# SERS-based detection and interaction of DNA bases with gold nanoparticles

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Surface-enhanced Raman spectroscopy (SERS) is a powerful tool for molecular detection as it is label-free, non-destructive and can potentially provide single-molecule sensitivity. In the context of DNA sequencing, SERS has many advantages over other sequencing methods, since it yields significantly better sensitivity and could eventually enable the detection of DNA modifications and protein sequencing.

In order to detect single DNA bases, the Raman signal must be strongly enhanced by carefully designed metallic nanostructures that can support surface plasmons. One option is to utilize the narrow gap between two gold nanoparticles (AuNPs) in a dimer, which can provide signal enhancement of up to 12 orders of magnitude in a very small region, called a hotspot. Since the Raman signal is dependent on the orientation of the molecules inside the hotspot, understanding the interaction of the DNA bases with the gold surface is a vital step towards enabling SERS-based DNA sequencing.

Even though a lot of experimental and theoretical work is already present on this topic, the precise orientation of the DNA bases on the gold surface is still debated. This work investigates the orientation of the DNA bases in the gap between two gold surfaces by exploring the changes in the relative size of the Raman peaks according to DNA base concentration and pH. It was found out that the ratio of the ring breathing mode to the stretching modes changes consistently with the gap size (Figure 1), implying that the DNA bases adopt a more perpendicular orientation at higher concentrations. The experimental results were supplemented by performing structural relaxations for adenine using DFT. Furthermore, the Zeta-potential of the AuNPs was measured over a wide DNA base concentration range, revealing that dimerization and colloidal stability can be achieved both at positive and negative Zeta-potentials. Finally, single-base sensitivity was verified by performing single-shot Raman measurements at very low adenine concentrations. It can be thus concluded that the gold nanoparticle dimer is a promising structure for enabling SERS-based DNA sequencing.

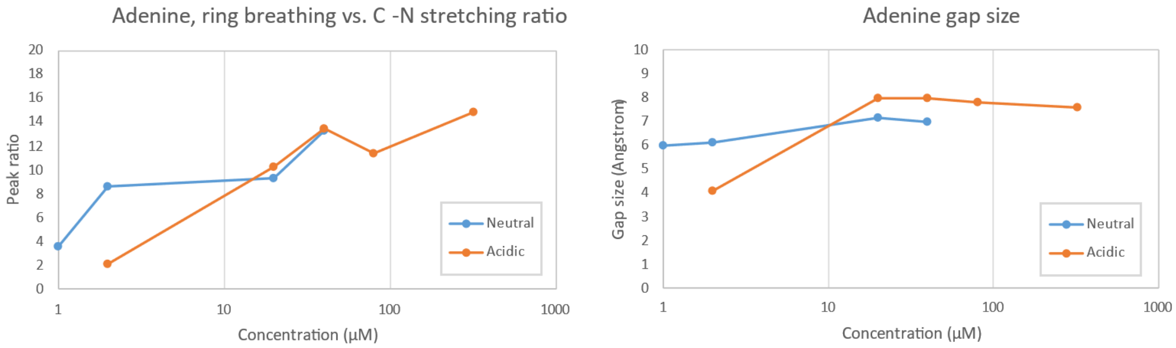


**Figure 1: The ratio between the ring breathing mode and the C-N stretching mode for adenine (left) and the dimer gap size (right) change consistently with adenine concentration.**