

Time-resolved electron spectroscopy of atomic inner-shell dynamics

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Abstract

The extremely fast evolution of core-hole relaxation was not yet observable directly in the time-domain. A novel technique combining core-hole creation with attosecond extreme ultraviolet (EUV) pulses and electron wave-packet sampling with a pulsed laser-field provides the necessary experimental tools. As a benchmark, the exponential decay of 3d holes in atomic krypton was tracked yielding a decay constant of 8 fs.

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1. Introduction

A single oscillation of the electromagnetic field of visible light leaves the electron of the hydrogen atom enough time to complete about a dozen classical roundtrips around the nucleus. More tightly bound electrons in heavier atoms are even faster. Energy exchange between electrons in an atomic shell can be expected to require several orbital periods, but still will the creation of a new stable state be finished after a few hundred attoseconds ($1 \text{ as} = 10^{-18} \text{ s}$) to a few femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$).

If we are interested in following in the time-domain how the electronic structure in the interior of the atomic shell evolves after an excitation event not only a sufficiently high excitation energy is necessary but also a method enabling extremely fast stroboscopic snapshots of the emerging electron waves. Electronic detectors of sufficient velocity are not available and even the fastest streak-cameras are limited to a temporal resolution of a few 100 fs. It is for these reasons, that up to now information about the inner-shell decay dynamics was deduced from measurements of the spectral linewidth $\Gamma = \hbar/\tau$, assuming an exponential decay with

time-constant τ and a corresponding Lorentzian line shape [1].

On the other hand, extremely high temporal resolution is promised by the pump-probe technique, where a pump pulse excites the system under study which then develops for a well defined time until its state is sampled by a second delayed probe pulse. Due to the rapid progress in the development of ultrashort laser sources with pulses as short as 5 fs this universal method has proven its utility in the field of femtochemistry [2]. Here, the typical molecular photoreactions like vibrational excitation or dissociation, governed by the coupling between electronic and nuclear movement, occur on a femtosecond to picosecond time scale. As with any cross correlation technique, the achievable temporal resolution is determined by the shortness of the electromagnetic pump- and probe pulses. A transfer of this technique to time-resolved studies of processes in the interior of the atomic shell therefore requires sub-fs pulses of ionising radiation in the extreme ultraviolet (EUV) or X-ray range. Such ultrashort pulses at such high photon energies are not provided by established light sources like X-ray tubes, synchrotrons or laser-driven plasmas. In the work reported here, high harmonics of few-cycle laser pulses provide the required photon energies as well as an ultrashort—attosecond—time-structure, making them

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a unique source for EUV-pump/laser-probe experiments on atoms. In order to utilise the pump-probe principle for time-resolved electron spectroscopy, a sufficiently fast physical mechanism must be found which correlates both light pulses with the atomic ionisation process under study. It turns out, that an acceleration of electrons liberated by the EUV-pump pulse in the field of the probing laser provides us with an extremely rapid ‘shutter’ for sampling the occurrence of electrons in the ionisation continuum. The capability of these novel tools is demonstrated by a first example of a time-based tracking of the atomic Auger decay—the MNN Auger decay in krypton.

2. Experimental techniques

2.1. A source of attosecond EUV pulses

For quite some time high harmonics of femtosecond laser pulses [3] were considered as potential candidates for sub-fs light bursts. In this technique odd multiples $h\nu_{\text{EUV}} = n \times h\nu_{\text{L}}$ of the laser frequency ν_{L} are generated if the ac-field strength approaches the Coulomb-field experienced by valence electrons of atoms in the laser-focus. The resulting high orders— $n > 300$ have been reached [4]—correspond to wavelengths in the EUV and soft X-ray range. Utilisation of fundamental laser pulses with a duration of a few tens of femtoseconds yields trains of radiation bursts [5,6] with a period of half a laser cycle ($T_{\text{L}}/2 \sim 1.3$ fs at $\lambda_{\text{L}} = 750$ nm). Accordingly, several schemes were proposed [7–9] for the selection of a more desirable isolated pulse. Recently, the generation of single EUV pulses with attosecond (250 –5/+30 as) duration could be demonstrated [10] by compressing the fundamental laser pulses to a few optical cycles and by spectrally filtering the emerging high harmonic radiation. An amazingly powerful semi-classical model [11] describes the high harmonic generation as a result of a three-step process: Initially, a weakly bound valence electron is emitted from an atom by tunnel-ionisation in the intense laser-field. The electron is then accelerated in the alternating electrical-field and may eventually return to the mother ion where it recombines upon emission of energetic radiation. The periodical nature of this process manifests itself in a discrete electromagnetic spectrum with odd harmonics up to a high energy cut-off which is determined by the maximum electron kinetic energy acquired in the laser-field. Owing to the pronounced non-linear character of tunnel-ionisation only the highest field strengths in the laser pulse contribute to this cut-off region. For sufficiently short pulses with a considerable contrast between subsequent field extreme radiation should consequently emerge only from a temporally well confined range around the strongest field amplitude thus forming an isolated attosecond EUV burst. The apparatus backbone for a realisation of this scheme is a laser system [12] delivering intense near-infrared (750 nm wavelength) light pulses of less than three oscillation pe-

