Advancing non-equilibrium ARPES experiments by a 9.3 eV coherent ultrafast photon source

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a b s t r a c t

The quest for investigating the non-equilibrium dynamics of the band structure of strongly-correlated materials over their entire Brillouin zone is a primary objective. However, the actual ultrafast UV light sources are not suitable for addressing several critical questions in the field. Here we report on a novel light source generating sub-250 fs, 9.3 eV photon energy light pulses at 250 kHz repetition rate, obtained via third-harmonic generation in Xe of frequency-doubled 50 fs laser pulses at 1.55 eV. By reporting the measured band dispersion of a Cu(111) crystal and the non-equilibrium dynamics of the Bi2Se3 topological insulator, we prove that this source is suitable for studying the non-equilibrium dynamics of the entire Fermi surface of several complex materials, with high signal statistics and limited space-charge effect.

1. Introduction

Time and angle-resolved photoelectron spectroscopy (TR-ARPES) is a stroboscopic technique based on two synchronized ultrashort optical laser pulses.

In this last decade, TR-ARPES has proved to be of paramount importance for studying the out-of-equilibrium electronic structure of novel materials [1–3] such as topological insulators (TIs) [4–8], graphene [9–12], charge-density-wave materials [93,14] and copper- [15–18] and iron-based [19,20] high temperature superconductors.

Despite many efforts aimed both to develop the laser technology and the photoelectron detection, ARPES experiments based on ultrashort laser pulses still have to face problems related to the limited energy and momentum resolution. Actually, produc-ing ultrashort laser pulses with a photon energy suitable to access the entire Brillouin Zone of most materials remains a challenging task, if the energy resolution has to be preserved. This fact leaves pending many important questions in the field of strongly correlated materials. For example, to address topical problems such as the nodal-antinodal dichotomy in cuprate superconductors or the role of the multiband structure of iron-based superconductors, it is mandatory to measure with high energy, momentum and time resolutions the out-of-equilibrium dynamics of the electronic states at the edges of the Brillouin zone (BZ), typically located at a momentum \( k \approx 0.85 \ \text{Å}^{-1} \).

Nowadays, these studies are partially precluded to TR-ARPES, since the maximal photon energy for actual TR-ARPES setups exploiting high repetition rate (250–1000 kHz) laser sources is limited to \( \sim 6 \text{ eV} \) [21,22], and only electronic states at \( k \ll 0.6 \ \text{Å}^{-1} \) can be probed. Conversely, photons produced by high-harmonic-generation (HHG) of ultrashort laser pulses [23] allow to map the entire BZ of any material. However, the ultimate energy resolution is intrinsically limited to several tens of meV [23] by the bandwidth of the harmonic pulses. Furthermore, the signal statistics is relatively poor because of the low repetition rate (typically few kHz) of the laser source, imposed by the high power density (of the order \( 10^{14} \text{ W/cm}^2 \)) required to generate these light pulses.

Hence the quest for an ultrafast light source operating at a repetition rate exceeding \( \sim 100 \text{ kHz} \), delivering photons suitable for covering the entire BZ of most materials and having a bandwidth of \( \sim 20–30 \text{ meV} \), is compelling. Recent out-of-equilibrium TR-ARPES studies performed at 6.2 eV probe energy indeed demonstrated

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the importance of ultrahigh energy and momentum resolutions (of the order $E \approx 20 \text{ meV}$ and $k_F \approx 0.003 \text{ Å}^{-1}$ [24,25] respectively), along with a high signal statistics, for the study of strongly-correlated materials.

Here we report on the development and commissioning of a coherent light source producing vacuum ultraviolet (VUV) 9.3 eV photons at 250 kHz repetition rate and characterized by a pulse length of $\sim 240 \text{ fs}$ and an estimated bandwidth of $\sim 55 \text{ meV}$. Our optical setup exploits the third-harmonic generation (THG) process in Xe gas of the second harmonics of a 250 kHz Ti:Sapphire regenerative amplifier producing $\sim 50 \text{ fs}$ laser pulses at 1.55 eV (800 nm) with an energy per pulse in the low-J regime.

