AIP | Applied Physics Letters

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Citation: Applied Physics Letters **106**, 083113 (2015); doi: 10.1063/1.4913853
View online: http://dx.doi.org/10.1063/1.4913853
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/106/8?ver=pdfcov
Published by the AIP Publishing

Ultrafast pump-probe force microscopy with nanoscale resolution

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(Received 9 January 2015; accepted 18 February 2015; published online 27 February 2015)

We perform time-resolved pump-probe microscopy measurements by recording the local force between a sharp tip and the photo-excited sample as a readout mechanism for the material's nonlinear polarization. We show that the photo-induced force is sensitive to the same excited state dynamics as measured in an optical pump-probe experiment. Ultrafast pump-probe force microscopy constitutes a non-optical detection technique with nanoscale resolution that pushes pump-probe sensitivities close to the realm of single molecule studies. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4913853]

Optical pump-probe spectroscopy comprises a popular set of techniques that enables a direct view of the time-ordered, ultrafast dynamics following optical excitations in materials.[1] Pump-probe measurements are typically carried out on large ensembles of particles or molecules, where the response of individual contributors combines with that from others to produce strong optical signals from the illuminated sample. In many studies, however, the sample is heterogeneous, and the unique response from individual particles is lost when averaging over the ensemble.

The ability to perform pump-probe measurements of single particles relies on technological advances that give rise to detectable signals from increasingly smaller ensembles of optical responders. Focusing light to diffraction-limited volumes, which is the excitation geometry used in various forms of pump-probe microscopy, increases the sensitivity to sub-micrometer scale particles.[2–4] The far-field optical microscope is sensitive enough for enabling pump-probe measurements of nanostructures with large optical cross sections, including metal nanoparticles,[5] semiconducting quantum dots,[6] and carbon nanotubes.[7]

Using optical excitation in combination with scanning probe techniques offers an opportunity to perform pump-probe measurements at sub-diffraction limited resolution, which can further increase the sensitivity of the measurement.[8,9] Recent examples of near-field pump-probe microscopy studies include ultrafast exciton dynamics in single quantum dots[10] and molecular nanocrystals,[11] and time-resolved plasmonic dynamics in graphene.[12] However, pushing the sensitivity of these techniques to the level of single molecules is challenging. Optical detection of the pump-probe effect is not background free: it relies on the ability to register a pump-induced intensity change in the scattered probe radiation. In the single molecule limit, despite recent successes,[13] the induced gain or loss in the probe detection channel may be well below the experimental shot noise. In this regard, detection strategies that circumvent the deleterious effects of the large optical background in nonlinear pump-probe measurements would be highly desirable.

Non-optical detection strategies offer a promising alternative for detecting the pump-probe response on the nanoscale. A particularly attractive approach is photo-induced force microscopy (PiFM). It has recently been shown that PiFM can detect optical transitions in chromophores by registering the changes in the electromagnetic forces between an atomically sharp tip and the sample.[14] The gradient force between the light-induced dipoles in the tip and molecule is a sensitive function of the molecule's polarizability, and thus offers a mechanism for nanoscale spectroscopy based on non-contact force detection.[15,16] PiFM is capable of probing various forms of optical interactions, including nonlinear optical excitation of the material, as recently demonstrated in force detection of stimulated Raman scattering in molecules using cw laser illumination.[17]

In this work, we show that the ultrafast excitation dynamics of a molecular chromophore can be monitored in a non-optical manner through time-resolved (tr-)PiFM. This approach enables sub-diffraction limited measurements on the 10 nm scale with a time resolution defined by the temporal width of the femtosecond pump and probe laser pulses. We demonstrate that the tr-PiFM signal is sensitive to the same excited state dynamics probed in far-field optical pump-probe measurements. A non-optical detection technique, tr-PiFM suppresses the impact of the optical background that is intrinsic to conventional optical pump-probe techniques, and offers a viable route for improving the detection sensitivity down to the single molecule limit.

