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Abstract. First experiments on atomic photoionization and molecular dissociation have been performed by taking advantage of the unprecedented characteristics of the Free Electron Laser in Hamburg (FLASH) combined with a separate near-infrared (NIR) femtosecond laser. In a series of two-color experiments, the photoionization of rare gases in the presence of a strong NIR dressing field as well as the polarization dependence of this process were investigated systematically. A detailed analysis of the partial cross sections for the two-color two-photon ionization process was carried out for low dressing fields. Higher dressing fields give rise to multi-photon processes, which are observed and analyzed without undesirable interferences, a beneficial consequence of the monochromaticity of the FLASH radiation. The experimental results are compared with theoretical descriptions for two-color above threshold ionization obtained by employing second-order perturbation theory and the "soft-photon" approximation. In addition, complementary information was obtained on the sequential two-photon double ionization of Ne, which was made possible by the short and intense FLASH pulses. As a starting point for future time-resolved studies on molecular dissociation, a proof-of-principle experiment on the hydrogen diatomic system was carried out. In a typical pump-probe arrangement, excited neutral fragments, which were formed during photo-induced dissociation by the FLASH radiation, were identified via single- and multi-photon ionization induced by the time delayed optical laser.

1. Introduction

The combination of two independently controllable photon sources, which provide radiation in very different wavelength regimes, has demonstrated in many applications that it is an ideal experimental tool to explore different various aspects of photon-matter interaction. High spectral resolution is achieved in experiments making use of the short wavelength emission from a synchrotron radiation (SR) storage ring and of the very narrow bandwidth of continuous wave dye lasers and enabling thereby the detailed study of a whole plethora of complex electronic excitation and decay processes in state prepared atoms and molecules (e.g. [1, 2]). High temporal resolution is provided for many photoionization applications by attosecond pulses, which are produced via high order harmonic generation (HHG) of an intense femtosecond infra-red laser and open unique access to the ultra-fast dynamics of electronic relaxation (e.g. [3, 4, 5]). As an extension of these studies, two-color experiments at Free Electron Lasers not only combine the short wavelengths and large spectral tunability known from SR with ultrashort femtosecond pulse duration on par with HHG, but also have the added advantage of providing the extremely strong fields necessary to drive and study non-linear effects at short wavelengths.

A wealth of new experiments have already been undertaken using the unprecedented characteristics of the Free Electron Laser in Hamburg (FLASH) (see for example recent reviews [6, 7, 8]). In particular, the extremely high photon flux (about $10^{12} - 10^{13}$ photons/pulse) and the ultra-short duration of 20 - 30 femtoseconds [9] provide an ideal basis for two-color studies combining the XUV pulses from FLASH with intense optical pulses delivered by a synchronized femtosecond laser (e.g. [10, 11, 12]). By employing a typical pump-probe excitation scheme, the high photon energy of the FLASH radiation opens access to processes which involve strongly bound innershell electrons and the optical laser enables controlled manipulation and characterization of the initial or the final states of the target under study. Non-linear phenomena and excitation processes in the presence of strong external fields can be investigated for the first time in the XUV wavelength regime by making use of multi-photon processes induced either by the optical or the FEL radiation. Moreover, the short temporal width of both XUV and optical pulses can be used for time-resolved studies on the femtosecond time scale.

Typical excitation schemes which are employed in two-color experiments at FLASH are shown in figure 1. In most of the studies, the short wavelength radiation of the Free Electron Laser (FEL) is used to ionize the atoms or molecules or to excite an innershell resonance by making use of its wavelength tunability. Good temporal and spatial overlap with a synchronized optical laser is needed (a) to prepare efficiently the target in a particular excited state, (b) to modify the ionization continuum or (c) to induce a coupling between two high lying resonant autoionizing states. In particular, the two-color above threshold ionization process (b) has been investigated in the first experiments, since it permits one not only to study this particular non-linear photoionization process, but also to perform a detailed characterization of the FEL

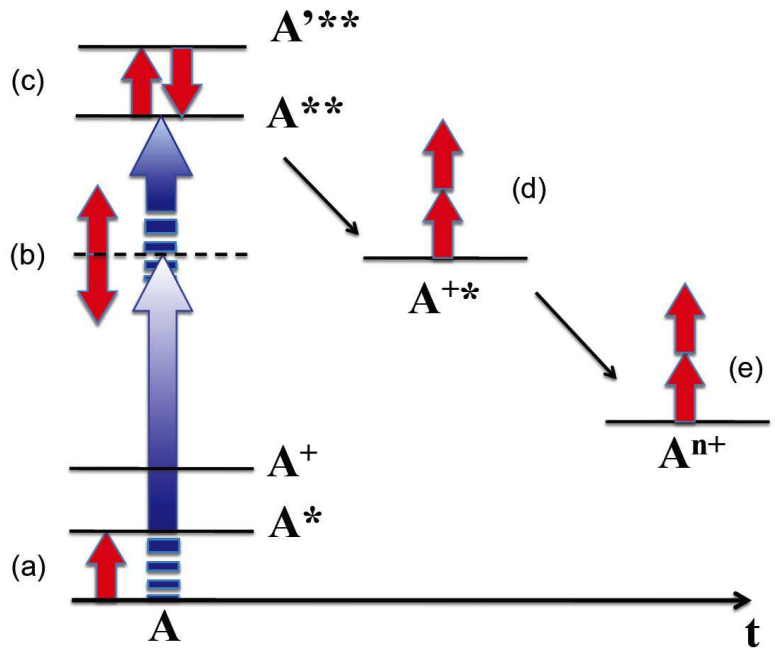

Figure 1. Schematic representation of typical two-color excitation schemes in atoms and molecules: (a) Photoionization of laser-excited species, (b) two-color above threshold ionization (ATI), (c) laser-coupling of autoionization states, and time-resolved studies of (d) intermediate and (e) final ionic states formed upon electronic relaxation or molecular fragmentation.

pulses [13, 14, 15, 16]. The possibility to control the temporal delay between both XUV and optical pulses serves finally to identify possible intermediate states of a relaxation process (d) or to characterize the appearance of a particular final state of a photoinduced process (e). The high intensity of the optical laser enables one to probe the species by single- or multi-photon processes.

