A femtosecond X-ray/optical cross-correlator

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For a fundamental understanding of ultra fast dynamics in chemistry, biology and materials science it has been a longstanding dream to record a molecular movie, where both the atomic trajectories and the chemical state of every atom in matter is followed in real time[1]. Free-electron lasers (FEL) provide this perspective as they deliver brilliant femtosecond X-ray pulses spanning a wide photon energy range, which is necessary to gather element-specific and chemical-state-selective information with femtosecond time resolution. The key challenge lies in synchronizing the FEL with separate optical lasers. We exploit the peak brilliance of the FEL in Hamburg (FLASH)[2,3] and establish X-ray pulse induced transient

changes of the optical reflectivity in GaAs as a powerful tool for X-ray/optical cross-correlation. This constitutes a breakthrough *en route* to a molecular movie and – equally important – opens the novel field of femtosecond X-ray *induced* dynamics, only accessible with high brilliance X-ray free-electron lasers.

The experimental foundation of femtochemistry[1] is time resolved pump/probe spectroscopy, which has been closely linked to the rapid development in ultra fast laser technology in the visible and near UV/IR regime[4]. Recently, the development of high harmonic generation, carrier-envelope phase stabilized laser pulses and X-ray optics has allowed to access even attosecond time scales in selected systems[5,6,7,8,9,10,11,12]. In a separate development, optical laser driven X – ray plasma sources (*e.g.* Kα lines of Cu, Al) have provided a first glimpse of sub-picosecond time resolved structural dynamics[13,14,15]. However, these optical laser based X-ray sources operate at very low intensity and repetition rate and are still very limited in photon energy.

In contrast, free-electron lasers excel in producing femtosecond X-ray bursts of variable photon energy at maximum peak brilliance and coherence using the principle of self amplification of spontaneous emission (SASE)[16,17,18,19,20]. Combined with optical lasers X-ray spectroscopic and diffractive methods allow to study ultra fast photo induced dynamical processes from low energy IR activated dynamics to excitations in the optical and UV spectral range. The selectivity of X-ray spectroscopy enables to monitor the temporal evolution of few selected active sites without the background of a large number of surrounding atoms from a passive matrix, as resonant X-ray excitation yields atom specific and chemical state selective information[21,22,23,24]. Thus disperse systems, highly relevant in biology and chemistry, e.g. in heterogeneous catalysis and colloidal systems, become accessible. Furthermore, the high peak brilliance provides sufficient X-ray pulse energy to study X-ray induced dynamics for the first time. This paves a new

route to radiation chemistry and to study, for example, the radiation induced processes at interstellar dust or the chemistry at particles in the upper atmosphere[25,26].

To carry out such investigations, we need to synchronize X – ray pulses to optical or infrared pulses of an external laser source with femtosecond accuracy. An important first step has been achieved by measuring the relative arrival time of the electron bunches within the linear accelerator structure through electro optical sampling (EOS)[34]. However, since the overall dimensions of FEL sources require to guide radiation pulses over approx. 100 m via various optical elements in separate X-ray and optical beamlines, we need to measure the precise time delay and spatial overlap directly at the interaction point of the experimental set-up. Such a cross-correlation measurement would allow eliminating the temporal jitter between the optical and X-ray laser pulses.

So far, approaches like laser induced side band generation and streaking in vacuum ultraviolet photoemission from noble gases have been put forward to measure temporal overlap [32,27]. This can only be done using dedicated electron spectrometers under high vacuum conditions[27] and is limited by space charge effects. Second harmonic and sum frequency generation, routinely used to correlate optical pulses from different lasers[4], suffer – when applied to X – rays – from low cross sections. In the following, we demonstrate that ultra fast transient changes of the optical reflectivity in GaAs induced by femtosecond X-ray excitation are an ideal tool for X – ray/optical cross correlation, which can be applied to any sample environment spanning the energy range of present and future FEL X–ray sources.