The photon energy provided by this source allows to access electronic states lying up to $\approx 1 \text{ Å}^{-1}$. At the same time, the accessible binding energy range allows to study the non-equilibrium dynamics of electronic states lying up to $\approx 2.5 \text{ eV}$ below the Fermi energy. The performances of this source have been tested in ARPES and TR-ARPES reference experiments. The outcome of these experiments demonstrate that this source advances those actually used for TR-ARPES experiments, meanwhile joining their advantages. In particular, the 250 kHz repetition rate ensures high statistics and almost space-charge-free experiments.

2. Motivation

An important achievement that would advance our under-standing of the physics of strongly-correlated materials arises from the possibility to completely characterize the nature and strength of the electronic correlations. An orbital-selective [26] or momentum-space-selective [27] degree of electronic correlation could be directly revealed by TR-ARPES experiments by measuring the temporal evolution of the quasi-particle scattering rate, provided that the out-of-equilibrium mapping of the electronic states over the entire BZ of these materials is possible. The results of such experiments will be of paramount importance in order to verify the ‘selective Mottness’ theory [26], that reconciles the unconventional properties of both the iron- and the copper-based high-temperature superconductors.

As an example, Fig. 1 reports the calculated Fermi Surface in the first BZ of the Bi2212 cuprate superconductor, obtained by using a tight-binding approach [28]. Two dashed circles enclose the momentum regions that can be mapped by using 6.2 eV photons (blue) and 9.3 eV photons (green).

In particular, at 6.2 eV probe energy the study of the antinodal region is precluded, whereas at 9.3 eV, the entire Fermi surface of the Bi2212 and other cuprates can be accessed.

A problem arising when studying electronic phases that can be easily vaporized by a light pulse, like the superconducting state [29], is that the excitation of the material must be performed at a very low fluence ($\sim 20 \text{ J/cm}^2$). Hence, a high repetition rate of the laser source is mandatory to provide a signal-to-noise ratio high enough to reveal low intensity out-of-equilibrium signals. Under these operating conditions the space-charge effect [30–35] is significantly reduced, and high energy and momentum resolutions are preserved. The ideal case is realized with a photoelectron-per-pulse, an experimental condition that is easily obtained with setups operating at a repetition rate in the 250–1000 kHz range, while challenging at the 1–10 kHz repetition rate of most of the HHG-based TR-ARPES setups.

3. The VUV Source

3.1. Optical and UHV apparatus

Fig. 2 shows the schematic of the TR-ARPES system, including the laser source, the optical setup for 9.3 eV generation and a sketch of the UHV ARPES chamber. The source is based on the THG in Xe gas of the second harmonics at 3.1 eV of a 250 kHz Ti:Sapphire regenerative amplifier delivering an energy per pulse in the low-J regime. In the figure the color-coding for the photon-energies involved in the setup is defined. The laser fundamental beam at 1.55 eV is indi-cated in red, its second harmonic beam at 3.1 eV in blue, while the 9.3 eV beam in light-blue.

The laser source produces $\sim 50 \text{ fs}$ FWHM (full-width at half maximum) pulses at $\sim 800 \text{ nm}$ ($\omega_0 = 1.55 \text{ eV}$), with a pulse-energy of $\sim 6 \text{ J}$ (1.5 W average power) when operating at 250 kHz. A fraction of the laser output (<10%) is used as the pump beam, and the pump-probe delay is controlled by a motorized translation stage. The pump beam is focused on the sample with a 750 mm focal length lens, and it has a full-width-half-maximum (FWHM) spot size of $500 \pm 20 \text{ m}$. The probe beam is frequency-doubled in a 0.5 mm thick barium borate (BBO) non-linear crystal, cut at an angle of 29.2°.

Using a 250 mm focal length lens to focus the radia-tion on the BBO crystal, we obtain a conversion efficiency of $\sim 40\%$, corresponding to 400 mW power (1.6 J/pulse) at 3.1 eV. This beam, with a FWHM diameter D = 5 mm, is used for third harmonic generation in gas. It is focused by a 36 mm focal length lens in the gas.