In the following, a short description of the experimental set-up is given before three typical examples of two-color experiments are discussed. Firstly, two-color above threshold ionization, which was one of the principal processes to characterize the FLASH facility and the starting point of all further applications; secondly, the dichroism in the atomic photoionization which was accessible due to the well-defined polarization of both sources and finally, the first study on molecular dissociation processes. A short conclusion and a brief presentation of possible future experiments is presented at the end of the paper.

2. Experimental

The experimental set-up used for the two-color experiments has been described in detail elsewhere [13, 14]. Briefly, it consists of a vacuum chamber, which includes the interaction region between an effusive gas jet and both the FEL and the optical

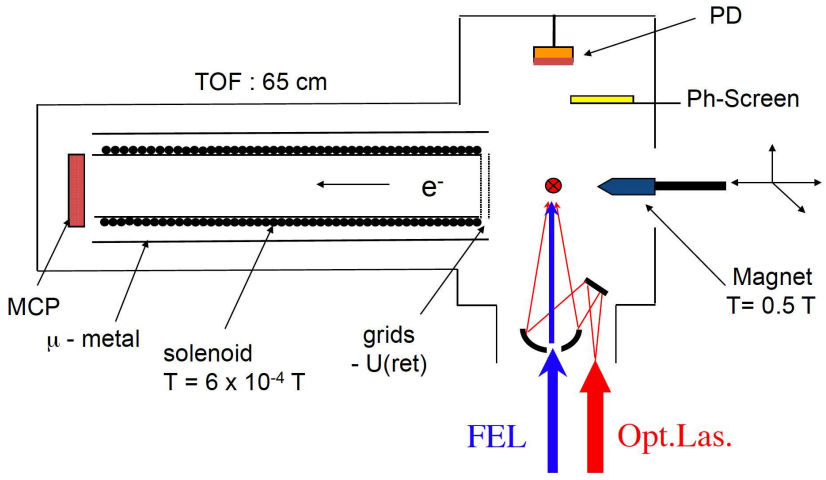

Figure 2. Experimental set-up used for the two-color pump-probe experiments at FLASH.

laser beam, various beam diagnostic tools, and a magnetic bottle electron spectrometer (MBES) (figure 2). Both lasers are introduced into the chamber in a collinear geometry and focus diameters of about 30 and 50 μm are achieved for the FEL and the optical laser, respectively. The slightly larger diameter of the optical beam enabled us to minimize the effect of the inhomogeneous optical field distribution in the ionization region and of the spatial jitter (due to small, relative beam pointing instabilities in the FEL and optical beams) for the two-color experiments. The spatial overlap was controlled and optimized by monitoring the spatial profiles of each beam on a phosphor screen, which could be inserted at the interaction region. The first calibration of the temporal overlap in the interaction volume was provided by a fast photodiode (rise time of 50 ps) [17]. The precise overlap is determined by the two-color signal itself.

As it is an ideal tool to measure the temporal overlap, measurements of the ATI process [18, 19] have been adapted to enable synchronisation of the XUV and NIR pulses by providing a unique time delay measurement, namely the point of maximum overlap (figure 3a). In the photoelectron spectra, the presence of the optical field during ionization by the FEL pulses is indicated by the formation of so-called sidebands in the photoelectron spectra. The intensity of these sidebands is extremely sensitive to the spatial and temporal overlap between both pulses and can be used to determine their relative temporal delay. Due to the large temporal jitter of 590 fs (FWHM) between both pulses [13], it was necessary to measure the delay for each individual pulse. A set of typical photoelectron spectra for atomic Xe is given displayed in figure 3b for nominally perfect overlap of both pulses. The different number of sidebands observed here at the high kinetic energy side of the main $5p$ photolines reflects directly the temporal position of the FEL with respect to the center of the optical dressing laser. The highest number of sidebands represents the maximal optical dressing field, only one or even the absence of sidebands represents minimal or no overlap. By sorting the electron spectra for each

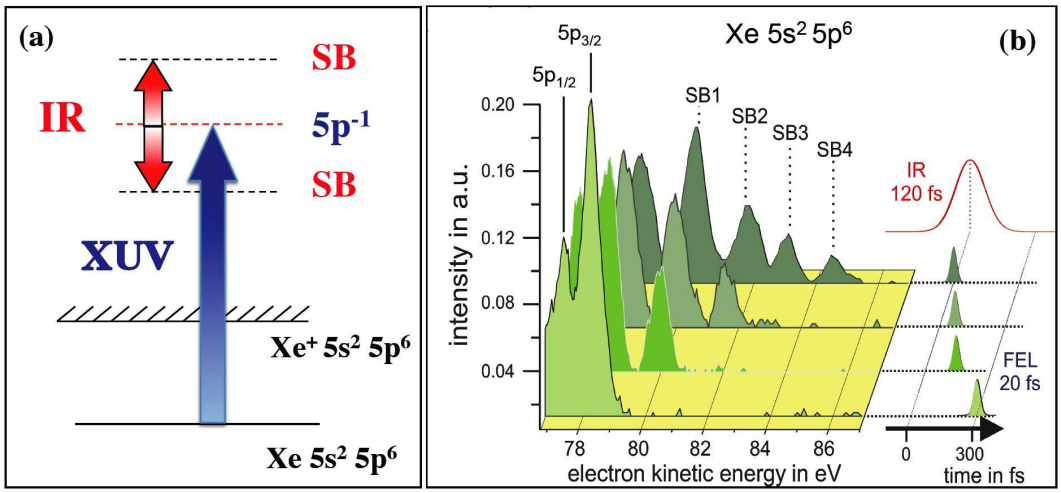

Figure 3. (a) Schematic representation of the two-color above threshold ionization (ATI) process for $5p$ ionization in atomic Xe. (b) Typical single-shot photoelectron spectra of atomic Xe recorded upon ionization with FLASH radiation of $h\nu = 90\,\mathrm{eV}$ (13.8 nm) and nominal maximum temporal overlap (Δ t = 0 fs) between the FEL and the near infrared (800 nm) dressing pulse.

shot with respect to number and intensity of the sidebands and comparing to theoretical models treating photoionization in strong fields [13], a precision of better than 50 fs can be obtained for the temporal resolution in the regime where both pulses overlap. The method is ideally suited for experiments requiring the temporal overlap between the two pulses, but for time resolved experiments it is limited by the duration of the dressing pulse and by the fact that negative and positive temporal delays provide the same field strength, i.e. the same number of sidebands.