The experiment was performed at the plane grating monochromator beamline PG2 at FLASH in Hamburg, Germany[28] in 0^{th} order, using the Hamburg inelastic X – ray scattering station. Clean, undoped GaAs(100) surfaces were prepared at a base pressure of 1×10^{-9} mbar by flashing off an As cap layer from molecular beam epitaxy

grown samples. The preparation regarding surface quality and stochiometry has been checked by core level photoelectron spectroscopy (XPS). As depicted schematically in Fig. 1, extreme ultraviolet radiation pulses of 39.5 ± 0.5 eV with a duration of < 50 fs impinge on the GaAs(100) crystal at 41.5° incidence angle with the electric field vector in the surface plane. The FEL was operated at a macro bunch repetition rate of 5 Hz consisting of bunch-trains of 30 micro-bunches with 2µs separation (500 kHz). The pulse energies reached up to 16µJ, as measured through the facility gas monitor detector[29] and independently by an intensity monitor within the PG2 beamline. With a spot size of (395 ± 23)µm x (274 ± 14)µm [30] the fluence stays well below the optical damage threshold of the GaAs surface (50 mJ/cm^2 for 30 fs pulse length at 800 nm)[31]. As shown in the upper part of Fig. 1, the induced change of optical reflectivity was probed at an angle of incidence of 53° by delayed optical pulses at 800 nm or optionally 400 nm with a duration of 120 - 150 fs (fwhm) delivered from an optical parametric amplifier system with 1 MHz repetition rate, electronically synchronized to the electron accelerator[32]. The optical pulse energies were detected in a reference path and after reflection with two fast photodiodes, allowing for transient reflectivity measurements pulse by pulse using a 2 GHz analog to digital converter (Acqiris) embedded into the distributed object oriented control system (DOOCS)[33] of FLASH. Operating the optical laser at twice the FEL repetition rate within each pulse train of 30 radiation bursts results in alternating measurements of the reflectivity with and without the X-ray pump pulse.

In Fig. 2 we present the FEL X-ray pulse induced transient optical reflectivity changes ΔR/R on time scales from femtoseconds to many hundreds of picoseconds, where from panel 2 a) to 2 c) different temporal delay ranges are presented. The intense X-ray excitation leads to an ultra fast drop in optical reflectivity, which recovers within a few picoseconds. Depending on the X-ray fluence and probe wavelength, ΔR/R can even overshoot to positive values before the system approaches equilibrium on the time scale

of more than 100 ps as shown for 800 nm probe. In the following, we focus on the femtosecond time scale of the ΔR/R transients, which is of key relevance for cross-correlation measurements of X – ray and optical radiation pulses. Fig. 2 b) shows that the rapid X-ray pulse induced drop in optical reflectivity occurs on the same time scale for both 800 nm and 400 nm probe wavelength, respectively. The time scale can be deduced from a measurement shown in Fig. 2 c), where we corrected for the major sources of temporal jitter within the accelerator (typically 0.25 ps RMS [27]) using electro optical sampling[34] to determine the arrival time of selected electron bunches relative to the optical laser. When we fit the reflectivity transient with an exponentially decaying response function convoluted with a Gaussian we obtain a full width at half maximum of 160 ± 44 fs. Thus the intrinsic time constant of the X – ray pulse induced initial drop in optical reflectivity is small compared to the cross-correlation width making it suitable for cross-correlation measurements of FEL X-ray and optical laser pulses.

To understand the physical origin of the ultra fast reflectivity drop we turn to the X-ray pump fluence and X-ray pump energy dependence as summarized in Fig. 3). At 800 nm probe wavelength, where in equilibrium only optical transitions across the direct band gap close to the Γ point are probed[35], the minimum of the ΔR/R transient scales linearly with the fluence up to 6 mJ/cm^2 and then stays almost constant. At 400 nm probe wavelength a smaller amplitude of the ΔR/R transient minimum is found and optical transitions at many k-values between the L – and Γ – points in the band structure are possible[35]. The absorption of the FEL radiation is governed by the atomic photoionization cross sections (Ga 3d: 3.6 Mbarn, Ga 4s: 0.17 Mbarn, As 4p: 0.3 Mbarn, As 4s: 0.21 Mbarn at 40.8 eV)[36, 37] leading preferentially to Ga 3d vacancies. Within 10 nm of the GaAs sample 10% of the incident photons are absorbed[38] (Fig. 3b), staying below the damage threshold of the GaAs surface (50 mJ/cm^2)[31]. Thus an excitation fluence of 10 mJ/cm^2 (equivalent to $1.6 \cdot 10^{15}$ photons at hv=39.5 eV) creates within the 10 nm thick surface layer a Ga 3d excitation density of approx. $1.6 \cdot 10^{20}$ cm^{-3}.

