# Plasmon activated forbidden phonon modes in defect-free graphene by tip-enhanced nano-confined light

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## 1. Introduction

When light interacts with a metallic nanostructure, two interesting phenomena occur: (1) field enhancement and (2) high photon confinement. Field enhancement occurs when light at an appropriate wavelength and polarization excites localized surface plasmon-polaritons (LSPs) on the surface of the metal nanostructure. A consequence of this highly-confined and enhanced field or *near-field* is the "field gradient effect" (FGE). A strong field gradient is generated due to the near-field that rapidly decays as it moves away from the source. The effect of these phenomena is quite evident in Raman spectroscopy. Placing a nano-sized metal close to a sample leads to either surface enhanced Raman spectroscopy (SERS) or tip-enhanced Raman spectroscopy (TERS) because of field enhancement and high photon confinement. The light-metal-sample interaction can also alter selection rules by the FGE [1]. Recently, Ikeda *et.al* reported that, in SERS, by controlling the gap between two Au nano-dimers (gap distance ~ 1 nm) and essentially the degree of photon confinement, the FGE could be controlled [2]. The breakdown of dipole selection rules was observed through the detection of forbidden D and D' Raman modes in defect-free graphene.

## 2. Results and Discussion

In this work, we demonstrate the activation of forbidden phonon modes in defect-free monolayer graphene on an Au(111) substrate via sub-nanometer resolution STM-TERS experiments using Au tips excited by 632.8 nm laser [3]. Owing to the gap distance (~1 nm) realized by the STM configuration comparable to the previous SERS experiment [2], we report the first observation, to our knowledge, of combination Raman bands, which we loosely attribute to either the D+D', D+G or a combination of both bands. The occurrence of the combination defect bands is due to the nano-confined light generated at the tip apex that, in turn, generates a strong field gradient.

TERS measurements were made on a CVD grown monolayer graphene on an Au(111) substrate [4]. Far-field spectra showed no D-band indicating that the measurement area is defect-free. The TERS spectrum, however, showcases a variety of defect-activated Raman bands alongside the $G^-$ (1569 $cm^{-1}$), $G^+$ (1594.6 $cm^{-1}$), and 2D (2656.2 $cm^{-1}$) bands. The D (1337.8 $cm^{-1}$) and the D' (1614.4 $cm^{-1}$) bands have been previously observed in SERS [2]. In our TERS measurements, both the D and the D' bands are quite prominent. We would like to note here that the TERS signal originates from a single point without any defect, whereas the SERS signal reported in Ref. 2 originates from several nano gaps that may contain a defect site. We also observed a broad combination band centered at 2919.1 $cm^{-1}$ whose peak assignment can be either D+D', D+G or a combination of both. To our knowledge, this is the first experimental observation of forbidden phonon combination bands in defect-free monolayer graphene [3]. In conventional diffraction-limited Raman spectroscopy, only zone-center optical phonons ($q = 0$) are observed ($G^-$, $G^+$ and 2D modes). In our near-field STM-TERS system, sub-nanometer spatial resolution is attained due to the highly confined optical field (diameter ~ 1 nm). The largest wavenumber present is determined by the inverse of the field variation distance, $k_{NF} \approx p/d \approx 10^7\ cm^{-1}$ – this value almost spans the wavevector $q$ of the full phonon dispersion curve. As a result, the $q = 0$ selection rule for Raman spectroscopy is altered, activating forbidden phonon modes, such as the defect-activated bands, D, D' and the combination defect bands, D+D' or D+G. The mechanism of activation is similar to double resonance [5]. But, instead of defect-mediated electron scattering, a plasmon-mediated process occurs. Due to the large $k$ wave number generated by the nano-confined light field at the tip apex, nonvertical optical transition is allowed [6].

## 3. Conclusions

We report the activation and the first observation of the defect-activated combination Raman bands: D+D', D+G or both, and also observe the D and D' defect induced peaks that have been previously reported. The activation of the forbidden modes is due to the breakdown of the Raman selection rules caused by the high photon confinement and the FGE induced by the tip-enhanced nano-confined light source used in our STM-TERS experiments.

## References

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