The possibility to record single-shot spectra is directly related to the high intensity of the FEL pulses and to the high acceptance of the MBES [20, 21]. Almost all electrons, which are produced in the interaction region are directed by a strong permanent magnet (0.5 T) towards a 65 cm long flight tube, where they are guided by a weak magnetic field field (0.6 mT) onto the micro-channel plate detector (MCP). The application of an electrostatic retardation field at the entrance of the flight tube enables measurements with a maximal energy resolution of 1 – 2 % of the kinetic energy. In order to reach this optimal value, additional broadening of the lines due to space charge effects has to be avoided by maintaining the gas pressure typically at less than 5×10^{-7} mbar with, and about 5×10^{-9} mbar without, gas load.

FLASH was operated mainly at 25.5 nm (48.5 eV) and 13.8 nm (90 eV) at a repetition rate of 5 Hz in single bunch mode. Typical pulse energies were of the order of 30 - 50 μJ recorded for each individual pulse by a gas monitor detector (GMD) [22]. The spectral bandwidth was determined to be 0.5 - 1% by means of a secondary high resolution spectrometer [23] and a pulse duration of 10 - 20 fs was estimated from the spectral distribution [9, 24]. The dressing field was provided by ultra-short optical

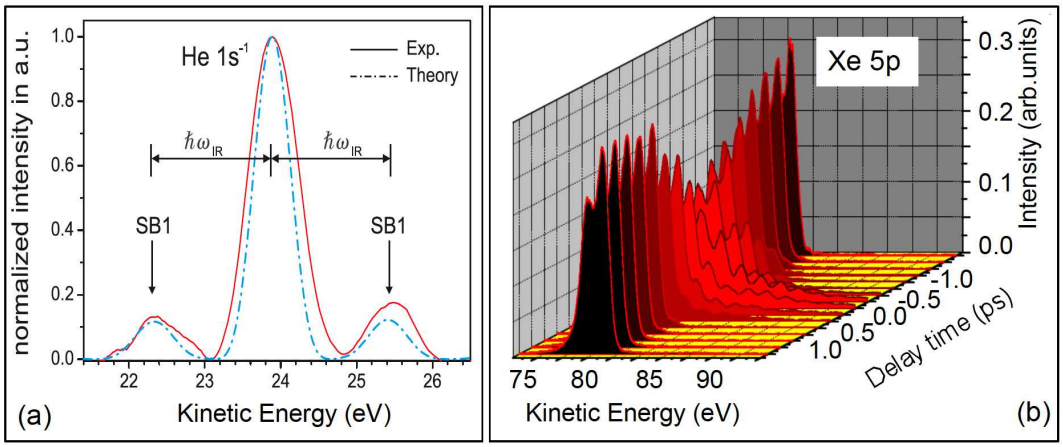

Figure 4. (a) Typical single-shot photoelectron spectrum of 1s ionization of atomic He for overlapping FEL and NIR pulses (hν(FEL)=48.5eV and I(NIR) = 2×10^{11} W/cm^2). The theoretical spectrum obtained from TDSE calculations is given as a dashed line for comparison (from [13]). (b) Series of electron spectra (average of 100 single-shot spectra) of atomic Xe as a function of the temporal delay between the FEL and NIR pulses ((hν(FEL)=91.8 eV and I(NIR) = 4×10^{13} W/cm^2).

laser pulses from an intense Ti-Sapphire laser (up to 2 mJ, 800 nm, 120 fs to 4 ps), synchronized to the radio frequency (RF) source driving the linear accelerator. In addition, the frequency-doubled output of a Nd:YLF burst mode laser can be used, delivering up to 0.4 mJ at 523 nm within a pulse width of 12 ps. The time delay between the optical lasers and the FEL pulses was varied by passing the 523 nm or 800 nm beams through a variable optical delay stage. Long term drifts between the two lasers were monitored by a fast streak camera with a resolution of better than 1 ps (r.m.s.).

3. Results and Discussion

3.1. Two-color Above Threshold Ionization

One of the fundamental processes, which can be investigated in two-color experiments with short and intense photon beams, is above threshold ionization or ATI (cf. figure 1). When both XUV and NIR pulses arrive at the same time in the interaction region, the strong NIR dressing field gives rise to the formation of sidebands in the photoelectron spectra, which can be interpreted as additional absorption or stimulated emission of optical photons by the XUV generated photoelectron. Their intensity and energy position are very sensitive indicators of the spatial and temporal overlap between both XUV and NIR pulses and have therefore been used to characterize the XUV femtosecond pulses produced by high order harmonic generation (HHG) from an intense femtosecond laser [18, 25, 19] as well as to determine the temporal stability of the FLASH pulses [13, 14, 20]

A typical spectrum resulting from two-color ATI is shown in figure 4a. The

spectrum was recorded upon photoionization in the 1s shell of atomic He by one single FLASH pulse operating at 25.5 nm (48.5 eV) and by using a NIR dressing field of about 2×10^{11} W/cm^2 created by a 800 nm, 120 fs, 20 μJ laser pulse. At this intensity of the dressing field, about 20% of the electron signal is transferred from the main photoline into the sidebands, which are energetically displaced from it by 1.55 eV, i.e. by the photon energy of the NIR laser. The process is well understood and the experimental data can be perfectly reproduced by a theoretical analysis using the so-called "soft-photon" approximation [26] or by numerically solving the time-dependent Schrödinger equation TDSE for a single active-electron, three-dimensional model of He [27]. The results of the TDSE simulation, corresponding to the experimental conditions, agree well with the measured spectrum within the limits of our experimental errors.