Within few femtoseconds Auger decay and autoionization converts the initial inner shell excitation[39] into twice the number of valence excitations (~ $3 \cdot 10^{20}$ cm^{-3}) and finally equilibration to the mean energy of electron-hole pair creation in GaAs of 4.2 eV[40] produces an electron-hole pair density of $1.5 \cdot 10^{21}$ cm^{-3}. With optical laser excitation at and above the optical damage-threshold photo-generated free carriers exceeding 10^{20} cm^{-3} lead to similar $\Delta R/R$ transients as we find for X-ray excitation below the damage threshold. There the free carrier absorption changes the dielectric function as described by the Drude model. Beyond that, screening of ionic potentials and electron many-body effects are important as they modify the band structure[35, 41]. Thus a full theoretical model of the X-ray pulse induced optical transient reflectivity will consider the response of the dielectric function to the distortion of the valence electronic structure through photoionization and ultra fast Auger decay of inner shell vacancies, electronic screening and electron-electron scattering as well as the structural changes to the crystal lattice.

Based on these considerations, we can estimate the applicability of our approach to the extended energy range of present and future FEL sources. In Fig. 3b) the photoabsorption in 10 nm GaAs is presented as the fraction of photons absorbed, which is decreasing towards higher photon energies. As long as the photoabsorption decreases less than inversely with photon energy, the reduced absorption probability is compensated by the higher photon energy, as the density of the excited carrier distribution responsible for the changes in optical reflectivity also depends on the absorbed energy. Taking our measurement at 39.5 eV photon energy as the reference, we expect comparable or higher $\Delta R/R$ signal strength up to 6.5 keV and at most a reduction by a factor of two up to 15 keV. Thus X–ray/optical cross correlation by means of transient optical reflectivity measurements should allow to easily monitor the temporal relation between FEL X–ray pulses and optical laser pulses at the interaction point within user experiments, suitable for a large variety of experimental conditions.

Let us in the following discuss how X-ray/optical cross correlation leads to important experimental applications: In Fig. 4 a) the transient optical reflectivity measurement is shown for FLASH operating with 30 micro bunches thus emitting 30 subsequent FEL femtosecond X – ray pulses separated by 2 µs each. As shown in Fig. 4 b) we observe a significant systematic drift of the delay by almost 1 ps over the first part of the pulse train stabilizing after ~10 pulses. Since this delay drift is caused by the electronic feedback systems of the accelerator structure and the coupling of subsequent electron bunches, it also varies with the operation condition of the accelerator. Thus its characterization and optimization are especially important for pump-probe experiments on a femtosecond timescale. Knowledge about the precise timing allows using drifts for a complete delay scan within a single bunch train or to alternatively correct the arrival time of all micro bunches. The investigation of these systematic timing drifts within the X-ray pulse trains could not be done before, as methods like electro optical sampling have been too slow in data acquisition for the 500 kHz repetition rate of FLASH.

We can also monitor the temporal overlap between optical and X – ray laser pulses over an extended period of time (Fig. 5). Due to the temporal jitter within the accelerator, we observe at a nominally fixed pump-probe delay a characteristic distribution of the optical reflectivity signal (Fig. 5). Characteristic differences in the $\Delta R/R$ intensity distributions are found for different delay positions in the femtosecond and picosecond range. In particular, around time zero the temporal jitter is translated into strong variations of the optical reflectivity. The reflectivity signal changes already significantly for a delay difference of 100 fs or 200 fs allowing for an online monitoring of pulse-to-pulse jitter. At larger temporal delay further variations of the $\Delta R/R$ intensity distribution function of optical reflectivity are found. The presented technique can even be extended to single shot X – ray pulse diagnostics by imaging the reflected optical pulses onto a spatially resolving detector mapping arrival time onto a spatial coordinate. In such a crossed beam experiment the temporal relation between X – ray and optical

pulses will be measured fully independent from any other temporal measurement. Finally, it might be possible to achieve full temporal and energetic characterisation of every radiation pulse by using an X-ray diffraction grating or crystal, where zero order light is delivered to the user experiment and parasitic to user operation, the first order spectral image is used to project energy and time information onto orthogonal axes.