The basic layout of the tr-PiFM experiment is shown in Figure 1. Two fs laser beams—a pump beam at frequency ω_1 and a probe beam at frequency ω_2—are incident on a microscope objective. The pump and probe beams are focused to a diffraction limited spot and optically excite the sample. A cantilevered, gold coated, scanning probe microscope tip is positioned in the focal spot forming a tip-

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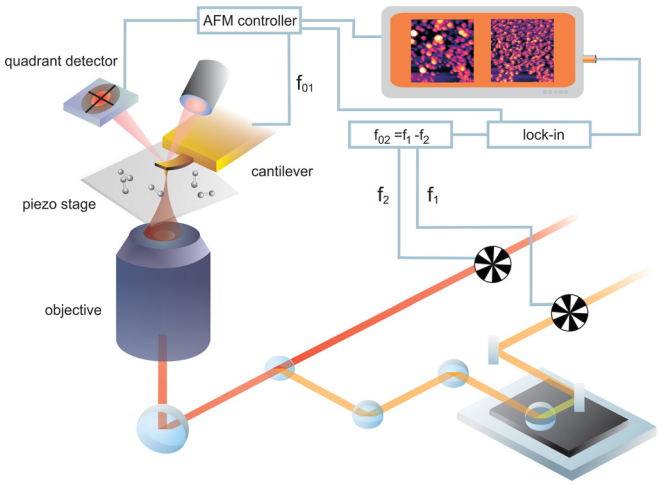

FIG. 1. Sketch of the time-resolved photo-induced force microscope.

molecule junction. The photo-induced dipoles in the tip and molecule mutually interact, and the field-gradient between them results in a force.[14–16] In case of a nonlinearly induced polarization in the molecule that is third-order in the fields, $P^{(3)}$, the time-averaged force can be written as[18]

$$\langle \mathbf{F} \rangle \propto \mathrm{Re} \int d\mathbf{r} P^{(3)}(\mathbf{r}) \cdot \nabla \mathbf{E}_2^*(\mathbf{r}), \tag{1}$$

where $\mathbf{E}_2$ is the total probe field in the junction and $\mathbf{r}$ is the position of the molecule relative to the tip dipole. It is interesting to compare Eq. (1) with the signal S in optical pump-probe microscopy experiments, measured at a far-field position $\mathbf{R}$, which is written as[19]

$$S \propto \mathrm{Im} \int d\mathbf{r} P^{(3)}(\mathbf{r}) \cdot \mathbf{E}_2^*(\mathbf{R}). \tag{2}$$

We see that both the photo-induced force and the optical pump-probe signal depend on the coherent mixing of the (complex) nonlinear polarization with the probe field. An important difference is that in optical measurements, the mixing is with the probe field at the far-field detector, whereas in PiFM, the mixing is with the field *gradient* in the near-field. In addition, the near-field force depends on the real part of the interaction, while the optical signal scales with the imaginary part.[15]

In the pump-probe process considered here, the pump excites the molecule from the ground state to an excited state population $|s_1\rangle\langle s_1|$. The probe pulse, time-delayed by τ, transfers population to a second excited state of higher energy, in a process called excited state absorption. The τ dependence of this process is determined by the lifetime τ_1 of $|s_1\rangle\langle s_1|$. In pump-probe experiments where the dynamics are governed by excited state populations, we expect the same time-delay dependence for the PiFM and the optical pump-probe signal: they both decay with τ_1. Our task is to show that the force- and optically-detected signals indeed follow the same time dependence.

To detect the pump-probe process in PiFM, the pump and Stokes beams are amplitude modulated at f_1 (pump) and f_2 (probe), respectively. Successive interactions of the molecule with the pump and probe radiation gives rise to a dipolar modulation at $\Delta f = f_1 - f_2$, which in turn produces a modulation of the photo-induced force at Δf. Note that neither f_1 nor f_2 couples to a mechanical resonance of the cantilever. tr-PiFM is based on sensitively detecting the cantilever's mechanical motion at Δf, which is achieved by tuning Δf to the second mechanical resonance of the cantilever at f_{02}. The $\Delta f = f_{02}$ resonance condition selectively amplifies the optical interactions induced by the *joint* action of ω_1 and ω_2, enabling a virtually background-free detection of the pump-probe response. The signal at f_{02} is demodulated with a lock-in amplifier, and its amplitude is plotted as a function of sample position, yielding nanoscale images with pump-probe contrast. A topographic image is simultaneously acquired at the fundamental resonance f_{01} of the cantilever.