The advantage of using monochromatic FEL radiation for this type of investigation is demonstrated when higher dressing fields are applied (figure 4b). Here a series of photoelectron spectra of atomic Xe obtained by photoionization at 13.5 nm (91.8 eV) in the presence of a NIR field of about 4×10^{13} W/cm^2 is shown as a function of the temporal delay between XUV and NIR fields. The ionization of the Xe 5p electron results in two photolines corresponding to the $^2P_{1/2}$ and $^2P_{3/2}$ spin-orbit components, which are energetically separated by 1.3 eV. The additional NIR dressing field causes numerous sidebands. Only the high kinetic energy side of the Xe 5p photoline is displayed, since in order to resolve the different structures, a retardation potential (-70V) was applied to the entrance of the MBES, which results in a strong reduction in transmission for the low energy sidebands. The figure illustrates nicely the sensitivity of the process to the temporal overlap between both pulses, since the sidebands appear only in the region close to perfect overlap. The redistribution of electron intensity from the main 5p photoline into the sidebands is directly related to the decrease of 5p intensity. The high number of sidebands is a clear manifestation of multi-photon processes induced by the NIR laser. Up to 8 sidebands, i.e. absorption of 8 additional NIR photons, are identified in the present spectra. The monochromatic radiation of the free electron laser provides in this situation the possibility to study directly two-color ATI involving many NIR photons. In similar experiments with HHG sources, the analysis and comparison to theoretical models is more complicated, since the different harmonic orders present in the beam cause many overlapping and interfering contributions from neighboring harmonics.

When the intensity of the dressing field is further increased, to values higher than 10^{14} W/cm^2, the impact of the NIR field is even more pronounced (figure 5a). For maximal temporal overlap, the main 5p photoline is almost completely suppressed and all photoelectrons are redistributed into a series of broad sideband structures, which extend to kinetic energies of more than 105 eV, i.e. more than 25 eV above the 5p line. A consequence of the high dressing field and especially of the procedure to record spectra in average mode is the strongly reduced resolution of the spectra. Due to the temporal jitter of about 600 fs, the individual photoelectron spectra are very different. Each spectrum is determined by different dressing fields, i.e. the number of sidebands

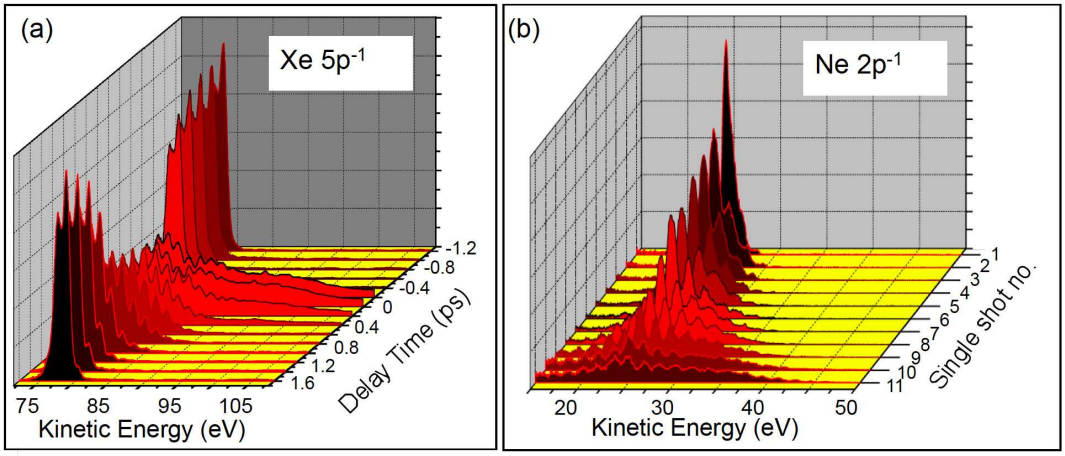

Figure 5. (a) Series of electron spectra (average of 100 single-shot spectra) of atomic Xe as a function of the temporal delay between the FEL and NIR pulses (hν(FEL)=90.5eV and I(NIR) $\geq 10^{14}$ W/cm^2). (b) Series of sorted single shot spectra of Ne recorded with FLASH operating at hν(FEL)= 46eV and by applying a NIR dressing field of about 3×10^{13} W/cm^2.

varies and, more importantly, the exact kinetic energy of the lines is slightly displaced for the high dressing fields as a result of the ponderomotive potential. In order to obtain a better basis for further analysis, it is necessary to record single-shot spectra at the position of optimal temporal overlap. A series of such single-shot spectra is presented in figure 5b. The $2p$ ionization of Ne at a photon energy of 46 eV is taken here as example. The single shot spectra are sorted with respect to the number of sidebands, i.e. the intensity of the dressing field. The spectra mirror directly the effect of the jitter, which is larger than the individual temporal width of FLASH and the NIR laser pulses, and explore the entire region between perfect overlap, i.e. maximum number of sidebands, and very little or no overlap evidenced by the observation of a pure one-photon ionization line. A detailed analysis of the data and a comparison of these multi-sideband structures with the corresponding theoretical treatments is in preparation [28].

In general, this type of experiment, i.e. the two-color ATI of rare gases, is well described by theory and has provided an ideal ground to characterize the new XUV Free Electron Laser sources, such as FLASH. The corresponding studies have been the starting point for a number of two-color pump-probe experiments at FLASH.

