Quantifying Ultrafast Three-Dimensional Transport Using Interferometrically Enhanced Pump-Probe Microscopy

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We present a novel microscopic technique to access local transient optical constants and carrier motion in thin-film materials in three dimensions, with sub-10 nm spatial precision and sub-15 fs temporal resolution. Our experimental scheme is based on imaging a traditionally defocussed plane in an interferometrically enhanced femtosecond pump-probe microscope, combining the amplitude and phase contrast between the perturbed and unperturbed probe due to the local photoinduced complex refractive index change. We find that our experimental approach is well described by a simple optical model based on a radially averaged Gaussian photoexcitation approximation, which we benchmark using finite-difference-time-domain calculations. Measurements on the organic semiconductor pentacene reveal an unexpected sub-1 ps out-of-plane motion of the correlated triplet-triplet exciton. Our approach is applicable to thin film materials in any pump-probe experiment, and holds promise for quantitative studies of three-dimensional transport in semiconductors, especially relevant to next-generation functional materials.

Elucidating the three-dimensional transport of excitations in condensed matter is key to advancements in our understanding and utilisation of functional materials ranging from novel quantum systems to next-generation optoelectronic materials [1–4]. Of particular interest are quantum coherent systems and heterogeneous, disordered systems which require both ultrafast time resolution and local measurements to study and develop their coherent transport characteristics [5–7].

The emerging field of optical pump-probe microscopy, which extends standard pump-probe spectroscopy to a microscope geometry, is well suited to explore these spatio-temporal realms, as it provides direct access to the transport of excitations via ultrafast transient spectra with sub-diffraction limited spatial precision [8–11]. While pump-probe microscopy has opened a variety of experimental possibilities, it has two key limitations: first, it exclusively probes two-dimensional in-plane carrier transport, and second, it lacks the ability to quantitatively characterise changes in the system’s complex refractive index. While other techniques, such as ultrafast ellipsometry, interferometric scattering microscopy, harmonic optical tomography and ultrafast off-axis holography have developed general routes to track objects over large areas in three-dimensions, they are currently not suitable to quantify the three-dimensional transport characteristics of local excitations in functional condensed matter systems [12–14].

In this Letter, we report a general experimental scheme that offers quantitative access to the three-dimensional motion of the material’s joint-density-of-states through changes in the photoinduced local transient complex refractive index. We demonstrate our approach by tracking the ultrafast photoinduced changes in local transient complex refractive index of the organic semiconductor pentacene. By developing a simplified optical model, which we benchmark against finite-difference-time-domain (FDTD) simulations, we are able to capture the ultrafast out-of-plane transport characteristics of the correlated triplet-triplet state.

The conceptual shift that enables this advancement is the treatment of a diffraction-limited optical perturbation in a thin film material as a well defined part-absorptive, part-refractive local object akin to a gold nanoparticle or polystyrene bead. Studying differential images of the presence and absence of this photoinduced object allows us to capture the key effects of this perturbation by removing computationally challenging aberrations. This allows us to photoinduce such local objects and subsequently track the magnitude of the complex refractive index change along with its two-dimensional lateral extent and vertical shifts in its principal plane which allows for quantitative tracking of the photoinduced perturbation in three-dimensional space with ultrafast time resolution.

Our experimental setup (Fig 1a,b) is based on a transmission widefield microscope equipped with an oil immersion objective (NA = 1.1). A pump pulse (560 nm, 13 fs) is focused onto the sample by the objective to produce a diffraction-limited (270 nm full-width-half-maximum (FWHM)) local photoexcitation. After a variable time delay, a counter-propagating widefield probe pulse (750 nm, 7 fs, ~20 μm FWHM) is transmitted through the sample and imaged onto an emCCD detector. Widefield probe images in the presence and absence of the pump excitation are recorded by chopping the pump pulse at 30 Hz. The pump and probe pulses are derived from a Yb:KGW amplifier (1030 nm, 5 W, 200 kHz) via white light continuum generation and subsequent spectral filtering and compression with chirped mirrors [8–9].
complex refractive index change, $\Delta n = \Delta n + i\Delta k$ (Fig 1a). This index change weakly perturbs the time-delayed plane-wave probe pulse incident on the sample, leading to local changes in its phase and amplitude [17]. The large background unperturbed probe field interferes with this perturbed probe field to form a spatial interference pattern along the propagation direction, attenuated by the coherence length of the probe ($\sim 2.1 \, \mu m$). The objective and imaging lens then image this spatial interference pattern combined with the attenuation of the probe on a camera. A variety of imaging planes are therefore available on the camera, and we study an interferometrically enhanced image that is spread over several pixels [18,19].