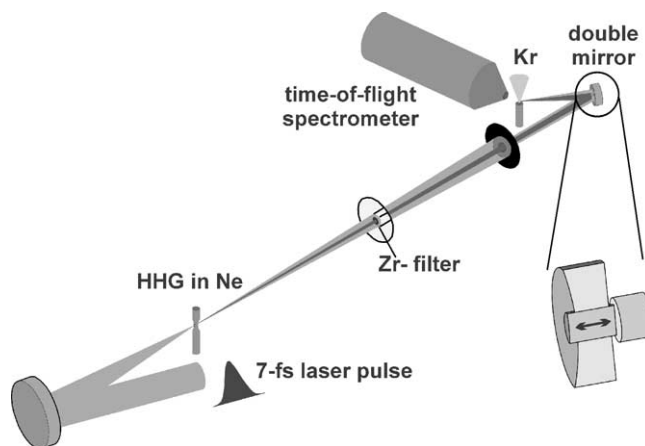


Fig. 1. Experimental arrangement for time-resolved electron spectroscopy. Attosecond EUV pulses are generated in neon as high harmonics of an intense few-cycle laser pulse. Spectrally filtered with a dedicated Mo/Si multilayer mirror, EUV- and a delayed laser-pulse are focused into the gaseous target under study. Delay-dependent variations in the kinetic energy of the emitted electrons are acquired with a time-of-flight spectrometer.

riods (approx. 6 fs) duration (Fig. 1) at a repetition rate of 1 kHz. In the laser focus located within a neon-gas filled tube intensities exceeding 10^{14} W/cm² lead to the generation of high harmonics with a cut-off at about 100 eV photon energy. Laser- and EUV beam are guided to interact once again in a second gas target using a dedicated double-reflector assembled from two concentric mirrors. The inner spherical X-ray multilayer mirror [13] filters a 3–10 eV wide spectral band in the 90–100 eV range from the high harmonic spectrum while the outer ring-shaped mirror of the same focal length refocusses the laser beam. In this way, both beams are spatially superimposed in the second gas medium. The temporal overlap can be varied by a piezo-electrical translation of the inner mirror with nanometer precision and reproducibility thus enabling pump-probe delays with attosecond resolution.

2.2. Ultrafast sampling of electron energies

The key to taking snapshots of the electron emission with unprecedented temporal resolution is the electrons' interaction with an intense laser-field, acting as an immaterial electron 'shutter' [14]. Rather than blocking the electrons, the laser-field introduces a modulation of their kinetic energy which can be detected with an electron spectrometer. Let us consider the photoionization of an atom in the presence of a visible laser-field being too weak to directly induce or even influence the electron emission process. Only after excitation with an ultrashort (assumed to be δ -like for this discussion) EUV pulse with sufficient photon energy the atom is ionised and a photoelectron leaves the ion with a defined momentum p_i . Once liberated, the electron experiences the laser-field and is accelerated in the direction of the light polarisation (Fig. 2). The classical analysis of the electron tra-