![Fig. 1. The Fermi surface of Bi2212 is reported as black lines representing the Fermi arcs. The dashed blue circle encloses the momentum space region that can be accessed using 6.2 eV photons (see text). Dashed green circle represents the situation when using 9.3 eV photons. These curves have been drawn by assuming a work function $\sim 4.5 \text{ eV}$ and a maximum emission angle $\sim 60°$. 9.3 eV photons determine a maximum accessible crystal momentum $\sim 70\%$ larger than at 6.2 eV, allowing to access the entire Fermi surface of cuprates. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 2. The block diagram of the experimental apparatus with the 9.3 eV source is sketched. M: mirror; DM: dichroic mirror; PBS: polarizing beamsplitter cube.](image2)
cell, with a spot size at the focus position of 10 m FWHM. The con-focal parameter in this geometry is $\approx 400$ m. The resulting power density at the waist position, available for harmonic generation, is of the order $1.5 \times 10^{13}$ W/cm$^2$.

The system for third-harmonic generation in Xe is based on a gas cell and a tube chamber, where the 9.3 eV harmonic beam is split from the 3.1 eV beam by a prism and is then focused on the sample in the UHV ARPES chamber. The limited energy-per-pulse avail-able requires a tight-focusing geometry for the seeding radiation, and allows for a compact design of the source. This tight focusing geometry is defined as the regime for which the confocal parameter $b$ of the focused Gaussian beam is much smaller than the length $L$ of the active medium, i.e., $b < L$. $L$ is typically the length of the gas cell, as it is the case of our experiment, or the size of the gas-jet. The opposite regime, $b > L$, is routinely used in HHG setups seeded by low ($\sim$kHz) repetition rate laser sources, where loosely focused beams and gas-jets are used.

The gas cell is constituted by a 34 mm CF16 UHV cube. The entrance window is a 1.5 mm thick fused-silica plate, while the exit window is a MgF$_2$ 20 mm focal length lens, with central thickness equal to 2.5 mm. One optics is used to both separate the two chun-ners and collimate the harmonic beam. The gas-cell is equipped with an evacuation port, a valve for introducing the gas and two pressure gauges. A Pirani sensor is used for measuring the vac-uum level after evacuation and a piezo-based sensor is used for measuring the Xe pressure. A precise pressure tuning in the gas cell is obtained by a limiting valve controlling the gas flow. Once the optimal pressure is set in the gas cell, operation of the source can proceed without requiring to replace the gas. The second vacuum chamber is constituted by an angled tube in which a LiF prism with 20° apex angle is mounted, for separating the 3.1 eV seed beam from its third harmonics at 9.3 eV. The prism is mounted on a motorized mount, ensuring a reproducible and remote-controlled operation. The angled tube was designed for ensuring that the trajectory of the 9.3 eV refracted beam matches the minimum dis-persion angle of the LiF prism, equal to 11.5°. After separation, the harmonic radiation is focused on the sample with a MgF$_2$ 550 mm focal length lens, to a spot size of 400 $\pm$ 50 m. The tube chamber is also equipped with a channeltron electron multiplier (CEM) detec-tor, mounted on a translation stage, for measuring the harmonic signal. Finally, the tube chamber ends with a double-side, 3 mm thick CF40 MgF$_2$ viewport, that physically separates the harmon-ics source from the UHV ARPES chamber. This window ensures a transmittivity of $\sim 50$% at 9.3 eV. The output signal from the CEM is amplified by a voltage-to-current converter with a $10^5$ V/A ratio and subsequently acquired via a fast digitizer. The conversion from the acquired voltage to the number of photons per second takes into account the gain of the CEM ($\sim 10^2$ at 1600 V, [36]) and its quantum efficiency ($\sim 0.01$ at 9.3 eV, [37]), and results of the order of $\sim 10^9$ V/A or $\sim 1.6 \times 10^6$ photons/(V s). These estimations are affected by a $\pm 30$% uncertainty arising from a possible inaccuracy of the val-ues of CEM gain and quantum efficiency. Finally, the polarization of the 9.3 eV beam can be easily tuned between linear-vertical ($s$) and linear-horizontal ($p$) by simply rotating a 1/2 waveplate placed on the second-harmonic beam, without affecting the VUV beam transmission to the sample.

### 3.2. Third harmonic generation in gases

Fig. 3(a) schematizes the non-linear interactions exploited for 6th harmonic generation (6HG). Generation of laser pulses in the VUV range via non-linear mixing processes requires exploiting gases as non-linear media, since for photon energies larger than $\approx 7$ eV, there are no crystals that can ensure a suitable phase match-ing and transparency [38]. In the past years the modeling of the phase-matching conditions in gaseous media has been matter of a few studies [39–44], and experiments where these generation schemes have been applied to spectroscopies have been reported [45–51].