We demonstrate our sensitivity to both absorptive and phase contrast induced by a photoexcitation by measuring the differential transmitted images of a photoexcited monolayer of MoS$_2$ for several image planes 200 fs after excitation (Fig 1c). We chose a monolayer to ensure that we characterise the experimental setup’s intrinsic interferometric capacity without convolution through the sample’s thickness. To access different image planes of the spatial interference pattern, we translated the imaging lens of our microscope to relay different planes from the image space onto the camera, akin to remote focusing [20]. The resulting z-stack resembles the 3D point-spread-function expected when coherently imaging a diffraction limited object and the asymmetry in the $z$ direction and the intensity structure about the focus establishes that phase contrast contributes to the measured signal [14].

We build a simplified optical model of this experiment motivated by the fact that the pump-probe experiment is a measurement of photoinduced polarisation change in the third-order susceptibility $\chi^3$ [21,22]. As the probe pulse is always temporally separated from the pump, time-ordering allows us to treat the pump-on and pump-off probe signals as measures of the photoexcited and ground state dielectric functions (or complex refractive index) of the material, respectively. The dielectric function $\epsilon$ measured by a weak probe is defined by,

$$D = \epsilon E = \epsilon_0 E + P$$

where $D$ is the displacement field, $\epsilon_0$ is the permittivity of free space, $E$ is the electric field of the probe and $P$ is the polarisation of the sample [23]. Before the pump pulse arrives, when the system is in the ground state (pump-off), the polarisation $P$ measured by the probe is given by, $P = \epsilon_0 \chi^{(1)} E$. Using Eqn. (1) the ground state dielectric function $\epsilon_{off}$ is therefore given by, $\epsilon_{off} = \epsilon_0 (1 + \chi^{(1)})$. After the arrival of the pump pulse, the system is in the excited state (pump-on), the polarisation $P$ measured by the probe is given by, $P = \epsilon_0 (\chi^{(1)} E + \chi^{(3)} E_{pu} E_{pu} E)$, where $E_{pu}$ is the pump electric field. Again, using Eqn. (1) the excited state dielectric function $\epsilon_{on}$ is therefore given by, $\epsilon_{on} = \epsilon_0 (1 + \chi^{(1)} + \chi^{(3)} E_{pu} E_{pu})$. Therefore the overall perturbation to the dielectric function,

$$\epsilon_{on} - \epsilon_{off} = \Delta \epsilon = \epsilon_0 \chi^{(3)} E_{pu}^2.$$
tinction coefficient for the pump [24]. For thin film samples of thickness less than $z_R$, and ignoring in-plane anisotropy, $\sigma$ can be approximated to be constant $O(z/z_R^2)$ through the thickness of the sample. We can therefore approximate the photoinduced refractive index change as,

$$\Delta n(r) = (\Delta n_0 + i\Delta k_0) \exp \left[ \frac{-r^2}{2\sigma_0^2} - \frac{\omega_{ps} \alpha z}{c} \right]$$  \hspace{1cm} (5)

over the sample length, where we have absorbed the constants and $\chi^{(3)}$ into the transient optical constants $\Delta n_0 + i\Delta k_0$.

The electric field of the probe directly after the photoexcited sample is typically obtained by numerically integrating the incident electric field over the spatially dependent refractive index profile along the propagation direction $z$ using Maxwell’s equations and propagating its plane wave decomposition to the plane $z_0$ [25]. We simplify this problem considerably by replacing these integrals with a constant profile through the depth of the sample, which is situated about its principal plane, $z_c$ [20]. We note that for a non-rigid optical object, a shift in $z_c$ may arise from a shift in the entire object or from a change in shape and it can be calculated using more advanced analytic approximations or the full numerical FDTD treatment [27]. The phase accumulated by the probe at the object plane $z_0$ after interacting with the sample is therefore sensitive to $\Delta z = z_c - z_0$ which allows us to track motion of the principal plane of the refractive index profile in $z$. This approximation allows us to compute the near-field electric field by multiplying the incident field with the laterally varying Fresnel complex transmission coefficients of a Gaussian disc situated about $z_c$,