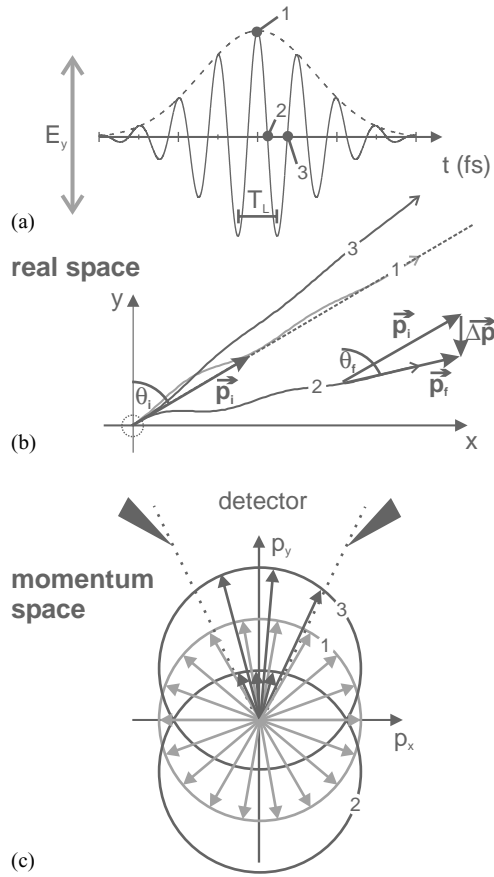


Fig. 2. The classical trajectories (b) of electrons liberated by the EUV pump pulse sensitively depend on the phase and magnitude of the probing laser pulse (a) at the instant of their emission. The momentum exchange (c) with the light-field leads to a bipolar shift synchronously with the laser-field oscillation.

jectories reveals, that the final momentum $p_f = p_i + \Delta p$ when the laser pulse has faded away strongly depends on the phase and amplitude of the laser-field at the instance of electron injection, i.e. the ionisation event. The transferred momentum Δp vanishes when the ionisation takes place in the field maximum and is strongest for the zero field transitions a quarter of a light period earlier or later (Fig. 2a). This extreme sensitivity of the electron momentum on the light phase builds the footing for temporal measurements with a resolution of a fraction of the laser period (approx. $T_L/20 < 200$ as for the current laser period of $T_L = 2.6$ fs). To this end the corresponding modulation of kinetic electron energies is detected with a time-of-flight spectrometer (Fig. 1) with a varying delay between the EUV pump and the laser probe-pulse [14]. The energy shift for an electron of initial energy W_i ionised in the laser-field

$$E_L = E_a(t) \cos(\omega_L t) \quad (1)$$

with a delay Δt with respect to the maximum of the field-envelope E_a can be expressed as

$$W_f(\Delta t) = W_i + \sqrt{8W_i k E_a^2(\Delta t)} \sin(\omega_L \Delta t) \quad (2)$$

with $k = e^2/4m_e\omega_L^2$. Even for a laser intensity of 10^{13} W/cm² corresponding to field strengths well below the Coulomb-field experienced by valence electrons this results in a bipolar shift of ± 20 eV. This steering effect [15] is therefore much stronger than the more familiar unipolar ponderomotive shift (or ac-Stark-effect) which amounts to only 600 meV at this intensity level.

So far we assumed that the electron wave-packet essentially mimics the intensity envelope of the incoming EUV pulse and has a duration τ_e of a fraction of the laser oscillation cycle, $\tau_e \ll T_L$. In this limit, the above classical description provides a reliable framework for the analysis of recent experiments characterising the temporal properties of sub-fs EUV pulses. A duration of less than 0.5 fs could be determined [10,15] and the isolated nature of the EUV pulses verified. However, an extension of this sampling technique to secondary electron emission—e.g. Auger decay following the creation of a core-hole—must account for a possible temporal extension of the electron wave-packet over one or more laser cycles, $\tau_e > T_L$. The analysis reveals [16], that in this regime different portions of the electron wave-packet interact coherently with the laser-field and lead to a modulation of the electron energy in the form of discrete side bands. In other words, for an interaction between electron and laser-field extending over more than half a laser cycle energy transfer occurs only in a quantized manner at multiples of the photon energy $h\nu_L$. This latter case applies for the time-resolved studies presented in the following.

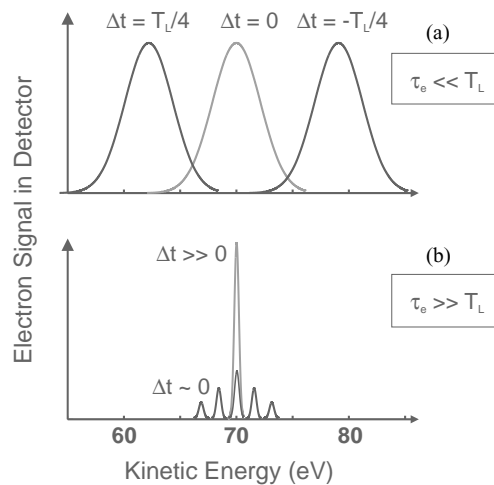


Fig. 3. (a) Schematically sketched electron spectra at different EUV-laser delays for an electron wave-packet considerably shorter than the laser period T_L . For an electron emission exceeding T_L , the distribution becomes modulated with spectral sidebands due to a quantized absorption/emission of laser photons.