In gases, having null even-order susceptibilities, the third-order susceptibility can be significant, especially in the vicinity of sharp resonance absorption lines. When the phase-matching condition $k = 0$ is fulfilled, the non-linear conversion efficiencies can be as high as $10^{-2}$ [52,53] for THG.

In the case of THG, the phase-mismatch between the harmonic radiation and the seed radiation writes $k = k_3 = 3k_1 = 6 / (n_3 - n_1)$, $n_j$ being the refractive index. Phase matching $k = 0$ can be obtained by proper gas mixtures, by gas pressure tuning or by selecting a couple of wavelengths such that $k = 0$. This last option is accessible by working across resonance lines of gases.

Harmonics generation seeded by laser pulses of moderate inten-sity requires to tightly focus the laser beam for achieving a power density exceeding $10^{12}$ W/cm$^2$ [38,56]. By focusing a Gaussian beam a phase shift $k_{geom}$, known as Gouy term, is introduced because of a slip in phase between the seed and the harmonic radiation [38,39], as the beam travels through the focal region. For sizeable harmonic production, this net phase-mismatch must...
be compensated by a wavevector mismatch coming from the dis-persion of the nonlinear medium, indicated as $k_{\text{gas}}$, in such a way the total wavevector mismatch $k_{\text{tot}} = k_{\text{geom}} + k_{\text{gas}}$ is zero.

It is worth noting that the geometry-induced phase slip modi-fies the ideal phase matching condition $k = k_{\text{gas}} = 0$ into the less stringent $k_{\text{tot}} = k_{\text{geom}} + k_{\text{gas}}$ condition. This is advantageous, since perfect phase matching $k_{\text{gas}} = 0$ can only be obtained for rare combinations of seed and harmonic frequencies depending on the dispersion of the medium. Conversely, the requirement $k_{\text{tot}} = 0$ with $k_{\text{gas}} \neq 0$ allows exploiting gas mixtures or gas pressure tun-ing for tailoring the gas refractive index and compensating the geometry-induced phase shift.

The value and sign of the geometry-related phase shift $k_{\text{geom}}$ depends on both the focusing geometry and the non-linear mix-ing process under consideration [39]. The simplest process leading to THG is a degenerate four-wave mixing, a third-order process described by $\omega_i = \omega_i^0 + \omega_i^0 + \omega_i^0$, with $\omega_i^0 = \omega_i^0 = \omega_i^0$. In this frame, the harmonic intensity, $I$, follows the form $I = (b k_{\text{gas}})^2 \exp(b k_{\text{gas}})$ in the limit $b L$ and $I = (b k_{\text{gas}})^2 \exp(b k_{\text{gas}})$ in the limit $b L$ ($b$ is the confocal parameter of the focused see-ding radiation and $L$ the length of the active medium). As a consequence, the opti-mal phase mismatch is obtained for $k_{\text{gas}} = -4 b$ in the limit $b L$, and for $k_{\text{gas}} = -2 b$ in the limit $b L$. These results come from the solution of the phase matching integral, as reported in [38,39]. Hence, THG as a result of a degenerate four-wave mixing process in the tight focusing geometry is only possible for a negative phase mismatch, i.e., $k_{\text{gas}} < 0$, corresponding to the negative-dispersion regime, whereas no THG is allowed in positive dispersion regime [40].

Xenon, as well as other inert gases, displays a positive phase mis-match between $\omega_i = 3.1 \text{ eV}$ and its third harmonics at $\omega_i^0 = 9.3 \text{ eV}$ [54,55,57], as shown in Fig. 3(b). For these energies, $k_{\text{gas}}$ is post-iwe and its magnitude can be tuned by adjusting the gas pressure, although its sign cannot be changed. Here we show that THG is also possible in this condition. Since the degenerate four-wave mix-ing interaction $\omega_i^0 = 3 \omega_i^0$ (the $\omega_i^0 = \omega_i^0$ ) $\omega_i^0$ ) cannot lead to THG with $k_{\text{gas}} > 0$, harmonic generation arises from a mechanism involving a higher-order non-linearity. In particular, as reported in [40], the interaction leading to THG is a six wave mixing phenomenon (a fifth-order process), described as $\omega_i^0 = 4 \omega_i^0 - \omega_i^0 (\omega_i^0 = \omega_i^0$, $\omega_i^0 = \omega_i^0$ ), which is instead allowed for positive dispersion of the gas. The harmonic-intensity $I$ in the case $k_{\text{gas}} \geq 0$ and in the tight-focusing limit $b L$ is given by $I \propto \exp(-b k_{\text{gas}})$ [40].