3.2. Polarization control of the two-color photoionization process

In one of the first applications, the well-defined linear polarization of FLASH and the NIR laser was used to obtain further information on the partial photoionization cross sections for two- and multi-photon ATI processes [10]. Taking as an example the $1s$ ionization of dressed He atoms by FLASH pulses, the intensity of the sidebands shows a characteristic dependence on the relative orientation between the linear polarization vectors of the two radiation fields (figure 6). Each individual spectrum represents

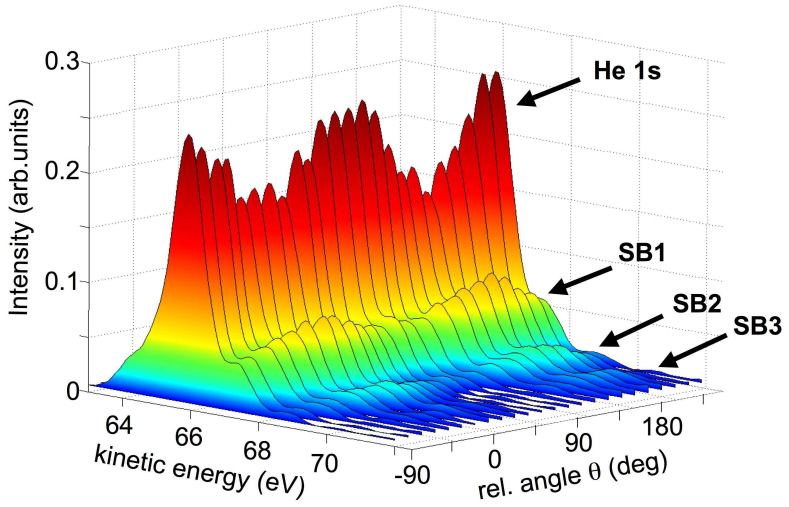

Figure 6. Photoelectron spectra of atomic He recorded with FLASH operation at 13.7 nm (90.5 eV) and for optical dressing fields of about $6\times\ 10^{11}$ W/cm^2 A series of spectra is presented for different relative orientations θ between the linear polarization vectors of FLASH and the NIR laser (from [10]).

the average of 100 FEL pulses, which were recorded for complete spatial overlap and at nominal temporal delay $\Delta T = 0$ fs between the XUV and the NIR pulses. Maximal intensity is transferred from the main $1s$ photoline to the sidebands for parallel orientation of both polarization vectors, i.e. $\theta = 0°$. The sidebands are much reduced when the orientation of the electric field vectors is perpendicular, i.e. $\theta = 90°$. Since the total photoionization yield remains constant, any increase or decrease in the sideband intensity is directly matched by the corresponding contra-variation in the main line intensity.

For low dressing fields ($I \leq 10^{11}$W/cm^2), i.e. when only one sideband is observed on each side of the main line, the sideband signal represents the direct signature of a two-color two-photon process. Following angular momentum conservation rules, the outgoing electron in the $1s$ photoionization process can be described in terms of partial waves with s and d symmetry:

$$He\,1s^2\,{}^1S_0 + h\nu(FLASH) + h\nu(NIR) \rightarrow He^+\,1s\,{}^2S_{1/2} + \epsilon s/\epsilon d. \qquad (1)$$

For higher dressing fields, the situation is more complex, since the higher sidebands are described as a mixture of electrons with alternating even ($s, d, g, \ldots$) or odd ($p, f, h, \ldots$) symmetries. In addition, interferences between different multi-photon pathways have to be taken into account for the interpretation of the experimental spectra. In the simplest case of two-photon ionization, the observed intensity variation can then be described analytically by means of a time-dependent second-order perturbation calculation, which is valid at low intensities, and is expressed as a function of the relative angle of the polarization vectors θ and the partial yields for emission of s and d electrons,

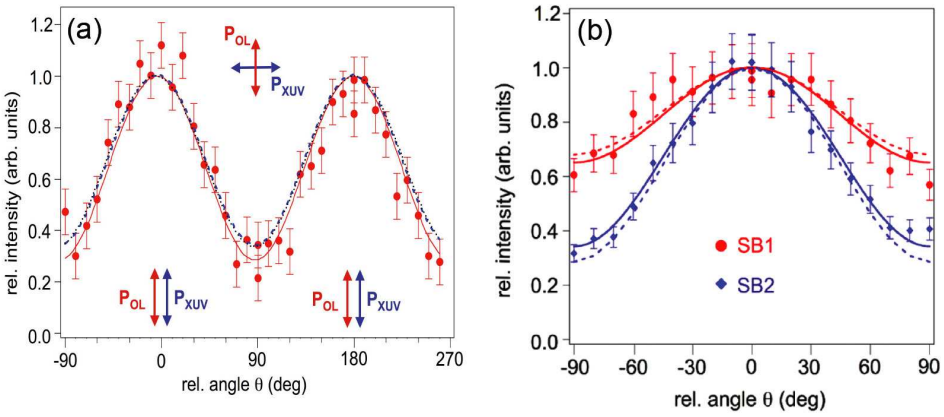

Figure 7. (a) Variation of the upper sideband yield for the 1s ionization of atomic He as a function of the relative angle θ between the linear polarization vectors of FLASH (13.7 nm) and the NIR laser (800 nm, I(NIR) $\leq 10^{11}$ W/cm^2). (b) Intensity variation for the first (circles) and second (diamonds) sideband of the He 1s ionization for high dressing fields (cf. figure 6). The solid line denotes the fit to the experimental data. The results of time-dependent second-order perturbation theory (dashed line) and "soft-photon" approximation (dotted line) are almost identical (from [10]).

respectively:

$$\sigma(\theta) \propto 3S_2 + (5S_0 + S_2)\cos^2\theta \tag{2}$$

with $S_i = |T_i|^2$, where T_i (i=0,2) are second-order radial integrals associated with the emission of s- and d-electrons, respectively [29]. In addition, the polarization dependence of the sidebands can also be described by the soft-photon approach, which can also account for higher intensities, i.e., for the departure from the lowest-order perturbation contribution.

