Towards single molecule femtosecond dynamics

Keke YUAN, Céline DABLEMONT, Serge CARREZ, Aimeric OUVRARD

Université Paris-Saclay, CNRS, Institut des Sciences Moléculaires d'Orsay, 91405, Orsay, France

**corresponding author: aimeric.ouvrard@universite-paris-saclay.fr*

Understanding ultrafast optical and vibrational processes in molecules on surfaces is a key for the design and performance of organic optoelectronic devices [1]. Optical processes can be probed at the single-molecule level using scanning probe microscopy and plasmon enhanced optical spectroscopies; however, their temporal resolution is intrinsically limited [2]. In this context, we aim to go beyond the diffraction limit of optical spectroscopy and beyond the temporal response of scanning probe microscopy. We propose to combine ultrafast sum-frequency generation (SFG) spectroscopy an ideal tool to probe molecules at surfaces [3], with scanning tunneling microscopy (STM), in order to probe the vibrational dynamics of single molecules. In a similar way to tip-enhanced Raman spectroscopy, the STM metallic tip will amplify both linear and non-linear local electric fields in the tip-surface junction thanks to the localized surface plasmon resonance.

First, we have conducted a feasibility study by numerical calculations using COMSOL, based on solving Maxwell's equations using the finite element method. We have simulated the linear optical response of a plasmonic tip close to a surface. The electric field distribution was computed. A parametric study was conducted to estimate the impact of tip geometry, laser wavelength and polarization. Simulations demonstrate the high sensitive of the field enhancement to the tip apex radius or laser wavelength. The strongest enhancement is reached when the laser field polarization is TM, parallel to the tip long axis. A strong enhancement factor of the electric field at the sum frequency is obtained, that is large enough to overcome the small surface of emission under the tip. Experimentally, an optical system was integrated into the STM microscope (Scienta Omicron) under ambient conditions. A short focal lens is used to focus the laser onto the tip apex to minimize the focused spot size and hence reduce the intensity of scattered SFG by the macroscopic spot, while another high numerical aperture lens is employed to efficiently collect the SFG signal emitted from the junction. In parallel to this work, we have develop an optical platform to test the short focal optical by performing SFG mapping of self-assembled molecules on gold surface with a spatial resolution around 1-2 µm, close to the diffract limit. Preliminary results will be presented. On the STM-SFG setup, we have found that thermal heating induced by the fs lasers is limited and the STM regulation loop remains stable under illumination. We succeed to combine STM and SFG using homemade Ag coated W tips, and find the SFG signal at the nanoscale, however the scattered SFG remained dominant. Future work include the improvement of light collection, beam focusing on the tip, the estimation of the lateral resolution and the mapping of vibrational response of the organic layer at nanoscale prior to demonstrate ultrafast Te-SFG spectroscopy.

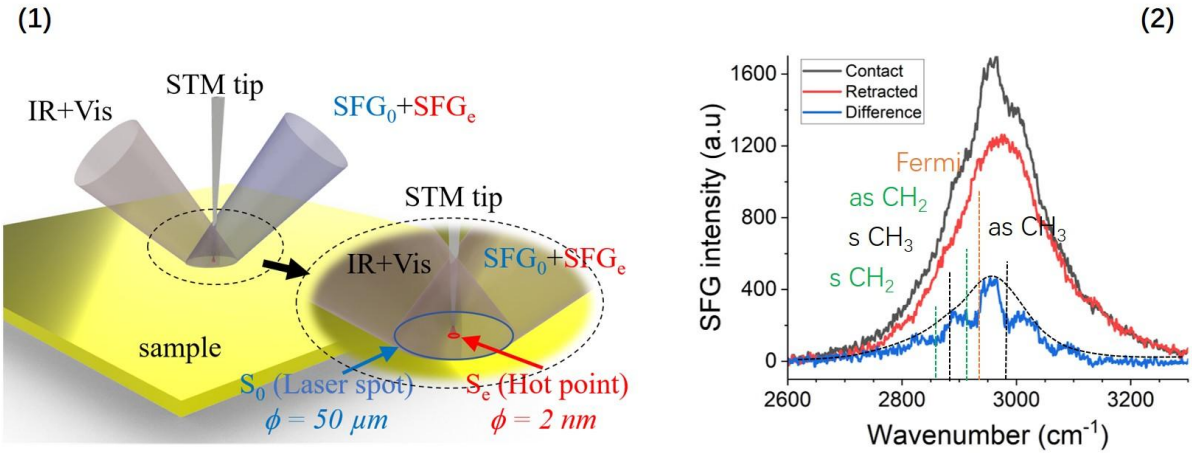

Fig 1 : (1) Principle of tip-enhanced SFG and (2) Preliminary results of Tip enhanced SFG signal from a self-assembled mon-olayer of octadecanthiol molecules.

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[2] Gutzler, R., Garg, M., Ast, C. R., Kuhnke, K., & Kern, K. Nature reviews physics, **3(6)**, 441-453(2021)
[3] N. Alyabyeva; A. Ouvrard; A.-M. Zakaria. J. Phys. Chem. Lett. **10**, 624-629(2019)