Plasmonic Heating effects in Tip-Enhanced Raman Spectroscopy (TERS)

Joel Rigor[1], Dmitry Kurouski[2], and Nicolas Large[1]
Department of Physics, University of Texas at San Antonio, San Antonio, TX[1]
Department of Biochemistry and Biophysics, Texas A&M University, College Station, TX[2]
Email: Joel.Rigor@utsa.edu

Tip-Enhanced Raman Spectroscopy (TERS) is well known for its applications in material science and nanotechnology. Performing TERS produces intense and highly confined electromagnetic fields at the apex of an atomically sharp tip which allows the detection of the chemical signature of molecules as well as providing insight to the underlying reasons for molecular changes within the system. However, these highly confined electromagnetic field interactions between the tip and the surface can cause photo- and thermal decomposition around the tip-surface junction. Here, we focus on the plasmonic behavior of various TERS systems: Local environmental changes on plasmonic heating effects with Au/Ag Tips on ITO substrate (Ag/Au – ITO TERS) and molecular changes of 4-Nitrobenzenethiol due to plasmonic heating effects on Au Tips on Au substrates (Au-Au TERS) [1]. Using numerical methods, such as electrodynamic and heat transport calculations, we can better understand the phenomena and processes occurring around the tip-surface junction, where the molecules experience high electromagnetic field interactions and temperatures. The absorption cross section given by each system is calculated and then used in order to generate thermal mappings of the tip-surface junction. With Ag/Au-ITO TERS, we observe the plasmonic behavior of a TERS system in air and a TERS system in water. A comparison is made at various wavelengths which shows a viable pathway to lessen the degradation found within the tip-surface region by performing TERS in water. With Au-Au TERS, we observe the possible plasmonic heating effects causing the thermal desorption of the 4NBT molecule. Numerical calculations show that the temperatures needed for thermal desorption of the 4NBT molecule are much lower than what is predicted by DFT theory. From this, the process of thermal desorption is not a product of plasmonic heating effects, but instead due to plasmon induced hot carriers.

References:

[1] Wang, R.; Li, J.; Rigor, J.; Large, N.; El-Khoury, P. Z.; Rogachev, A. Y. & Kurouski, D., "Direct Experimental Evidence of Hot Carrier-Driven Chemical Processes in Tip-Enhanced Raman Spectroscopy (TERS)." *J. Phys. Chem. C,* **2020**, *124*, 2238

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