3. Results and discussion

Having a source of attosecond EUV pulses at hands with sufficient photon energy for a ionisation of atoms from inner shells, we aimed for a tracking of the subsequent core-hole relaxation using the light-sampling method described above. One of the most comprehensively studied systems (in the energy domain) of atomic Auger decay is the non-resonant MNN Auger decay in krypton following excitation of the 3d shell above the ionisation threshold at 93.8 eV. Information about the Kr-3d core-relaxation time τ_h has been deduced previously from a thorough analysis of the spectral width of highly resolved photo lines [17]. For a time-based measurement of τ by directly sampling the Auger wave-packet krypton atoms were excited with an EUV pump-pulse in a 3 eV wide band centred at 97 eV, corresponding to a (Fourier-limited) duration of 0.9 fs. A typical electron spectrum acquired in the 40 cm long time-of-flight spectrometer after integration over 300,000 laser shots is shown in the upper right corner of Fig. 4. Combining 20 of such spectra taken at different delays Δt between the EUV and the laser pulse a map of the temporal evolution of the electron emission is obtained, displayed as a surface plot in Fig. 4. According to the above discussion for an electron emission extending over a few femtoseconds, the interaction with the laser-field should lead to the emergence of sidebands separated by multiples of $h\nu_L \sim 1.6$ eV from each Auger line. For the case of the $M_{4,5}N_1N_{2,3}$ Auger lines investigated here this spacing approximately coincides with the typical separation between the Auger lines thereby obscuring most of the sidebands. Only for the least energetic (1P_1) line the -1 st sideband is well isolated and will be considered in the following. The onset of this sideband together with the corresponding depletion of the mother line at times after the hole creation ($\Delta t = 0$) clearly indicates a delayed

electron emission. For a quantitative analysis, the area of this sideband is evaluated which corresponds to the overlap between the envelopes of the Auger emission rate $R_0 \times \exp(-t/\tau_h)$ and the laser pulse intensity raised to a power α , $E_a^{2\alpha}(t)$ [18]. While $\alpha=1$ in the perturbative limit at very low laser intensity, for the intensities around 5×10^{11} W/cm² used in this experiment we determined $\alpha = 0.5 \pm 0.2$ by varying the intensity at a fixed delay Δt . Since the sideband area displayed in Fig. 5a represents a convolution of the Auger emission rate and the laser envelope the latter must be precisely known for an extraction of the desired value of τ_h . This calibrating information is simultaneously embedded in the acquired electron spectra in the delay-dependent broadening of the 4p photo line (Fig. 4). Since the direct ionisation process can be considered as instantaneous on the relevant time scale, according to Eq. (2) the spectral broadening of the 4p photo line (Fig. 5b) directly maps the evolution of the laser-field envelope $E_a(t)$. With this information as an input a fit procedure with τ_h as the only varied parameter is capable of extracting the temporal evolution of the Auger emission rate. Taking into account the uncertainty in the determination of the non-linear exponent α this analysis yields $\tau_h = 7.9 (+1.0/-0.9)$ fs for the lifetime of $M(3d_{5/2})$ vacancies in krypton [16]. This value corresponds to a natural line width of 84 ± 10 meV, well in accordance with the measured value of 88 ± 4 meV from [17]. However, those energy-domain measurements were performed on photo- rather than Auger electrons with exciting photon energies well above the ionisation threshold in order to avoid a distortion of the line profiles by post-collision interaction (PCI) [19]. In contrast to that, by definition PCI does not alter the hole-relaxation itself; therefore our time-based approach is not subject to such perturbations and the measurement of τ_h very close (<3 eV) to the ionisation threshold underlines that τ_h does not depend on the excess excitation energy.