In figure 7a, the result of both theoretical descriptions is compared to the experiment. From the experimental data, a contrast between maximal and minimal intensity of 3.4 is extracted, which leads to a value of 1.25 ± 0.3 for the ratio of the parameters S_0 and S_2. Both theoretical approaches are in good agreement with the experiment and values of 0.98 and 1.0 are obtained from the second-order perturbation theory calculation and the soft-photon approach, respectively. From this analysis, a 1.5 times higher relative yield for the emission of s (equivalent to $5S_0$) than of d (equivalent $4S_2$) electrons is extracted for parallel polarization ($\theta = 0°$). This value, obtained far above the 1s ionization threshold, is very different from that predicted by the normal propensity rules, which would favour, upon absorption of one photon, transitions corresponding to an increase of the angular momentum ($\Delta l \geq 1$). In the region closer to the threshold at a photon energy of 48.6 eV, a smaller ratio S_0:S_2 of about 0.9 ± 0.3 was determined, and theory predicts a value of 0.34 at threshold (24.5 eV), which corresponds to a 2.3 times higher yield of d than of s electrons for the case of parallel orientation of the polarization vectors [30]. This trend underlines

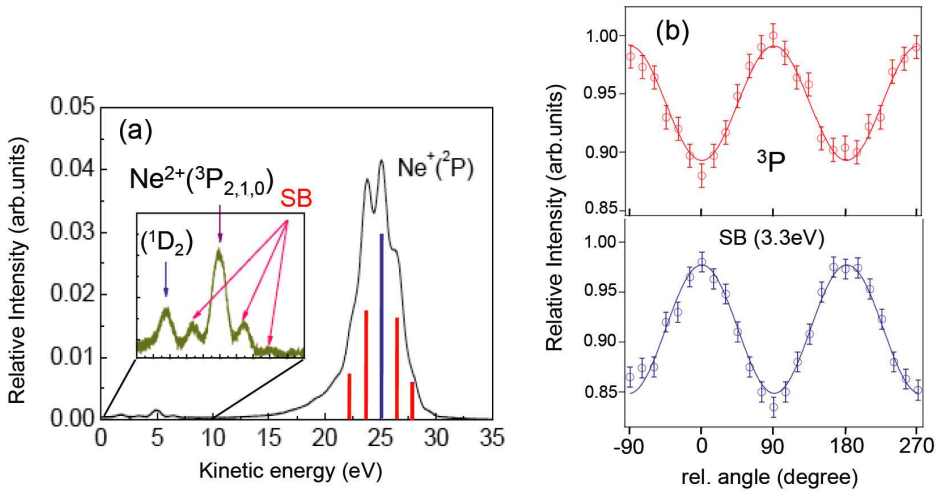

Figure 8. (a) Typical photoelectron spectrum of atomic Ne recorded upon ionization with FLASH radiation of wavelength 26.9 nm (photon energy 46 eV) in the presence of a NIR dressing field of about 5×10^{12} W/cm^2. (b) Intensity variation of the $Ne^{2+}\, 2p^4\, {}^3P_{0,1,2}$ photoline arising from the sequential TPDI and of the corresponding low-energy sideband (at 3.3 eV kinetic energy) as function of the relative angle θ between the two linear polarization vectors.

the general tendency that the contribution of the d wave increases at lower excitation energies, in better agreement with the propensity rules.

For the case of a stronger optical dressing field (10^{11} W/cm^2), when more than one sideband is observed, the amplitude of oscillation of the first sideband is less pronounced (figure 7b) exhibiting a contrast of only 1.5±0.3. The "soft-photon" approach describes satisfactorily the main features of the experiment, and the reduced contrast in the polarization dependence of the sideband intensity is explained as a consequence of contributions from numerous quantum paths, i.e. processes due to the exchange of many photons and hence to the population of higher angular momentum states. For parallel orientation of the polarization vectors of the XUV and the NIR fields, this results in a destructive interference in the case of the first sideband (SB1) and thus to a reduced contrast. This behavior is also observed for the second sideband (SB2). The intensity variation of SB2 is again much more pronounced with values of 3.3 and 3.5 in experiment and theory, respectively, but it does not reach the limiting value of $2n + 1 = 5$, that is predicted by the soft-photon approximation.

The two-color excitation scheme and the control of the polarization of both beams was also used to get more information about fundamental processes, which are caused by the strong XUV field, namely two-photon double-ionization (TPDI). Many experiments and theoretical works have already been performed on the TPDI of atomic He highlighting the competition and the intensity dependence of the two principal mechanisms, i.e. direct two-photon ionization and sequential double ionization (e.g.[31, 32, 33] and references therein). More recently, the angular distribution of the

sequential TPDI of atomic Ne has been measured and theoretically described [34, 35]. When ionizing the Ne atoms with FLASH pulses of 46 eV photon energy, i.e. below the double-ionization threshold, and applying pulse energies of about 50 μJ, which provide an XUV field of about 10^{12} W/cm^2 in the interaction region, the electron lines corresponding to the sequential TPDI are observed in the low kinetic energy region of the spectrum (figure 8a). One-photon processes give rise to the strong lines at high kinetic energies, which are assigned to the ionization of the Ne 2p electron (binding energy of 23 eV). The subsequent ionization of the Ne^+ ion by the same FLASH pulse results in the appearance of smaller lines in the region below 10eV, which are assigned to the $Ne^{2+}\,2p^4\,{}^1D$ and ${}^3P$ final states. The one-color spectrum using only FLASH pulses was already measured [36]. For the present two-color spectrum (figure 8a), a strong NIR field (about 5×10^{12} W/cm^2) was added, which causes sideband structures on the $2p$ photolines as well as on the lines corresponding to sequential TPDI. In contrast to the discussion above, the sidebands in the low kinetic energy region are now a mixture of different contributions arising from the different pathways, since the individual $2p^4$ multiplet lines are separated by about 3.2 eV, i.e. twice the photon energy of the NIR laser (1.55 eV).

Similar to the $1s$ ionization of He, the intensities of the $2p$ lines of Ne and the corresponding sidebands depend strongly on the relative orientation between the linear polarization vectors of the ionizing FLASH radiation and of the NIR dressing field (figure 8b). Since the dressing field simply redistributes the photoelectrons among the photolines and the sidebands, both curves are characterized by oscillations that are out of phase by 90 degrees, i.e. minima in the sideband intensity correspond to maxima in the photoline intensity and vice versa. The amplitude of the intensity variation is determined by the relative partial cross sections in the two-photon ionization process. However, in contrast to the case of He $1s$ ionization, for Ne $2p$ ionization the one-photon process is already described by two outgoing partial waves with ϵs and ϵd symmetry. In an earlier work on the two-color ATI process in Ar using HHG sources [37], it was shown that in the case of ionization from a p shell it is possible to extract from the intensity changes of the sidebands the asymmetry parameter of the one-photon process. The measured polarization dependence of the sidebands arising from the sequential TPDI should therefore provide additional and complementary information on the angular distribution of the TDPI.

