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Nano-FROG: Frequency Resolved
Optical Gating by a nanometric object

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Abstract: We present a technique to characterize ultrashort pulses at the focal plane of a high numerical aperture objective with unprecedented spatial resolution, by performing a FROG measurement with a single nanocrystal as nonlinear medium. This approach can be extended to develop novel phase-sensitive techniques in laser scanning microscopy, probing the microscopic environment by monitoring phase and amplitude distortions of femtosecond laser pulses.

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excitation and harmonic generation yield [3]. Intra-pulse micro-CARS [4, 5] and coherent microscopy. For instance, pulse-shaping has been applied to temporally recompress femtosecond pulses in the fields of time-resolved and coherent spectroscopy have recently been bridged to sample is typically achieved by ultrashort laser pulses, a large number of techniques developed including higher spatial resolution, deeper sample penetration, better spectral separation between signal and excitation, and virtually no out-of-focus bleaching. [1] As nonlinear excitation of the sample is typically achieved by ultrashort laser pulses, a large number of techniques developed in the fields of time-resolved and coherent spectroscopy have recently been bridged to microscopy. For instance, pulse-shaping has been applied to temporally recompress femtosecond pulses at the measuring site, to improve spatial resolution [2], and to increase fluorescence excitation and harmonic generation yield [3]. Intra-pulse micro-CARS [4, 5] and coherent con-
trol microscopy have demonstrated successful for obtaining higher selectivity in the imaging of structures in very diverse samples [6]. More recently, interest has been focused on the effects of pulse polarization, and the related capability to achieve control of optical near field. [7]

To fully exploit the potential of these techniques, equally developed pulse diagnostics capabilities are necessary. In particular, considering that femtosecond pulses are prone to undergo modifications during their propagation (temporal stretching by group velocity dispersion, higher order distortions in the spectral-phase induced by microscope objectives [8], spectral amplitudes modulation by sample scattering [9] and absorption) an in situ measurement of the excitation pulse is customary for any advanced application. Since the early work of Muller et al. [10], several techniques, largely based on Frequency Resolved Optical Gating (FROG), have been proposed, but until present none of them incorporates the spatial resolution necessary to resolve features inside the focal region of a high numerical aperture (NA) objective [11]. The starch-based FROG approach proposed by Amat et al. [12] and the scanning SEA TADPOLE technique by the group of Trebino [13] represent a clear progress in this direction, but unfortunately both techniques are limited to a spatial resolution of a few micrometers.

We propose a technique to achieve unprecedented spatial resolution, without renouncing at the tenability of the FROG technique. Our approach, which can be implemented on a conventional or an inverted laser scanning microscope, is based on the use of individual noncentrosymmetric nanoparticles (NPs) as nonlinear medium. Considering the recent interest towards the use of NPs as exogeneous contrast agents for multiphoton microscopy of cells [14], the approach described here can be further developed to provide phase-sensitive information by monitoring the distortions induced by the microscopic local environment around the NP on femtosecond pulses.

2. Experimental

Set-up. As illustrated in Fig. 1, the output of a Synergy 20 Femtosource Ti:Sapphire oscillator (40 nm bandwidth) is temporally stretched to 364 fs by a grating compressor (C) to precompensate for dispersion of transmissive optics,[15] The beam is then split at beamsplitter BS1 into the two arms of an interferometer. A delay stage (DS) with 0.017 μm step resolution is used to induce a difference between the optical paths. The two pulses from the interferometer, after being recombined at BS2, are collinearly injected into an inversed microscope equipped with a 1.3 NA 100 × oil immersion objective. Notice that the collinear geometry of the set-up is imposed by the necessity to fully fill the whole aperture of the objective to maintain high spatial resolution. The SHG signal generated by single NPs dispersed on a standard glass slide is collected in the backward direction by the same objective, spectrally dispersed by a scanning monochromator (2 nm resolution), and detected by a photomultiplier. Lockin detection is used to increase detection sensitivity. Considering the long irradiation of a single NP, shutter 1 (S1) is used to reduce photodegradation by regularly blocking the laser for a few seconds to allow heat evacuation at the sample site. Shutter 2 (S2) is closed to measure the reference SHG signal generated by a single arm of the interferometer for further data correction.