$$E^{nf}(r, z_c) = E_i[(1 - r_1(r))[1 - r_2(r)]l(r)]$$  \hspace{1cm} (6)

where $t = e^{i\tilde{\Delta}n r \sigma}$ captures the attenuation of $E_i$ through the sample, $r_1 = \frac{n_u - n}{n_u + n}$ captures the reflection at the air-sample interface and $r_2 = \frac{n_0 - n_s}{n_0 + n_s}$, captures the substrate-sample interface. Here $n_s$ is the substrate refractive index, $L$ is the sample thickness and $k$ is the probe wavevector. The amplitude and phase of $E^{nf}$ therefore encodes three-dimensional spatial information of photoexcited carrier motion through $\Delta \tilde{n}(r)$ and $z_c$.

The probe electric field at the objective’s input aperture can be approximated as the Fourier transform of the near-field electric field, $E^{ff}(k_r, z_c) = \mathcal{F}(E^{nf}(r, z_c))$, where $k_r$ is the spatial frequency of the probe in the radial direction and $\mathcal{F}$ is the Fourier transform (Fig 1). To study the spatial interference of the probe in different planes in the object space where the field is interferometrically enhanced, we calculate the far-field electric field of the plane $\Delta z = z_0 - z_c$ by propagating the plane wave decomposition an extra distance $\Delta z$,

$$E^{ff}(k_r, z_0) = e^{i\Delta z \sqrt{k^2 - k_r^2}} E^{ff}(k_r, z_c).$$

![FIG. 2. Approximations and benchmark against finite difference time domain (FDTD) calculations. a) Comparison of the optical model and FDTD calculated three-dimensional point-spread of the differential transmission in the far field of a pure refractive and pure absorptive profile. b) Cross-sections along the dotted lines showing excellent quantitative agreement between the optical model and FDTD calculations.]

To calculate the image on the camera by the objective-imaging lens system, we compute an inverse Fourier transform after filtering the high spatial frequencies as the objective’s $NA$ specifies, yielding,

$$E^{im}(r', \Delta z, n, k) = \int_{-\kappa NA}^{\kappa NA} E^{ff}(k_r, \Delta z)e^{-iknr'} dk_r$$  \hspace{1cm} (7)

which is a simplified version of the Richards-Wolf integral [25][30].

We calculate the widefield normalised differential transmitted image of a photoexcited refractive index change (at a given probe wavelength), $\Delta \tilde{n}(r) = \Delta n(r) + i\Delta k(r)$ centred at $z_c = z_0 - \Delta z$ on a spatially constant, static background $\tilde{n}_0(r) = n_0 + ik_0$ centered about $z_0$,

$$\frac{\Delta T}{T}(r', z_0 - \Delta z, \Delta \tilde{n}) = \frac{|E^{im}(r', \Delta z, n_0 + \Delta \tilde{n})(r)|^2}{|E^{im}(r', z_0, n_0)|^2} - 1.$$  \hspace{1cm} (8)

Experimental control over the image plane $z_0$ is achieved by translating the imaging lens in the infinity space of the objective to relay different conjugate planes to the camera [20]. The effective axial distance accessible by moving the imaging lens by a distance $z_0'$ is given by the axial magnification of the imaging system (Fig 1). Ensuring that neither the imaging lens nor the objective move during a pump-probe measurement fixes $z_0$, allowing us to track changes in $z_c$, $\sigma$ and transient refractive index $\Delta \tilde{n}$ as a function of pump-probe delay.

We performed FDTD calculations at a variety of $\Delta n(r)$, sample thicknesses, substrate refractive indices and wavelengths in order to benchmark the validity of our approximations (in particular, Eqn. 6) in the true experimental configuration. We include the refractive index mismatches with the immersion medium and consider a spatial $n, k$ material with a radial Gaussian disc profile. In all cases we find that the nearfield amplitude and phase are very well approximated by Gaussians. In order to
highlight any shortcomings of our model we demonstrate here a purely refractive ($\Delta n(r) = -0.5$, $\Delta k(r) = 0$) and purely absorptive ($\Delta n(r) = 0$, $\Delta k(r) = -0.5$) photoexcitation perturbation on a sample of refractive index $\tilde{n} = 1.5 + 1i$ (Fig 2). We find excellent agreement in the far-field differential transmission images, demonstrating that the near-field approximations are systematically cancelled in the differential far-field images. These results confirm that our simple model manages to capture the relevant optical effects of the local refractive index perturbation and can be used to retrieve the transient optical constants, lateral expansions and vertical shifts in the principal plane from experimental data.