In conclusion, we have established the technique of X – ray induced transient optical reflectivity on a GaAs surface as a powerful tool for cross correlation between femtosecond optical and X – ray pulses, spanning the energy range of present and future X-ray free-electron laser sources. Furthermore, X-ray induced non-equilibrium dynamics opens a new field of time resolved studies of matter which is highly relevant for X-ray induced chemistry in biological systems, solids and interfaces e.g. present in atmospheric and interstellar dust. Thus our findings pave the way towards time resolved structural dynamics in chemistry, biology and materials science.

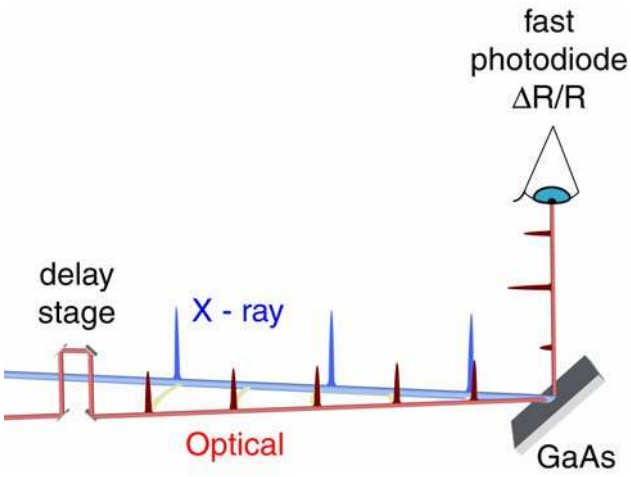

Fig. 1: Transient X-ray induced optical reflectivity (ΔR/R) measurement - schematic overview:

Extreme ultraviolet FEL pulses (39.5 eV, 25 fs, < 16µJ) impinge onto a crystalline GaAs(100) surface and generate photoexcited carriers. The transient changes of the dielectric function are probed by visible laser pulses (800 nm or 400 nm, 120 fs, < 10 nJ) reflected from the GaAs surface at 53° as a function of their temporal delay relative to the FEL radiation pulse. The visible laser operates at twice the repetition rate (1 MHz) of the FEL (500 kHz) to measure the pumped and unpumped surface as a reference.

