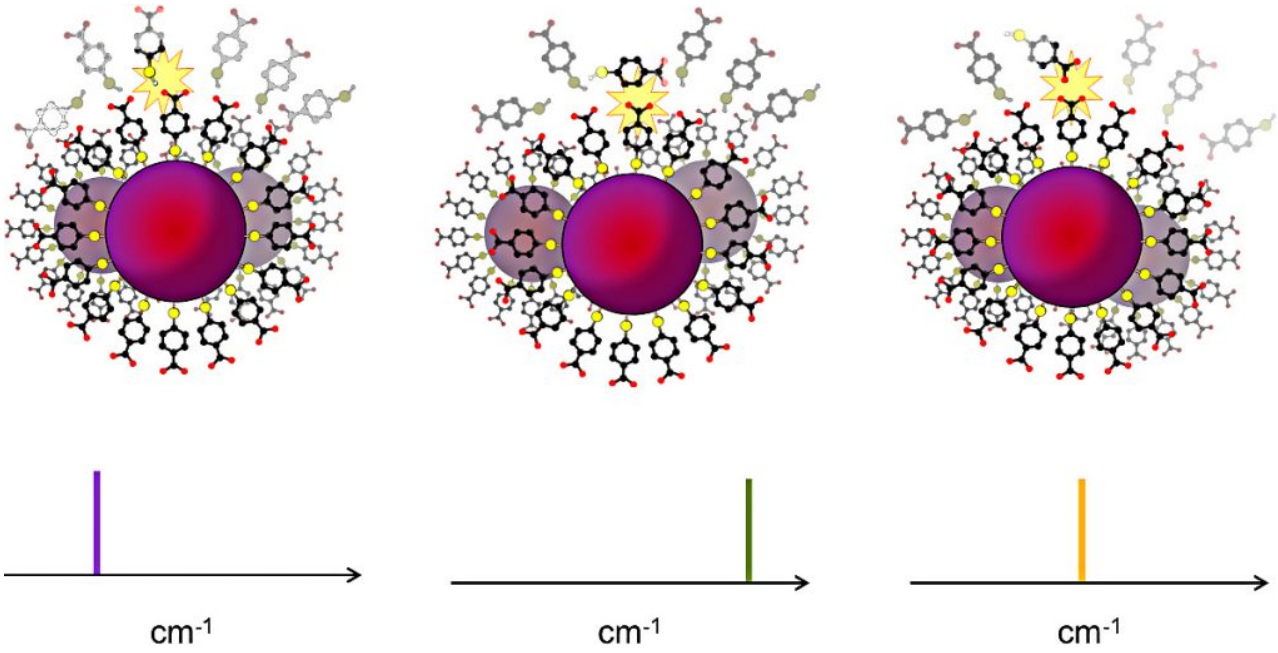

Fig. 1. Schematic representation of the "gate opening" mechanism putting into a play the Brownian motion of gold nanoparticles in conjunction with the orientation of a single molecule from the second layer. This "resonant" structure gives rise to a signal corresponding to a molecular group of the involved single molecule.

Taking advantage of the offered possibility to record hundreds of high quality spectra in a couple of minutes, it is possible to analyze the fluctuations of the SERS features arising from a layer of p-mercaptobenzoic (p-MBA) molecules chemisorbed onto gold nanoparticles by means of a proper statistical description. In particular, “individual events” corresponding to the abrupt and reversible

observation of original spectral signatures which lifetime did not exceed one second were identified and investigated.

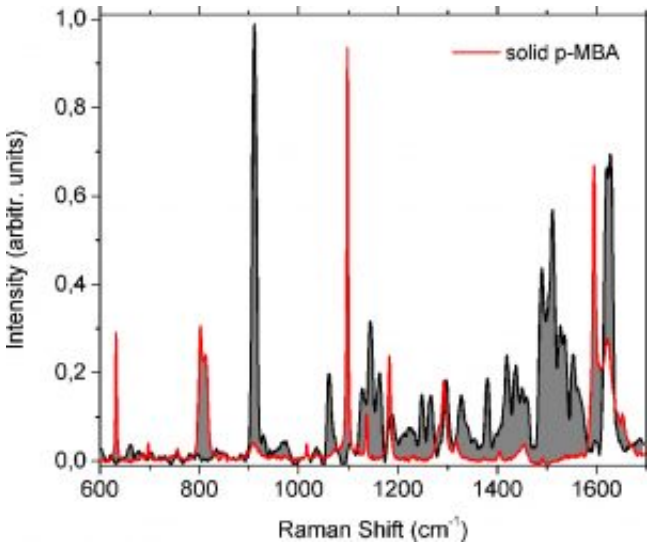

Fig. 2. Spectral representation of the comb (in black) obtained from a systematic Kurtosis analysis over more than 8000 SERS spectra and conventional Raman spectrum of solid p-MBA

After due analyses, it turned out that those individual events occurred randomly in time whereas the spectral region affected by those new features was alike a comb of vibrational frequencies. The latter can be seen as individual channels which gates open at time. The mechanisms involved in the switching from an “closed’ to an “open” state within a time scale of the second were proposed to arise from the formation of transient resonant structures allowing the detection of the second layer of p-MBA.

In this resonant structure, only a part of the molecule belonging to the second layer of p-MBA contributes to the enhanced signal. This transient phenomenon is proposed to originates from the morphology and orientation of the gold nanostructures, and thus, reveal their mobility. Adding the “individual” spectral events together made it possible to reconstruct SERS features of an isolated molecule of p-MBA.

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Publication

Dynamics of a plasmon-activated p-mercaptobenzoic acid layer deposited over Au nanoparticles using time-resolved SERS.

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