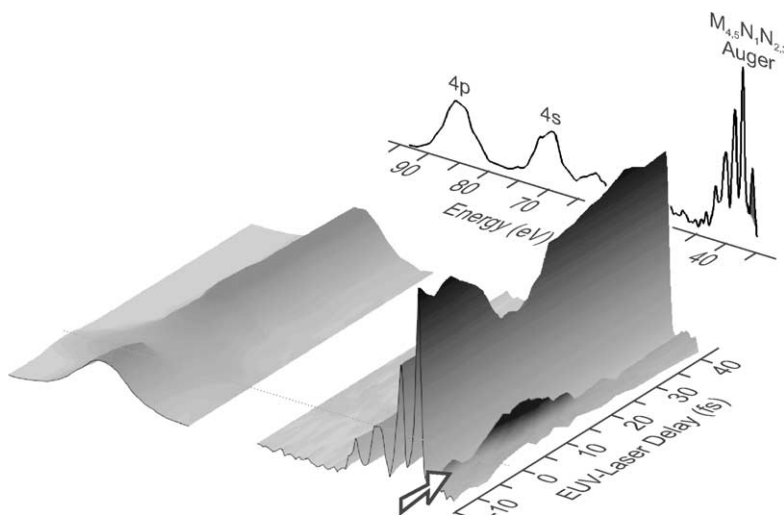


Fig. 4. Single Kr spectrum at $\Delta t = 4$ fs (upper right) and delay-dependent measurement of the $M_{4,5}N_1N_{2,3}$ Auger group as well as the 4p photo line. The sideband (arrow) area is determined by the temporal overlap between the exponentially decaying Auger signal and the field-envelope of the laser pulse, the latter being directly mapped by the broadening of the 4p-photo line, as clearly discernible around $\Delta t = 0$ fs.

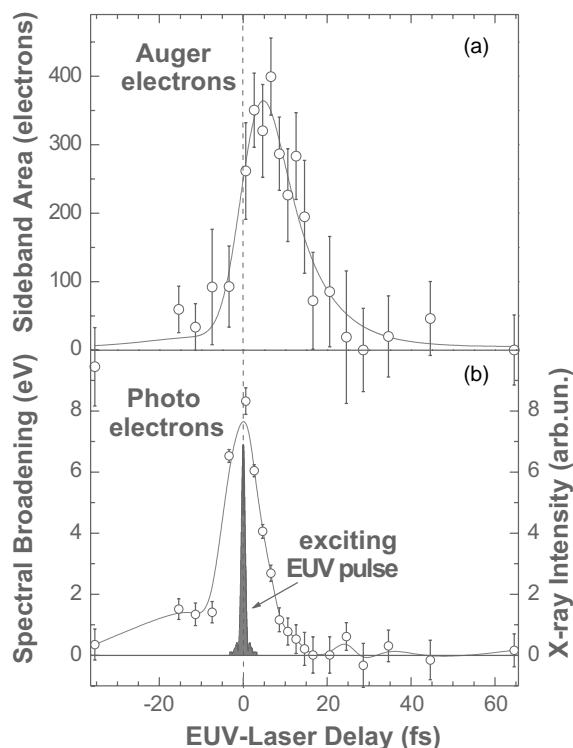


Fig. 5. (a) Sideband area (circles) of the first-order sideband (arrow in Fig. 4) of the lowest-energy Kr $M_{4,5}N_1N_{2,3}$ Auger line. Deconvolution with the laser-field envelope (b), determined from the broadening of the Kr 4p photo line, yields the desired time-constant of the exponential Auger decay of the Kr $3d_{5/2}^{-1}$ hole.

Moreover, the good correspondence between the lifetime results from Auger line [16] and photo line [17] based measurements indicates that the Kr 3d core-hole relaxation is clearly dominated by the non-radiative Auger channel while the radiative (fluorescence) channel is much weaker.

4. Conclusion

The exponential decay of inner-shell vacancies—hitherto been inferred from energy-domain measurements—has now been investigated directly in the time-domain. The decay of krypton M-shell-holes excited with ultrashort EUV pulses served as a benchmark process for proving the feasibility of time-resolved atomic inner-shell spectroscopy. The utilised EUV-pump/laser-probe technique makes use of a momentum transfer between the laser-field and electrons at the instant of their emission and does therefore not depend on particular transitions in the probing step. Accordingly, direct photoionization as well as indirect photoemission phenomena like Auger-decay are becoming accessible to time-resolved studies.

Advances in the light source development will lead to an extension of the experimental capabilities. With higher photon energies [4] deeper atomic shells—with generally faster decay processes—can be excited. The introduced

ultrafast electron-sampling principle is capable of resolving dynamics on a sub-laser-cycle time-scale. Very recently, fundamental laser pulses with a locked phase between the laser carrier and envelope have become available [20] and provide sufficient phase stability and reproducibility to improve the temporal resolution to a few hundred attoseconds.