Xe was selected because it allows high conversion efficiency (it has the lowest ionization energy among inert gases, thus it is more polarizable yielding to a large non-linear coefficient) and because its resonances lie far from both the seed and harmonic energy, thus avoiding resonant effects [41].

The optimization of the harmonic production is performed via gas pressure tuning. The optimal condition is obtained when the geometrical phase mismatch $k_{\text{geom}}$ is compensated by the phase mismatch due to the medium, $k_{\text{gas}} > 0$, that depends linearly on the gas pressure $p$ as: $k_{\text{gas}} = 6 / (1 - (3 (p) - n_1 (p))),$ where $n_1 (p) = 1 + d_1 (p - p_0) / p_0$, $1$ being the fundamental wavelength in vacuum, $n_1$ the refraction indexes, $d_1$ a coefficient independent on pressure and $p_0$ a reference pressure. Hence, pressure tuning allows to obtain the optimal phase matching condition $k_{\text{tot}} = 0$ for the seed beam at $3.1 \text{ eV}$ and its third harmonics at $9.3 \text{ eV}$, for maximal harmonic production. Fig. 1(c) shows the generated $9.3 \text{ eV}$ beam intensity, detected by the CEM detector, as a function of Xe pressure in the gas cell.

The inset of Fig. 3(c) shows two clearly resolved features assigned to the $3.1 \text{ eV}$ seeding beam and the $9.3 \text{ eV}$ harmonics beam, detected upon scanning of the incidence angle of the dis-persing prism. The width of the peaks does not reflect their actual spectral bandwidth. It is given by the fact that the angle of a beam of finite size is scanned across the active area of the detector, which is $10 \text{ mm wide in our experiment.}$

The angle of minimum deviation of the $9.3 \text{ eV}$ beam is found to be in good agreement (within $\pm 0.5\%$) with the calculated value of $11.5^\circ$, determined by simulating the dispersion angle of a LiF prism with apex angle equal to $20^\circ$ and refractive index $n = 1.569$ [58] at $133 \text{ nm.}$ This minimum dispersion condition is obtained for an incidence angle on the prism equal to $16 \pm 0.5^\circ$, at which the maximum of the $9.3 \text{ eV}$ beam peak is recorded.

The optimal phase matching condition is found by tuning Xe pressure till the maximum harmonic generation is recorded. In our setup this is obtained at $P_{\text{opt}} = 145 \pm 10 \text{ mbar.}$ At this pressure, the measured voltage is $-50 \text{ mV}$ (see Fig. 3(c)), corresponding to a flux of $\sim 10^{13} \text{ photons/s.}$ The generation efficiency, considering the $3.1 \text{ eV}$ beam power of $400 \text{ mW}$, is slightly larger than $10^{-9}$ . Considering an overall transmittivity $T \sim 50\%$, a flux of $\sim 4 \times 10^{13} \text{ photons/s}$ at the sample position is estimated. It is worth noting that optimization of the conversion occurs at progressively higher pressures as the beam is focused more tightly ($P_{\text{opt}}$ increases as the confocal parameter $b$ is reduced), hence harmonic production increases as the beam is focused more tightly.

For interpreting the pressure tuning curve reported in Fig. 3(c), it is important to consider that, when the optimization of the har-monic intensity is performed by varying the gas pressure, both the gas density $N$ and the phase mismatch $k$ are affected, and the phase matching integrals must be modified [39]. In particular, the quantity that maximizes the harmonic production is obtained by multiplying the square of the phase-matching integrals by $(b)^2$. Thus, in the limit $b L$, the functional form that describes THG via the 5th order process $\omega_i^0 = 4 \omega_i^0 - \omega_i^0 (\omega_i^0 = \omega_i^0$, $\omega_i^0 = \omega_i^0$ ) is $b (k_{\text{gas}})^2 \exp(-b k_{\text{gas}})$, for $k_{\text{gas}} > 0$, while the one expected for THG via the 3rd order process $\omega_i^0 = 3 \omega_i^0 (\omega_i^0 = \omega_i^0$, $\omega_i^0 = \omega_i^0$ ) is $b (k_{\text{gas}})^3 \exp(b k_{\text{gas}})$, for $k_{\text{gas}} < 0$.

