Nonlinear nonlocal infrared plasmonic arrays for pump-probe studies on protein monolayers

SHYAMSUNDER ERRAMILLI, RONEN ADATO, ALAN GABEL, AHMET ALI YANIK, HATICE ALTUG, MI K. HONG, Boston University — Infrared spectroscopy is an exquisite bond-specific tool for studying biomolecules with characteristic vibrational normal modes that serve as a molecular “fingerprint”. Intrinsic absorption cross-sections for proteins are significant ($\sim 10^{-19} - 10^{-21}$ cm$^2$), although small compared to label-based fluorescence methods. We have shown that carefully designed plasmonic nanoantenna arrays can enhance the vibrational signatures by $\sim 10^5$ (Adato et al, Proc Natl Acad Sci USA, 2009). Theoretical modeling combined with polarized FTIR-microscopy show that enhancement is due both to localized effects and nonlocal collective effects, governed by the dielectric properties of silicon and gold nanoantennae, coupled to protein molecules. The resonance properties can be modulated by photoinduced excitation of charge carriers and excitons, causing both a shift in the resonance frequency and a change in the enhancement factor. An ultrafast visible pump laser can then be used to extend visible pump-infrared probe studies to protein molecules even when the molecules lack a chromophore. This provides a toolkit for biophysical studies in which the nonlinear, nonlocal interaction between a 35-fs visible or near-infrared laser and the designed plasmonic nanoantenna arrays are used to study dynamics of protein molecules.

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