Tip-enhanced THz-Raman spectroscopy: an all-optical method for precise determination and control of local temperature at the nanoscale

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Signal enhancing techniques, such as tip-enhanced Raman spectroscopy (TERS), provide high chemical sensitivity and spatial resolution making it possible to study and understand the nanoscale realm. Although signal enhancement has many advantages, one disadvantage that has to be addressed is heating caused by the generated enhanced field. In the case of TERS, heating is observed at the tip apex that is directly in contact with the sample and, so far, only several groups [1-3] have reported this issue of heating in TERS. To ensure accurate data analysis, determining the temperature and temperature changes at the sample is important, especially at the low temperature regime (< 100˚C). Aside from determining the temperature, temperature control during TERS experiments is just as important to prevent both tip and sample damage, particularly samples that are thermally sensitive. In this work, we have developed an all-optical technique called tip-enhanced terahertz Raman spectroscopy (TE-THzRS, THz-Raman < 200 cm^{-1}) to precisely determine and control the local temperature at nanoscale volume in the low temperature range (< 100˚C) via incident laser power while maintaining sufficiently high tip-enhancement [1]. Heat transferred via conduction and radiation from the enhanced electric field at the tip to single-walled carbon nanotubes (CNTs) was studied. The intensity ratio of the anti-Stokes/Stokes Raman scattering of the CNTs' radial breathing mode (RBM) was modulated following the Boltzmann distribution. Due to the RBM's low energy feature, the local temperature of the probing volume was extracted successfully with high sensitivity. The dependence of the temperature rise beneath the tip apex with respect to incident laser power was demonstrated experimentally and coincided with analytical results calculated by finite element method based on tip-enhancement effects and steady state temperature via Joule heating. This work can be extended to biological samples and can be utilized to explore the various intermolecular and intramolecular interactions whose Raman signatures can only be detected in the THz-regime.

References:

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