Fe(IO₃)₃ nanoparticles. The NPs used in this work can be easily obtained by a cost effective co-precipitation synthesis as a dispersion of nanocrystals with typical grain size ranging from 20 to 300 nm [16]. Fe(IO₃)₃ nanocrystals possess a series of attracting properties, including low-chemical reactivity, stability in aqueous environment in a wide thermal and pH range, and possibility of surface functionalization. The non-centrosymmetric crystal structure (space group P6₃) determines their polarization-sensitive nonlinear optical response.[17] Fe(IO₃)₃ nanocrystals are very efficient frequency doublers (nonlinear coefficients about 10 pm/V) and are transparent from visible up to 12 μm.[18] Moreover, given that their size is smaller than the...
Fig. 1. Experimental set-up. C: folded compressor for dispersion precompensation; I: interferometer; DS: stepper motor; MC: scanning monochromator; PMT: photo-multiplier tube. The excitation polarization is controlled by a zeroth order \( \lambda/2 \) plate (PWP). Shutter S1 is used to completely block the beam, while S2 for blocking one arm of the interferometer.

excitation wavelength, no phase-matching constraints apply to the frequency-mixing process, allowing complete spectral doubling of broadband femtosecond pulses.[19] To provide a comparison with bulk crystals limit, the phase matching conditions have been calculated within the usual description of sum-frequency generation for a crystal of 1 \( \mu \)m length using the dispersion properties of Li(IO₃) [20] since Fe(IO₃)₃ bulk properties are still partially unknown. In configuration ooe for SHG, this results in a phase-matching acceptance angle greater than \( \pi \) radians, and in an acceptance bandwidth larger than 800 nm. [21]

A SHG image of an ensemble of nanocrystals deposited on a microscope slide is shown in Fig. 2(c). From previous comparisons with atomic force microscopy [17], the size of the crystals deposited on a glass substrate by evaporation of a solution droplet is expected to be in the range between a few tens to a few hundreds of nanometers. The particle highlighted by the 1 \( \mu \)m side square in Fig. 2(c) was used as nonlinear medium for the measurements presented in the following. The NP size is slightly larger than the two-photon spatial resolution of our set-up (~500 nm FWHM) along one axis, and limited by the resolution along the other. [17]

3. Results

The autocorrelation trace reported in Fig. 2(a) was recorded after maximizing the SHG response as a function of the incident laser polarization as described in [17]. The time increment corresponds to 1.8 fs, the interference fringes of the two electric fields at 800 nm (T=2.66 fs) are therefore not fully resolved. On the other hand, the expected 8:1 ratio between the trace maximum and the wings is almost perfectly recovered: as remarked by Fittinghoff et al., small deviations from the theoretical ratio are expected in presence of high NA objectives. [22].

The retrieval of a symmetric autocorrelation trace, showing the theoretical fringes-to-offset ratio confirms the good alignment of the two interferometer arms, the balance among their intensities, and the absence of saturation in the frequency-mixing process. After this preliminary characterization, which indicates a FWHM pulse duration of 69 fs, we could proceed to acquire the full collinear-FROG (cFROG) trace of Fig. 2(b). Due to the long acquisition time necessary for measuring the full cFROG curve, it was necessary to correct for slow sample photodegradation. To this end, we systematically monitored a reference value corresponding to the SHG generated by a single arm of the interferometer. The correction procedure incorporates
the experimental time-dependence extracted from the autocorrelation trace to associate the right weight at different time delays to the photodegradation baseline correction. For the measurement in Fig. 2(b) photodegradation amounts to \( \sim 50\% \) decrease of the SHG signal intensity over the complete scan.

The resulting trace can be interpreted considering the superposition at varying time delay \( \tau \) of two interfering pulses of complex electric field \( \hat{E}(t) = E(t) \exp(i2\pi v_0 t) \) and carrier frequency \( v_0 \):

\[
I_{cFROG}(\tau, \nu) \propto \left| \int_{-\infty}^{\infty} (\hat{E}(t) + \hat{E}(t-\tau))^2 \exp(-i2\pi \nu t) dt \right|^2
\]  

(1)

This expression can be developed as:

\[
I_{cFROG}(\tau, \nu) \propto 4 \left| \int_{-\infty}^{\infty} E(t)E(t-\tau) \exp(-i2\pi \nu t) dt \right|^2 + 2 \left| \int_{-\infty}^{\infty} E^2(t) \exp(-i2\pi \nu t) dt \right|^2 + + 2 \int_{-\infty}^{\infty} E^2(t) \exp(-i2\pi \nu t) dt \right|^2 \cos(2\pi(2v_0 + \nu) \tau) + + 4 \text{Re} \left\{ \int_{-\infty}^{\infty} E^2(t) \exp(+i2\pi \nu t) dt \int_{-\infty}^{\infty} E(t)E(t-\tau) \exp(-i2\pi \nu t) dt \cdot (\exp(-i2\pi v_0 \tau) + \exp(i2\pi (v_0 + \nu) \tau)) \right\}
\]  