The fitting of the expression for the 5th order process to the experimental data shows excellent agreement between the data and the phase-matching model (see Fig. 3(c)). Only at the higher gas pressures, where competing phenomena are likely to be at play, a small departure is observed. This fact confirms that the non-linear interaction leading to THG is of fifth order, i.e., $\omega_i^0 = 4 \omega_i^0 - \omega_i^0$. The maximum conversion efficiency is obtained for a pressure corresponding to the condition $k_{\text{gas}} = 42 / b$. On the contrary, the simulation of the curve that would have been obtained for a third-order degenerate sum-frequency mixing (represented by the dashed line in Fig. 1(c)) indicates that this process (beyond the wrong sign of the dispersion of the medium) cannot be responsible for the observed harmonic production.

4. Results and discussion

To prove that this source can open new important routes it has been tested in ARPS and TR-ARPS experiments using a Cu(111) single crystal and the Ti Bi2 Se3 . Cu(111) presents a non-dispersing d-band and dispersing 4 sp bands both within the accessible energy and momentum range of the present setup [59], and thus consti-tutes an ideal benchmark. Likewise, TIs are known for their peculiar electronic structure, consisting in a bulk insulating or semicon duct-ing band gap and in a spin polarized metallic surface state [60]. They have recently attracted a large attention as promising materials for realizing opto-spintronic devices. Extensive information about their electronic structure studied by ARPS [61–63] and TR-ARPS [4–8] is available in the literature. In particular, TIs exhibit a large variation of the occupation of both the bulk and of the topologically protected surface state, when excited by ultrashort infrared laser pulses [4].
The result of the fitting procedure yields $= 2.8$ ps for the exponential decay, as measured at $T = 120$ K. Both the topological surface state and the Shockley surface states are clearly detected. An additional dispersing band, orig-inated from hybridized sp states, is also detected. These results are in good agreement with the literature [64]. Fig. 4(b) shows an energy-distribution-curve (EDC) integrated over a $0.01 \, \text{Å}^{-1}$ window centered at $k_F = 0.1 \, \text{Å}^{-1}$, as indicted by the white box in Fig. 4(a). We stress the capability of the setup developed to access electronic states lying $-2 \, \text{eV}$ below the Fermi level, that is precluded to ARPES at $6 \, \text{eV}$ photon energy.

Fig. 5(a) shows the ARPES data from a high quality TI Bi$_2$Se$_3$ single crystal measured at $T = 120$ K. Both the topological surface state and the conduction band are resolved. Fig. 5(b) shows an EDC extracted at $k_F = 0$ across the Fermi level, integrated over a $0.02 \, \text{Å}^{-1}$ window (solid white box in Fig. 5(a)). Fitting a function given by the product of a Lorentzian peak (accounting for the conduction band) and a Fermi–Dirac function at $T = 120$ K, convoluted with a Gaussian function accounting for the experimental energy resolution, to the EDC, we are able to extract the overall energy resolution achieved with this setup. The FWHM of the Gaussian resulted $dE = 100 \pm 10 \, \text{meV}$, overall determined by the electron analyzer pass energy ($10 \, \text{eV}$) and slit aperture ($0.5 \, \text{mm}$), both set for achieving a reasonable acquisition time ($\sim 10$) with the moderate flux available at present. With the data reported in Fig. 5(a) we prove the capa-bility of our setup to resolve the topological surface state from the conduction band of Bi$_2$Se$_3$, a performance which is not achieved with current HHG sources [8].

