

Ultrafast infrared near-field molecular nano-spectroscopy

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Abstract. We demonstrate molecular radiative infrared vibrational free-induction decay on the nano-scale and its control via near-field coupling between the transient molecular polarization and optical antenna properties of the metallic scanning near-field probe tip. This allows for pushing the sensitivity of infrared vibrational spectroscopy into the single molecule regime.

1 Introduction

The extension of ultrafast spectroscopy to the nanoscale to access the underlying spatial inhomogeneities of far-field ensemble averaging spectroscopy has been a long-standing challenge [1,2]. Its application to infrared vibrational molecular spectroscopy is particularly underdeveloped yet highly desirable for its chemical sensitivity and access to chemical dynamics. In this work we combine scattering scanning near-field optical microscopy (*s*-SNOM) with femtosecond infrared spectroscopy for ultrafast molecular vibrational nano-spectroscopy in the mid-infrared. The metallic scanning probe tip provides a nanoscale field localization and near-field coupling via evanescent modes with the induced coherent vibrational polarization. Via its enhanced coupling to the far-field electromagnetic density of states this gives rise to tip scattered *radiative* emission of the vibrational molecular free-induction decay (FID) in competition against the rapid intra- and inter-molecular nonradiative decay in the condensed phase. With increasing degree of near-field coupling between molecular excitation and metallic antenna tip we can control the rate of mode transfer and thus controllably *enhance* the vibrational relaxation from $T_2^{\text{FF}}=720$ fs to $T_2^{\text{NF}}=250$ fs. We demonstrate a drastic tip-enhanced increase in *sensitivity* of ultrafast IR spectroscopy by $>10^4$ probing ensembles as low as 100 vibrational oscillators reaching the realm of single molecule IR spectroscopy. This approach allows for spatio-temporal imaging on nanometer length and femtosecond time scales including extension to multi-dimensions IR nano-spectroscopy [2].

2 Method

The schematic of the experiment is shown in Fig. 1a). Mid-IR radiation tunable from 5-10 μm with pulse duration of 220 fs is generated by difference frequency generation from a high power Ti:S oscillator pumped OPO. The IR beam is focused onto the apex of a metallic scanning probe tip of a modified atomic force microscope operating in dynamic force mode. The tip-scattered IR light is collected in epi-detection, interferometrically heterodyned with the reference field of variable time

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delay, detected by an MCT detector, and demodulated using a lock-in detector at higher harmonics of the tip dither frequency for near-field signal discrimination. Multiple harmonics are recorded simultaneously while scanning the reference mirror for heterodyne recoding of the interferograms. As samples polytetrafluoroethylene (PTFE) serve as a model system for its high transition dipole moment of the C–F bond and high oscillator density. For spatially resolved studies self-assembled monolayers of mercaptohexadecanoic acid (MHDA) on gold are used.

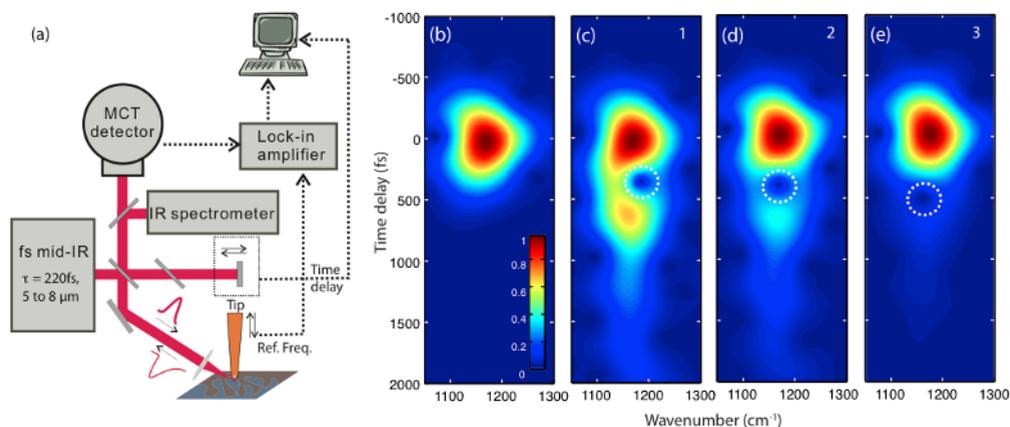


Fig. 1. Near-field control of vibrational coherence: a) Experimental setup for infrared vibrational scattering scanning near-field optical microscopy (s-SNOM). Spectrogram of 220 fs mid-IR laser pulse (b), and radiative tip-scattered near-field free induction decay of molecular polarization in C – F. With increasing tip-sample coupling and polarization transfer to the tip this leads to an associated decrease of the FID decay from 570 to 250 fs (c-d) [6].