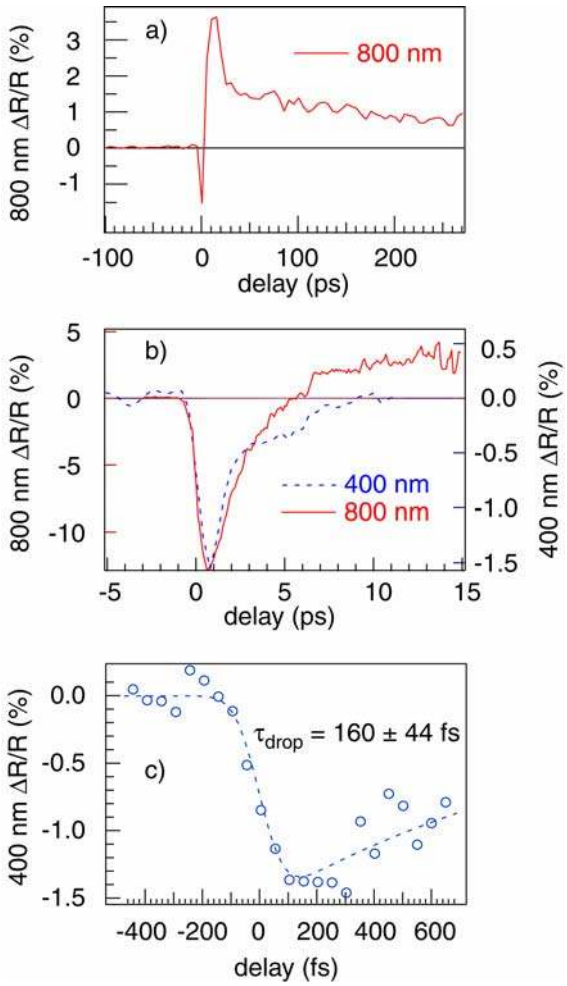

Fig. 2 Transient X-ray induced optical reflectivity (ΔR/R) – temporal characteristics: a) X-ray pulse induced dynamics: A rapid initial electronic response is followed by slower lattice dynamics on a picosecond timescale b) Ultra fast electronic response after X-ray pump: The rapid drop of ΔR/R observed for 400 nm and 800 nm probe wavelength is followed by a recovery which depends on the GaAs band structure and the time scale of electronic relaxation. c) The width of the initial drop in optical reflectivity as determined fitting an exponentially decaying response function convoluted with a Gaussian (full width at half maximum of 160 ± 44 fs) is limited by the pulse length of the optical laser pulse (120 – 150 fs). To eliminate temporal jitter from the accelerator the delay is corrected for the electron bunch arrival determined with electro optical sampling (EOS)[34].

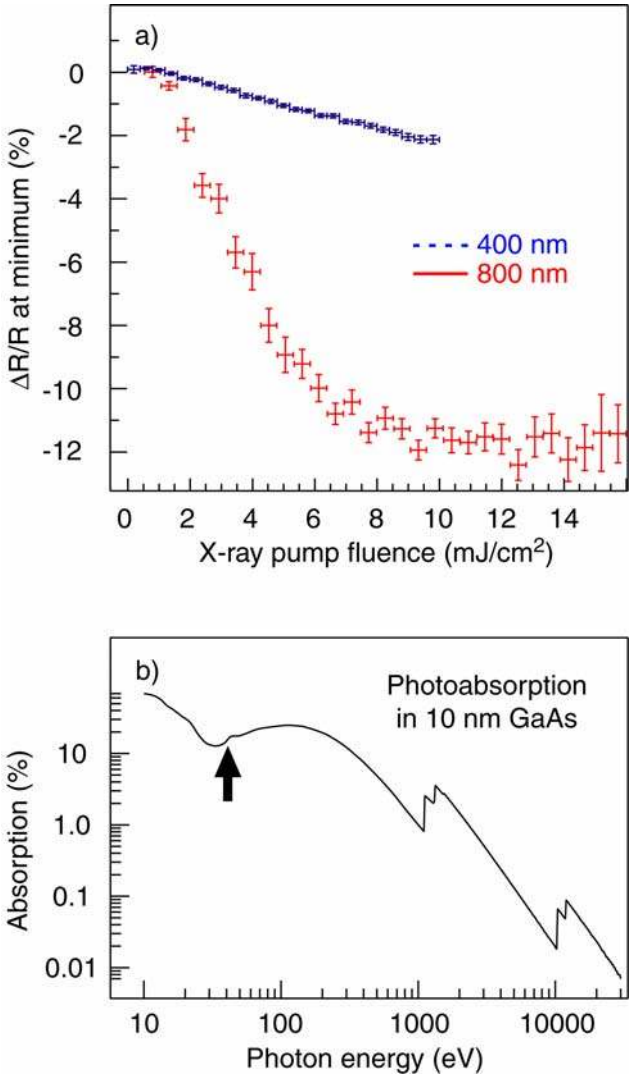

Fig. 3: Transient X-ray induced optical reflectivity (ΔR/R) – energy dependence: a) Dependence of the initial drop of ΔR/R for 800 nm and 400 nm probe light on the fluence of the X-ray pulses. The error bar in X-ray pump fluence reflects the finite binning intervals used. The error bar of ΔR/R is the standard deviation of events within the corresponding fluence binning interval.

b) Photoabsorption within 10 nm GaAs across the energy range of present (arrow: this report) and future X – ray free-electron lasers computed from Ref. 36, 38, 37. The excited carrier distribution responsible for the change of reflectivity is mainly determined by the absorbed fluence which stays in the same order of magnitude up to 10 keV.