The most exciting perspectives of the method are connected with studies of such phenomena that are not directly reflected in the kinetic electron energy spectrum. Whenever continuum states are involved in the atomic relaxation, several interfering relaxation pathways may connect the same initial and final state, resulting in a complex non-exponential temporal behaviour. As an example, the coherent excitation of two or more competing reaction channels is known to result in an oscillation of the transition moments. Finally, for the current work a low laser intensity was chosen in order to rule out perturbations of the electronic process under study. However, we could also intend to influence the process with an external laser-field. The objective would be to achieve—as recently demonstrated in femtochemistry for molecules [21]—a certain degree of control over fundamental atomic photoreactions.

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References

- [1] V. Schmidt, *Electron Spectroscopy of Atoms using Synchrotron Radiation*, Cambridge University Press, Cambridge, 1997, p. 54.
- [2] A. Zewail, *J. Phys. Chem. A* 104 (2000) 5660.
- [3] T. Brabec, F. Krausz, *Rev. Mod. Phys.* 72 (2000) 545.
- [4] M. Schnürer, C. Spielmann, P. Wobrauschek, C. Strelt, N.H. Burnett, C. Kan, K. Ferenc, R. Koppitsch, Z. Cheng, T. Brabec, F. Krausz, *Phys. Rev. Lett.* 80 (1998) 3236.
- [5] N.A. Papadogiannis, B. Witzel, C. Kalpouzos, D. Charalambidis, *Phys. Rev. Lett.* 83 (1999) 4289.
- [6] P.M. Paul, E.S. Toma, P. Breger, G. Mullot, F. Auge, P. Balcou, H.G. Muller, P. Agostini, *Science* 292 (2001) 1689.
- [7] V.T. Platonenko, V.V. Strelkov, *Quant. Electron.* 28 (1998) 749.
- [8] I.P. Christov, M.M. Murnane, H.C. Kapteyn, *Opt. Commun.* 148 (1998) 75.
- [9] F.L. Kien, N.H. Shon, K. Hakuta, *Phys. Rev. A* 64 (2001) 051803.
- [10] R. Kienberger, E. Goulielmakis, M. Uiberacker, A. Baltuska, V. Yakovlev, F. Bammer, A. Scrinzi, Th. Westerwalbesloh, U. Kleineberg, U. Heinzmann, M. Drescher, F. Krausz, *Nature* 427 (2004) 817.
- [11] P.B. Corkum, *Phys. Rev. Lett.* 71 (1993) 1995.
- [12] S. Sartania, Z. Cheng, M. Lenzner, G. Tempea, C. Spielmann, F. Krausz, *Opt. Lett.* 22 (1997) 1562.
- [13] Y.C. Lim, T. Westerwalbesloh, A. Aschtrup, O. Wehmeyer, G. Haindl, U. Kleineberg, U. Heinzmann, *Appl. Phys. A* 72 (2001) 121.
- [14] M. Drescher, M. Hentschel, R. Kienberger, G. Tempea, C. Spielmann, G.A. Reider, P.B. Corkum, F. Krausz, *Science* 291 (2001) 1923.

- [15] R. Kienberger, M. Hentschel, M. Uiberacker, C. Spielmann, M. Kitzler, A. Scrinzi, M. Wieland, T. Westerwalbesloh, U. Kleineberg, U. Heinzmann, M. Drescher, F. Krausz, *Science* 297 (2002) 144.
- [16] M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, T. Westerwalbesloh, U. Kleineberg, U. Heinzmann, F. Krausz, *Nature* 419 (2002) 803.
- [17] M. Juvansuu, A. Kivimäki, S. Aksela, *Phys. Rev. A* 64 (2001) 012502.
- [18] A. Bouhal, R. Evans, G. Grillon, A. Mysyrowicz, P. Breger, P. Agostini, R.C. Constantinescu, H.G. Muller, D. von-der-Linde, J. Opt. Soc. Am. B 14 (1997) 950.
- [19] M. Borst, V. Schmidt, *Phys. Rev. A* 33 (1986) 4456.
- [20] A. Baltuska, Th. Udem, M. Uiberacker, M. Hentschel, E. Gouliemakis, C. Gohle, R. Holzwarth, V. Yakovlev, A. Scrinzi, T.W. Hänsch, F. Krausz, *Nature* 421 (2003) 611.
- [21] T. Brixner, N.H. Damrauer, P. Niklaus, G. Gerber, *Nature* 414 (2001) 57.