In the experiments reported here, the pump and probe beams are derived from a synchronously pumped optical parametric oscillator (OPO) source (Inspire OPO pumped by MaiTai, Spectra-Physics), which produces 80 MHz, 200 fs pulse trains. The pump beam is set at 809 nm and the probe beam is tunable throughout the visible range. The pump and probe beams are amplitude modulated at $f_1 = 1000$ kHz and $f_2 = 2098$ kHz, respectively, using acoustic optic modulators. The excitation pulses are pre-compressed with a prism compressor to account for dispersion in the microscope optics. The average power of the two laser beams in the focal plane of the microscope objective (NA = 1.4 oil) is adjusted to $\sim$350 μW. The force measurements are carried out on a custom-modified non-contact/tapping-mode atomic force microscope (Resonant Force Microscope from Molecular Vista Instruments and FlexAFM from Nanosurf). We use a cantilever with $f_{01} = 178$ kHz, quality factor $Q_1 = 490$ and stiffness constant $k_1 = 58$ N/m at the fundamental resonance, and $f_{02} = 1098$ kHz, quality factor $Q_2 = 588$, and stiffness constant $k_2 = 2267$ N/m at the second resonance, operated with a free oscillation amplitude of $A_{01} = 47$ nm at the fundamental resonance. Note that $\Delta f = 1098$ kHz, which coincides with the second mechanical resonance f_{02} of the cantilever.

We first study the excited state dynamics of bulk silicon naphtalocyanine (SiNc). The energy of the pump beam coincides with the transition from the ground state to the S_1 state of SiNc. The time- and spectrally-resolved transient absorption of bulk SiNc is given in Figure 2, using standard optical detection. It can be seen that at negative time delays, when the probe proceeds the pump, the pump-probe signal is negligible. At positive time delays, SiNc displays a strong excited state absorption that peaks at a probe wavelength of 605 nm,

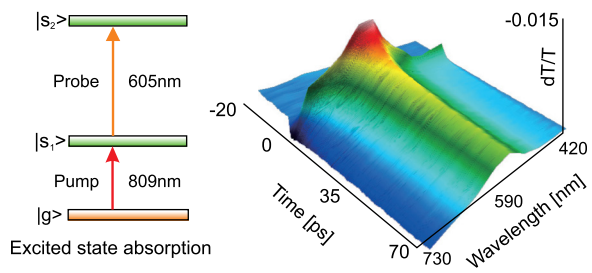

FIG. 2. Energy level diagram (left) and time-resolved transient absorption spectrum (right) of SiNc using optical detection.

and decays exponentially with a lifetime of $\tau_1 = 7.9$ ps. Beyond a probe wavelength of ~700 nm, the signal reverses sign, an indication of ground state depletion.

We next examine the pump-probe response of SiNc at the nanoscale using tr-PiFM. The sample consists of SiNc nanoclusters, which vary in size between several micrometers to less than 10 nm in diameter, spin cast from solution onto a borosilicate coverslip. Figure 3 depicts images of sub-100 nm SiNc nanoclusters taken at two different time delays and the probe wavelength tuned to 605 nm, where we expect a strong excited state absorption. The left column shows the topography (3(a)) and PiFM (3(c)) images when the time delay is set to −5.9 ps. Whereas the topography image indicates the presence of multiple clusters, the PiFM image, measured at Δf, displays limited contrast. The situation changes when the pump-probe time delay is tuned to 0.7 ps. As expected, the topography image (3(b)) remains unaltered upon changing the time delay. The PiFM image (3(d)), however, changes dramatically and now clearly reveals the SiNc structures. The PiFM signal at positive time delays indicates the presence of a force modulated at Δf, as induced by the joint action of the pump and probe pulses.