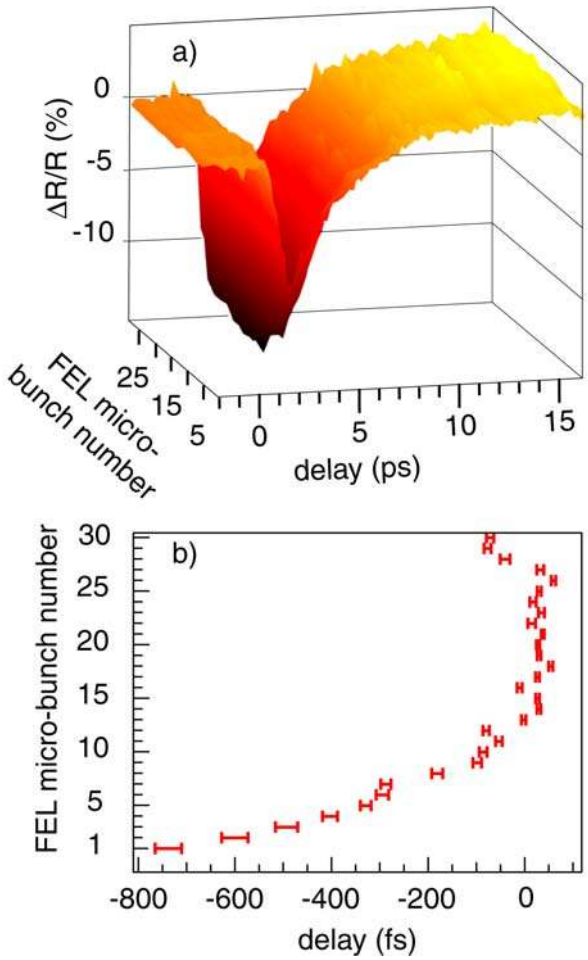

Fig. 4: X-ray pulse arrival for 30 FEL radiation pulses (500 kHz repetition rate) relative to 800 nm laser pulses:

a) Overview of experimental data.

b) X-ray pulse arrival time from the reflectivity drop within the pulse train. The uncertainty results from fitting the turning point of the falling flank. The drift in arrival time results from the accelerator feedback system and coupling phenomena within the electron accelerator at present operating conditions.

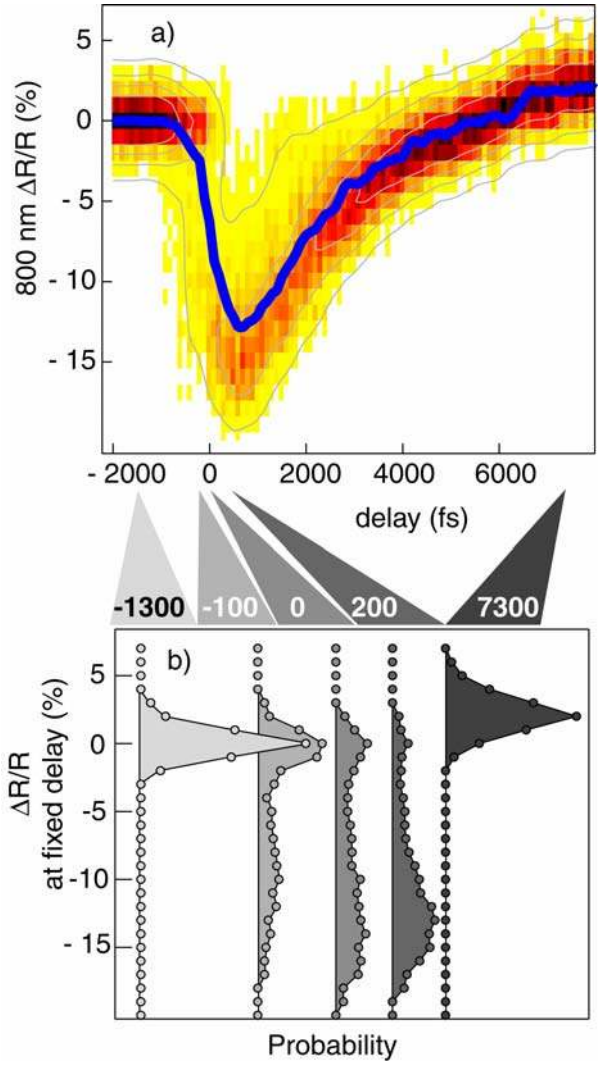

Fig. 5: Femtosecond X–ray/optical delay monitor:

a) Transient optical reflectivity with single shot fluctuation from temporal jitter at nominal delay positions. The blue solid line represents the average optical reflectivity.

b) Characteristic ΔR/R transients at various delays.

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