3.3. Multi-photon effects in molecular dissociation

The high intensity of the optical laser can also be used to probe molecular dissociation processes induced by the XUV radiation of FLASH. In a first series of experiments, H_2 molecules were ionized far above threshold by FLASH pulses of 90.5 eV photon energy. The subsequent dissociation of the highly excited molecular ionic states results also in the formation of excited neutral atoms, which correspond to the dissociation channel leading to a proton (H^+) and an excited atom ($H^*(nl)$). The dissociation mechanisms

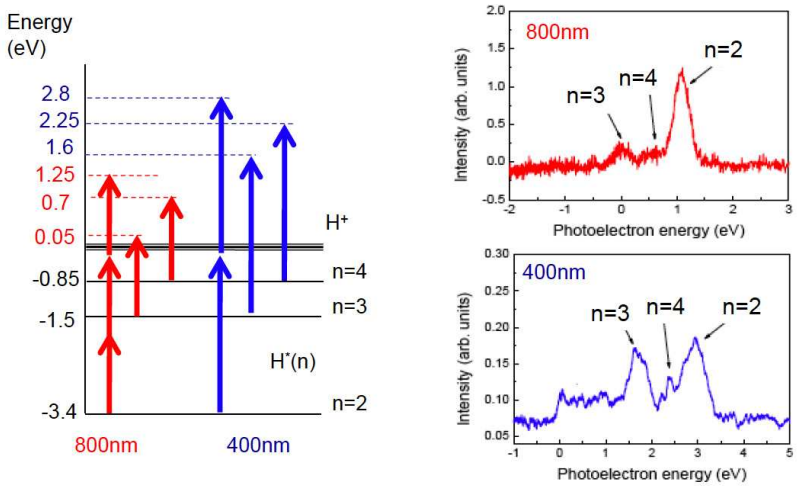

Figure 9. (Left-hand side) Schematic representation of the ionization pathways for excited hydrogen atoms. (Right-hand side) Typical photoelectron spectrum of excited H atoms recorded upon dissociation of hydrogen molecules with FLASH radiation at 13.7 nm (90.5 eV) and ionization by an optical laser of (bottom) 400 nm, 200 μJ, 120 fs and (top) 800 nm, 1.5 mJ, 120 fs (from [30]).

of this prototypical molecule have been largely investigated at lower excitation energies and dissociation into excited neutral atoms was studied up to $h\nu = 60eV$ by fluorescence spectroscopy in order to probe the excited states (e.g. [38, 39]). In contrast to these studies, photoionization of the excited atoms by the optical laser and analysis of the photoelectron spectrum was used in the experiment at FLASH in order to characterize the production of excited states. By using the 800 nm (1.55 eV) NIR laser or the frequency doubled 400 nm (3.1 eV) output of the laser, it is possible to ionize in a one-photon process hydrogen atoms with the excited electron in orbitals with principal quantum number $n \geq 3$. Ionization of the $n = 2$ shells requires already a multi-photon process (figure 9a) for both 800 nm and 400 nm laser light. For the experiments reported here, the temporal delay between the pulses of FLASH and the optical laser was set to about 1 ps, i.e. the optical pulses always arrived in the interaction region after the corresponding FEL pulse. The experimental spectrum (figure 9b) obtained upon ionization with the 800 nm laser is dominated by a strong line at about 1.2 eV kinetic energy, which is attributed to the three-photon ionization of the $n = 2$ states. One-photon ionization from $n = 3$ and 4 produces the smaller structures at lower kinetic energies.

The comparison of relative intensities of the observed lines provides an indication of the relative populations of the excited atomic states. The strong intensity of the line attributed to the ionization of orbitals with principal quantum number $n = 2$ shows that these orbitals are predominantly populated after dissociation of the molecule. The fact that ionization from $n = 2$ requires two (400 nm) or even three (800 nm) photons supports further this statement, since multi-photon ionization cross sections

are generally much weaker than those for one-photon processes, which have to be taken into account for the intensity of the $n = 3$ and 4 photolines. The surprisingly high intensity for the $n = 2$ line observed in the spectrum recorded with the 800 nm laser and attributed to a three-photon process may be explained by resonant excitations of intermediate Rydberg states close to the ionization threshold, which can be reached by a two-photon process. This interpretation is corroborated by the results obtained with the 400 nm radiation, where the ionization process may again be enhanced by a resonant intermediate state. Further studies taking into account the intensity dependence of the different photoelectron lines, comparison with theoretical results for the multi-photon rates as well as the use of an even shorter wavelength for the optical laser allowing all final products to be probed by a one-photon process, will enable finally the determination of the relative populations of H atoms in $n = 2, 3$ and 4 excited states. In addition, time-resolved experiments will provide insight into the dynamics of the dissociation process. The two-color pump-probe scheme employed here is directly applicable to other molecules and the results obtained on the photodissociation of molecular hydrogen therefore represent the starting point for time-resolved two-color studies in the femtosecond time regime.

4. Conclusion and Outlook

Some of the exciting opportunities that two-color experiments on atoms and molecules, provide have become possible due to the unique characteristics of the Free Electron Laser in Hamburg and are demonstrated here with various illustrative examples. For atomic photoionization processes, two-color above threshold ionization was investigated at different intensities of the optical dressing field as well as for different relative orientations of the linear polarization vectors of both XUV and optical photons. In these experiments, it was possible, having first used them for a detailed characterization of FEL pulses and of the temporal stability of the pump-probe set-up, to determine partial photoionization cross sections in two-color ATI as well as to explore multi-photon processes induced by the strong optical field. In general, the experimental results are well reproduced by theoretical treatments obtained by employing second-order perturbation theory or the "soft-photon" approximation. For molecular dissociation processes, the fragmentation of molecular hydrogen has been studied in a proof-of-principle experiment. In particular, the dissociation channel leading to excited hydrogen atoms could be characterized via single- and multi-photon ionization induced by the time delayed optical laser.