In order to estimate the overall temporal resolution of this setup, a TR-ARPES experiment on the TI Bi$_2$Se$_3$ has been performed. Fig. 5(c) shows the temporal dynamics of the ARPES intensity, inte-grated over the area delimited by the white box drawn in the inset. For maximizing the statistics, the slit width of the analyzer was set to $2 \, \text{mm}$. The dynamics, induced by an absorbed pump fluence of $100 \pm 10 \, \text{J/cm}^2$ at $1.55 \, \text{eV}$, has been recorded over a $6.6 \, \text{ps}$ delay range. In order to extract the ultimate temporal reso-lution of the setup, we fit a single-exponentially decaying function convoluted with a Gaussian function accounting for the temporal cross-correlation (dt) to the time trace of Fig. 5(c). In performing the fitting procedure, we also take into account a $350 \, \text{fs}$ rise time that is needed to fit equivalent time traces acquired with the conventional $6.2 \, \text{eV}$ setup [4], that presents a cross-correlation of $250 \pm 10 \, \text{fs}$, as measured with an optical cross correlation technique. The result of the fitting procedure yields $= 2.8 \, \text{ps}$ for the exponential decay, in excellent agreement with previous results [4–7], and $dt = 260 \, \text{fs}$ (FWHM) for the cross-correlation, a result which is mainly due to the chirp acquired by the VUV beam as it traverses the optical elements of the setup.

After deconvolution of the pump pulse FWHM (70 fs), we obtain a pulse FWHM of $240 \pm 10 \, \text{fs}$ for the 9.3 eV pulse at the sample position. This value represents a novel experimental determina-tion of the pulse duration of THG obtained in the positive dispersion regime, by seeding the generation process with femtosecond laser pulses. This result seems to confirm the predictions reported in [40], suggesting that an ultrashort VUV pulse can be generated in the case of positive dispersion of the gas with a six-wave mixing process.

Finally, we provide an estimate of the energy bandwidth of the VUV pulse. This is obtained starting from the knowledge of the pulse temporal FWHM at the sample position, sample = $240 \pm 10 \, \text{fs}$, taking into account the temporal chirp acquired by the VUV beam as it travels from the source to the sample. Under the reasonable assumption that the chirp of the VUV pulse is only acquired because of the propagation of the beam through optical elements, it is pos-sible to calculate the VUV pulse duration at the source, source , through the relation sample = source $\left( \frac{1}{\text{source}} + 16 \ln 2 \right)^2 \text{GDD}^2$, describing the propagation of Gaussian beams in dispersive media. The 9.3 eV beam travels through four optical elements, contributing with overall $-7.5 \, \text{mm MgF}_2$ glass and $-1 \, \text{mm LiF}$ glass. At 9.3 eV, the Group Velocity Dispersion (GVD) is equal to $+517.29 \, \text{fs}^2 / \text{mm}$ for MgF$_2$ glass [65] and $+413.68 \, \text{fs}^2 / \text{mm}$ for LiF glass [66]. This means the total Group Delay Dispersion (GDD) is $4293 \, \text{fs}^2$. Hence,
we obtain the value source = 50 ± 5 fs for the VUV beam at the source position. This implies a 35 ± 3 meV FWHM bandwidth at 9.3 eV. This value sets the ultimate energy resolution that could be achieved in ARPES measurements, and also indicates that by reducing the num-ber of optical elements in the setup, the temporal resolution can be further improved.

\[5.\] Summary and perspectives

In summary, we report on the development and character-ization of an ultrafast 9.3 eV VUV laser light source that can be driven by high repetition rate Ti:Sapphire regenerative lasers. With this source the momentum matching capability of TR-ARPS setups reaches \(\Delta \mathbf{p} \ll 1\), allowing to measure the non-equilibrium dynam-ics of the electronic states over the entire BZ of most materials, with a temporal resolution of the order \(\Delta t \approx 200\) fs. With our exper-iment, we proved that THG in inert gas is a suitable method for producing ultrashort VUV light pulses to be used in TR-ARPS experiments. At the same time, this source overcomes the prob-lems of a low statistics production.

Only very recently many novel setups for achieving HHG at high repetition rate have been presented. Development of these novel sources have been made possible by the recent progress of laser technology. In particular, high-power laser sources (with an average power that can be in excess of \(\sim 100\) W) working at high repetition rate (50-600 kHz) are exploited. However, common to most of these sources is an intrinsic harmonics bandwidth of the order 50–100 meV, thus limiting the overall energy resolution in ARPES experiments.

Considering the results of the experiments reported, the 9.3 eV ultrafast VUV source opens the way to the investigations, with high statistics and high energy-momentum resolutions, of the non-equilibrium electron dynamics over the entire BZ of materials with a complex Fermi surface or a multiband structure.

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