(2)

The first term represents the actual FROG trace measured in non-collinear geometry, while the second one corresponds to the DC offset associated to type-I frequency generation.[25] The remaining terms arise from the interferences at \( 2\nu_0 \) between the two SHG pulses, and at \( \nu_0 \) between the SHG fields generated by the two individual pulses and the cross-SHG field \( E(t)E(t-\tau) \). The idea of the analysis is to extract the standard FROG trace by filtering out the oscillatory components at \( \nu_0 \) and \( 2\nu_0 \). As demonstrated by Stibenz and Steinmeyer, these modulational components can be also exploited for an alternative pulse retrieval procedure.[23]

The result of a numerical Fourier transform along the time axis of the cFROG trace is displayed in Fig. 2(d). Note that the frequency of the modulation at \( \nu_0 \), expected at 375 THz is...
downshifted to \(\sim 180\) THz due to undersampling, while the \(2\nu_0\) component is not resolved. It has been shown that undersampled acquisition of a cFROG trace can be safely performed under certain conditions without loss of information on the final FROG.[23, 24]

The FROG in Fig. 3(a) was extracted by first filtering out the modulation components in the Fourier space, and then by applying the inverse transformation back to the time/wavelength space. After this operation, we subtracted the DC offset from the trace, i.e. the second term in Eq. 2. The treated data were successively fed into a commercial FROG-inversion program [26] to determine the pulse characteristics. The retrieval error corresponds to \(2.50^{\circ}/0.00\). The retrieved FROG trace is shown in Fig. 3(b), along with pulse electric field intensity temporal profile (corresponding to a pulse duration of 75 fs) and spectrum reported in (c) and (d). The corresponding phase-functions are also shown. The latter indicate the presence of a residual quadratic chirp on the pulse due to group velocity dispersion accumulated during propagation through the microscope optics, which is not fully corrected by the grating compressor. By comparing the pulse duration at the input of the microscope and at the focal plane, we can quantify the second-order dispersion parameter to \(4416\) fs\(^2\), in line with the values determined by Wolleschensky et al. for similar but not identical optical systems.[15]

4. Discussion

In the present work the particle investigated has dimensions comparable to the size of the nonlinear focal spot (\(\sim 500\) nm), the spatial resolution is therefore already one order of magnitude higher than the spatially-resolved FROG and TADPOLE techniques recently proposed.[12, 27] Our approach can be easily extended to smaller NPs down to a dimension of a few tens of nanometers. The major experimental difficulty is represented by the extremely long acquisition time (five hours) compared to the photostability of the nanoscopic samples: the use of an imaging spectrometer equipped with an array detector capable of simultaneous acquisition of the whole spectrum would reduce the acquisition time by orders of magnitudes, allowing stable measurements on smaller samples. Note that size-dependent signal intensity does not represent a limitation: thanks to the very good frequency conversion efficiency of \(\text{Fe(IO}_3)_3\), we recently succeeded in imaging and measuring the polarization response of NPs with sizes as small 40 nm on the same experimental set-up.[17] For NPs smaller than the focal spot of a high NA objective, the resolution of sub-focal features theoretically predicted in the framework...
of phase and polarization shaping microscopy will be reachable. Recent calculations indicate, for example, that clearly different spatio-temporal evolution of the electric field are expected at locations 400 nm apart in the focal plane for tightly focused shaped pulses.[28] In addition, the polarization-dependent response of Fe(IO₃)₃ NPs can be exploited to characterize the polarization evolution by combining two orthogonal cFROG measurements of the same shaped pulse.[29] The absence of phase-matching constrains for subwavelength NPs can be useful for broadband pulse characterization allowing the frequency mixing of virtually any wavelength in the transparency window of Fe(IO₃)₃. This possibility can result particular advantageous for microCARS and coherent microscopy, which are increasingly based on the use of supercontinuum broadened pulses in photonic crystal fibers.[5]

Finally, we are currently exploring the possibility of functionalizing the NPs’ surface to embed them into biological samples. This in vivo nano-FROG measurement would open the way to elucidate the interactions between the different spectral components of femtosecond pulses and the NP local environment (cell membranes, biological solutions, local pH). There is in fact a growing evidence of the applicability of pulse shaping techniques for improving functional imaging [30, 31], for reducing photo-bleaching of fluorescent labels [32], and for acquiring excitation selectivity [33, 34] also with respect to the local fluorophore environment [30]. Our in situ pulse diagnostic technique could in principle be used to decipher the control mechanism underlaying these observations.

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