In future studies, the possibility to tune the wavelength of the FEL and of the optical laser will become more and more important. In particular it will enable the excitation of highly excited autoionization states (c.f. process (c) in figure 1). By combining both the intense XUV and optical radiation, and adjusting precisely their photon energies, resonances can be excited which are inaccessible by a one-photon process from the electronic ground state due to parity conservation rules. The relaxation pathways and

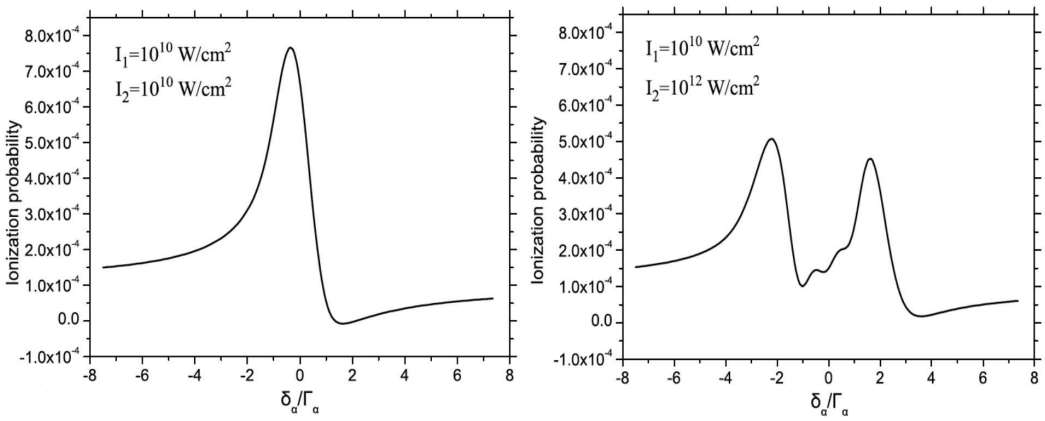

Figure 10. Photoionization probability of atomic He for two different intensities of the optical laser (from [41]). The x-axis corresponds to XUV photon energy detuning δ_a from resonance in units of the Fano resonance width Γ_a. The intensities of the XUV (I_1) and the optical (I_2) lasers are given in the figures while the duration of the pulses is 200 fs and 150 fs, respectively.

dynamics of these resonances are still almost completely unexplored. The possibility to vary widely the wavelength, the temporal delay, the polarization and the intensity of both pulses provides a unique basis for a detailed characterization of these resonances. Beside the investigation of the electronic relaxation of the two-photon resonances, the strong optical field can also be used to shift the energy position of the resonances, i.e. to control the transparency of the medium at a particular wavelength. Moreover, the wavelength of both photons can be chosen to coincide with a doubly resonant excitation. The underlying physics for such doubly optically resonant processes has already been investigated in many theoretical papers (e.g. [40, 41, 42]), but only one experiment has been performed up to now, and only at very low excitation energies [43]. An illustration of the expected effect of optical coupling between two autoionization states, here $2s2p\,^1P$ and $2s3d\,^1D$ of atomic He, is given in figure 10 [41]. For weak optical fields, the effect of the $He^*\,2s2p\,^1P$ autoionizing state is observed as the usual enhancement of the photoionization cross section in the vicinity of 60.1 eV excitation energy. The resonance profile is described by the typical asymmetric Fano-type lineshape, which is the result of interference between the direct and the resonant ionization process. For higher optical fields, the photoionization cross section is strongly modified by the coupling of the two autoionizing resonances. The opening up of new ionization continua has to be taken into account and results in a very different resonance profile. The sensitivity of the resonance profile to the applied optical field provides thereby a new and very sensitive control on the dynamics of these highly excited autoionization states.

Beside the wavelength tunability of the FEL, the temporal width of its intense XUV pulses offers various possibilities for experimental studies of atoms and molecules. In particular, the option to use XUV pulses with a temporal duration of only a few femtoseconds, shown recently at LCLS [44], is a very promising development, since

the lifetimes of core-excited resonances are generally on similar timescales. When combining XUV pulses with a NIR laser, the pulse width of the ionizing FEL radiation is similar to the width of one optical cycle. Under these conditions the formation of the photoelectrons is determined by interference effects, which completely govern the angular distribution of the photoelectrons [45].

In addition, the study of molecular dissociation dynamics will largely benefit from the different two-color excitations schemes involving FEL radiation. Similar to the given example of photoinduced fragmentation of H_2, the various dissociation pathways and final products for the dissociation of larger molecules can be probed by multi-photon excitation or ionization induced by the optical laser. Special attention will certainly be given to investigations on molecules, which are spatially aligned by an intense optical field (e.g. [11]), allowing the extraction of information for well-defined and fixed geometries of the molecules under study. Finally, many theoretical suggestions for time-resolved studies of core-excited molecules have already been given, focusing often on the phase sensitivity of the processes (e.g. [46, 47]). Based on the combination of XUV and NIR femtosecond pulses, the excitation of vibrational wavepackets can be used to explore the potential curve of core-excited states outside the Franck-Condon region or to investigate the dynamics of proton transfer in water dimers. These two examples deliver insight into the rich and exciting possibilities for future two-color experiments on molecular dissociation.

5. Acknowledgements

We would like to acknowledge the contributions and the exchange with many collaborators during the last years. Especially, we appreciated various help during the experiments at FLASH from A. Azima, D. Cubaynes, J. Dardis, J. Feldhaus, P. Hayden, P. Hough, E. T. Kennedy, H. Redlin and V. Richardson as well as substantial theoretical support and stimulating discussions with A. N. Grum-Grzhilailo, E. V. Gryzlova, P. Lambropoulos, A. Maquet and R. Taieb. We greatly appreciate the work of the scientific and technical team at FLASH, in particular the machine operators and run coordinators. Support from the EU RTD-project X-Ray FEL Pump-Probe HRPI-CT-1999-50009, from Science Foundation Ireland, IRCSET and from the France-Ireland ULYSSES program are acknowledged.

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