3 Results

Fig. 1a) shows the detected tip-scattered interferogram at third cantilever harmonics with Au as non-resonant reference sample after wavelet analysis with a 200 fs gate function, representing the driving laser field in the near-field of the apex with laser tuned to 1170 cm^{-1} center frequency (70 cm^{-1} bandwidth). Fig. 1c) shows the corresponding results for the PTFE sample. Radiative resonant free-induction decay dominated by the symmetric C–F stretch mode ($\nu_1=1160\text{ cm}^{-1}$) is discerned with a dephasing time of $T_2 = (570 \pm 30)\text{ fs}$ and enhanced compared to non-radiatively dominated far-field response of $T_2 = 720\text{ fs}$. With increasing tip-sample coupling (c-e), and increase in efficiency of mode transfer from molecular polarization to the tip, further decrease in vibrational lifetime via $T_2 = (480 \pm 40)\text{ fs}$ (d) to $T_2 = (250 \pm 60)\text{ fs}$ (e) is achieved. The results can be described using a dipole-dipole model reproducing FID behaviour and interference features (dashed white circle) and their evolution with increasing degree of coupling [6].

The resulting increase in sensitivity and spatial localization of the FID signal allows for nanometer spatially resolved imaging with unprecedented sensitivity. Fig. 2 (a-d) demonstrate the molecular monolayer sensitivity of the MHDA SAMs on gold, probing the C=O resonance [67]. With a spatial resolution of 30 nm and a molecular density of $1/\text{nm}^2$ with the contrast and s/n obtained this demonstrates a sensitivity of 100 vibrational oscillators or less, exceeding far-field IR spectroscopy sensitivity by 10^4 .

Our experiments are the conceptual extension of surface-enhanced infrared absorption (SEIRA) [3], phonon IR s-SNOM [4] and tip-enhanced fluorescence [5] into the ultrafast regime. The observed decrease in C–F decoherence time from far-field to tip-enhanced near-field is summarized in Fig. 2e) together with a schematics illustrating the underlying decay channels. Without near-field coupling the vibrational relaxation proceeds primarily through non-radiative intra- and intermolecular coupling corresponding to $T_2^{\text{FF}}=1/\Gamma_{\text{nrad}}$. With increasing coupling of the metallic tip

to the excited molecule coherent polarization transfer into the tip results in a decrease in molecular coherence time. This energy is dissipated via non-radiative scattering in the metal (ohmic loss) and detectable radiative emission $\Gamma_{\text{tip}} = \Gamma_{\text{ohmic}} + \Gamma_{\text{rad}}$.

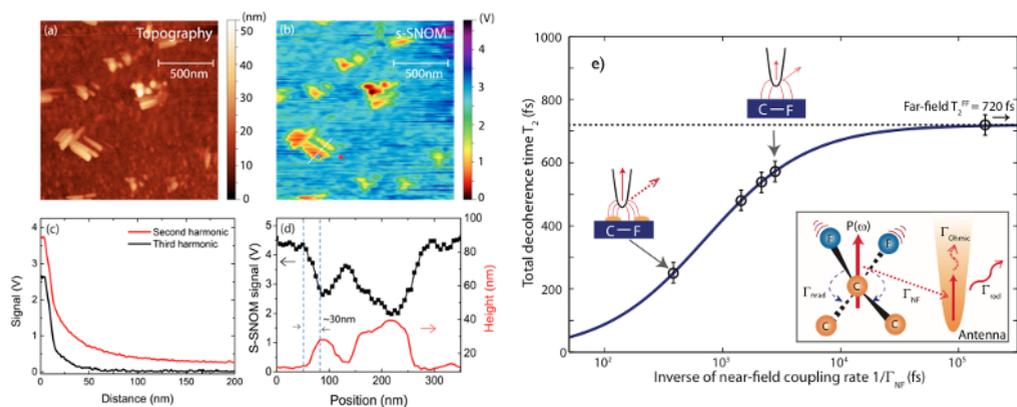


Fig. 2. Ultrahigh spatial resolution tip-coupled FID imaging and sensitivity: Topography (a) and integrated FID image (b) of C=O mode of MHA monolayer, with few 10's nm near-field FID localization (c) and resolution (d) [6]. Model of microscopic optical tip-molecule interaction (e): Decrease of measured near-field vibrational C–F dephasing T_2 with increasing degree of tip-sample coupling plotted as $1/T_2$ (total) = $1/T_2^{\text{FF}}$ (non-rad) + Γ_{NF} . The dipole-dipole coupled mode transfer into the tip/antenna subsequently decays non-radiatively (ohmic loss) or by far-field radiation (detected signal) [7].

In summary we have demonstrated the extension of ultrafast coherent infrared spectroscopy into the near-field regime. We take advantage of the optical antenna properties and field localization of the metallic scanning probe tip. They mediate the mode mismatch between the near-field molecular coherent polarization and far-field density of states succeeding in the competition against the otherwise dominant non-radiative decoherence. This results in enhanced sensitivity of coherent IR spectroscopy and its nano-scale implementation. We expect that the generalization of this approach to any form of linear and nonlinear wavemixing techniques including multi-dimensional spectroscopy will allow for vibrational quantum coherent control and full spatio-temporal imaging of vibrational dynamics on the nanoscale.

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