Note that unlike the topography image, which shows nanoscale height variations among the clusters, the signal magnitude in the PiFM image is nearly uniform. This response is expected from the spectroscopically sensitive gradient force, which is a local force that is exclusively manifested at nm distances from the surface and relatively independent of volume effects.[16] In addition to larger clusters, Figure 3(d) shows smaller structures down to a width of ~10 nm, which corresponds to the spatial resolution of the PiFM microscope. Under the excitation conditions used, the magnitude of the photo-induced pump-probe signal at zero time delay is ~500 μV, which translates into a force of 370 pN. When either of the optical beams is blocked, the signal is reduced to less than 5 μV, which is also the background signal in the absence of light.

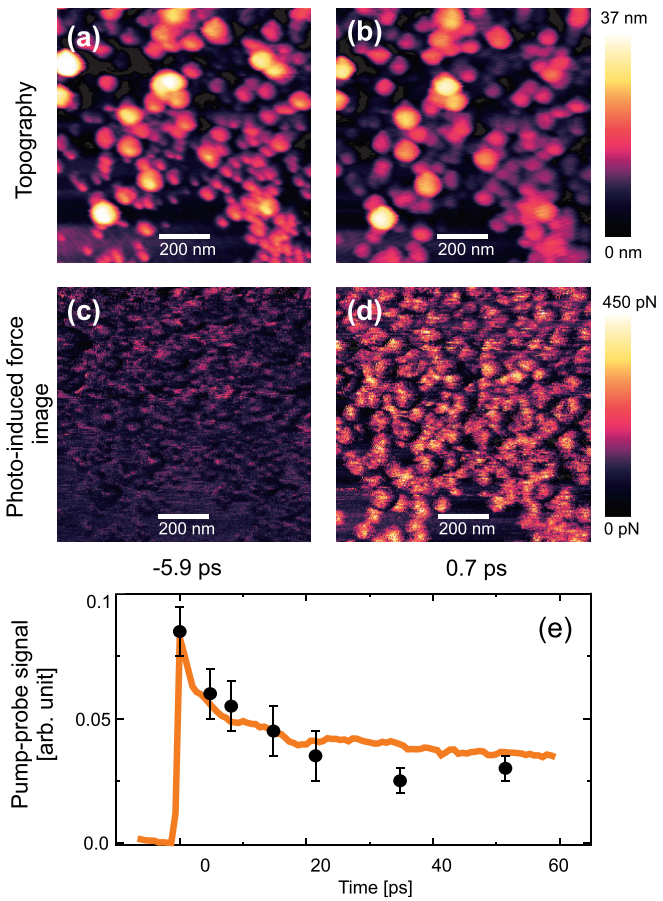

FIG. 3. Topography image (a) (or (b)) and optical force image (c) (or (d)) are simultaneously recorded at negative time delay −5.9 ps (or positive time delay 0.7 ps). (e) direct comparison between the optically detected pump-probe signal (orange solid line) and the tr-PiFM signal (black circle dots).

In order to further investigate the pump-probe signature in tr-PiFM, we record images of a single cluster at various positive time delays. The magnitude of the photo-induced force is shown by the solid dots in Figure 3(e), revealing that the tr-PiFM signal decays on the picosecond timescale. The tr-PiFM signal is compared with the time-resolved pump-probe signal of a larger cluster, using far-field optical detection in the same microscope. It can be clearly seen that the force-detected signal and the optically detected signal display the same dynamics: they both decay with the excited state lifetime of the S_1 state in SiNc.

This work demonstrates the feasibility of probing the ultrafast nonlinear optical response of nanoscopic materials in a non-optical manner by measuring changes in the local forces between a sharp tip and the sample. The PiFM approach can be used to examine various pump-probe transitions in the material, as shown here for excited state absorption, at a resolution far below the diffraction limit of light. Because the sensitivity in PiFM is not primarily limited by the large optical background that affects the sensitivity of conventional optical pump-probe measurements, the technique represents an attractive means of interrogating the nonlinear optical properties of small quantities of molecules. This work shows pump-probe PiFM signals from molecular assemblies as small as 10 nm, which is near the resolution of the microscope. Further optimization may push the sensitivity well into the limit of individual chromophores, setting the stage for a wide array of single molecule ultrafast spectroscopy studies at the nm/fs space-time resolution.

This work was supported by the National Science Foundation, Grant No. CHE-1414466.

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