We applied our technique to study the three-dimensional transport of excitons in a thin film of the organic semiconductor pentacene. Upon photoexcitation, pentacene forms spin-correlated triplets pairs through the ultrafast quantum coherent process of singlet fission. This process has wide relevance in the fields of photon multiplication and quantum computing where insights into the transport of excitations are critical. We photoexcite a 100 nm evaporated film of pentacene with the described experimental setup and image the interferometrically enhanced probe using a bandpass filter at the energy of interest.

Fig. 3a,b demonstrates that our developed optical model (Eqn. 8) satisfactorily describes the experimental data. The photobleaching spectral feature at 1.85 eV in pentacene thin films serves as a signature of the photoexcited singlet exciton population, which converts to a correlated triple-triplet pair state of overall singlet character in 50-80 fs. The presence of the triplet state is associated with a photoinduced absorption spectral feature at 1.68 eV. As shown in Fig. 3c,d, we find that the magnitude of the real and imaginary part of the refractive index at both probe energies changes over ultrafast, sub-100 fs timescales with $\Delta k < 0$ and $\Delta n > 0$ at 1.85 eV and $\Delta k > 0$ and $\Delta n < 0$ at 1.68 eV, in agreement with a Kramers-Kronig analysis of the transient transmission spectra retrieved from ensemble transient transmission experiments. We note that dynamics within 100 fs after photoexcitation (Fig. 3) grey highlighted) suffer from coherent artefact contributions, which our model does not accurately describe due to the violation of the time-ordering assumption. Irrespective, after $\sim$100 fs at both energies, the population of excitations remains constant, as neither $\Delta k$ nor $\Delta n$ changes significantly, implying that the joint-density-of-states ($\propto \text{Im}(\epsilon)$, where $\epsilon = \tilde{n}^2$) at these energies is fixed.

At 1.85 eV, we observed a lateral expansion in $\sigma$ of $\sim 10$ nm and no observable change in $\Delta z$ over 2 ps (Fig 3a). At 1.68 eV, however, we identified over the first 500 fs a contraction of $\sigma$ by $\sim 15$ nm and a correlated out-of-plane motion of the principal plane of the signal by $\sim 6$ nm (Fig 3c). As the joint-density-of-states remains constant (compare to Fig 3a), this correlated lateral contraction and motion of the principal plane implies that the excitons expand along the $z$-direction. The timescale of this motion matches a recently discovered 1 THz lattice vibration associated with triplet-pair separation, and could be related to the finite momenta of the triplet excitons in pentacene exhibiting a non-zero group velocity upon formation from zone-center singlets, however detailed physical insights are beyond the scope of this study.

It is interesting to note that the absolute size of the near-field $\sigma$ retrieved from our technique is substantially larger at 1.68 eV compared to 1.85 eV, and also larger than the size of the pump ($\sigma_p = 115$ nm). This observation suggests that the sub-100 fs singlet fission dynamics in pentacene cause a lateral expansion that our method cannot capture due to complications arising from coherent artefact contributions.

These results remain qualitatively unchanged when performed under different photoexcitation densities of the pump pulse. We further note that the higher signal-to-noise at 1.68 eV compared to 1.85 eV is due to the larger $\Delta n$ and potentially due to the selection of an imaging plane with a more unique solution to Eqn. 5 which increases the interferometric sensitivity of our model. This appears to ultimately limit the signal-to-noise and localisation precision of this experiment.

In conclusion, we have developed an interferometrically
enhanced femtosecond pump-probe microscope to characterise three-dimensional transport of local excitations in thin film materials. We have successfully characterised the magnitude and spatial extent of three-dimensional photoinduced refractive index change in a thin film semiconductor pentacene where our approach revealed an ultrafast out-of-plane expansion of the correlated triplet-triplet pair state. Our technique is not limited to optical pump-probe techniques or femtosecond timescales, but can be equally applied for other pump-probe schemes involving electron or X-ray sources over any experimentally accessible timescale [20]. Going forward we believe that our approach in conjunction with further modelling, will enable direct insights into the transport of excitations in a range of condensed matter systems over a variety of timescales.

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