Non-recollisional diabatic electronic excitation of krypton in an ultrafast laser field

W. A. Bryan*, I. C. E. Turcu, J. M. Smith, E. J. Divall, C. J. Hooker, S. J. Hawkes, A. J. Langley and J. L. Collier
Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., OX11 0QX, UK

E. M. L. English, J. Wood, S. L. Stebbings# and W. R. Newell
Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, UK

J. McKenna, C. R. Calvert and I. D. Williams
Department of Mathematics and Physics, Queen's University Belfast, Belfast, BT7 1NN, UK

* Also at Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, UK
# Present address: Department of Physics and Astronomy, University of Southampton, Southampton, SO17 1BJ, UK

Main contact email address w.bryan@rl.ac.uk

Introduction

Modern intense ultrafast pulsed lasers generate an electric field of sufficient strength to tunnel ionize one or more valence electrons from an atom. Such processes are generally treated as a rapid succession of isolated events, in which the states of the remaining bound electrons are unrelated to the preceding ionization events. While such a description has been shown to be more than adequate at predicting single, and in certain cases double ionization, a number of recent experimental studies have indicated the necessity to consider more than one active electron. Following the recent suggestion that intense field tunnel ionization may be accompanied by a 'shake-up' process[1], the authors observed recollision-free multi-electron excitation in argon in a circularly polarized laser field[2]. The current study[3] follows up our recent work, and we present evidence for the same mechanism of indirect non-recollisional excitation of the bound valence electrons during tunnel ionization (TI) of krypton. In the present article, we will address previous theoretical treatment is more detail, and discuss why this mechanism has not been observed before.

The foundation of the modern theoretical description of intense AC-field nonlinear photoionization was laid by Keldysh[4], who derived the dependence of the rate of TI on the frequency and strength of the optical field and the binding energy and quantum state of the ion and electron: for a detailed review see[5]. In the ultrafast regime (optical pulse duration of the order of femtoseconds, 1 femtosecond = 10^{-15} s), the ionization of an atom is either a perturbative process (peak intensity less that approximately 10 TWcm^{-2} where 1 TW = 10^{12} W), or a strong-field process, described by tunnel theory. In the present work, we concern ourselves purely with the strong field regime.

Immediately following ionization, the liberated electron is in a Volkov state, and is initially fully correlated with the parent ion. The electron is driven on a trajectory defined by the ellipticity of the laser radiation and the optical phase at which ionization occurred. An intriguing phenomenon in the strong field regime is that of *recollision* whereby electron impact excitation[6] or further ionization[7] can arise in a linearly polarized laser pulse, which drives electron(s) back to the parent ion. Recollision is the key mechanism for coherent attosecond XUV pulse generation[8], whereby energy absorbed by the electron from the field is dissipated photonically upon recombination with the parent ion.

In the present work, we make recollision ionization (RI) events extremely unlikely by employing circularly polarized light. In undergoing TI, an atom must absorb a large number of photons which, when absorbed from a circularly polarized laser pulse, transfer considerable angular momentum to the liberated electron, dramatically reducing the probability of returning to the ionic core, i.e. the impact parameter will be very large. In terms of the laser-induced electric field, following TI, the field drives the free electron on a spiral path: the pitch of the spiral is defined by the temporal envelope of the pulse. As the pulse intensity increases, the electron is rapidly removed from the vicinity of the ion. By negating recollision processes, the masking effects of electron-impact excitation and ionization are removed, allowing us to probe the many-electron dynamics of neutral and ionic krypton atoms.

While ionization in ultrafast laser pulses is well documented, minimal theoretical studies have investigated the possibility of simultaneous excitation of the parent ion during TI. The contemporary work of Zon[1,9] introduced the idea of 'inelastic tunnelling' whereby the parent ion can be left in an excited state following the ionization of one of N identical valence electrons. The excitation process is through 'shake-up', first employed by Carlson[10] to explain single UV photon absorption leading to the ionization of a first electron with the excitation of a second electron. The ionization event diabatically distorts the bound electron wavefunctions, resulting in the excitation of a bound electron. Recently work by the authors[2,3] supports the existence of such diabatic excitation in ultrafast ionization; the lowest lying states are populated. Furthermore, it is also necessary to allow for all combinations of excitation + ionization to some final charge state after the laser pulse has finished, irrespective of whether it is a ground or excited state. To distinguish such processes from standard sequential TI, we refer to such processes as multi-electron tunnel ionization (METI). This distinction is necessary, as Eichmann *et al.*[11] previously proposed the mechanism of collective tunnel ionization (CTI), whereby two electrons can simultaneously tunnel away from the atom. This process was predicted to only arise if the tunnelling electrons have highly correlated momenta, otherwise recapture of one of the electrons would occur; this requirement results in a very low probability.

Experimental procedure

In general, previous experimental measurements of ion yield as a function of laser intensity are unavoidably a convolution of the probability of ionization with the focal volume producing the signal. By simply changing the energy of the laser pulse, the spatial distribution of laser intensity also changes; frequently, the complexity of this situation is compounded by diffraction associated with the spatial profile of the laser. A direct comparison with theory is made impossible without introducing the specific experimental geometry. Through a contemporary method by Bryan *et al.*[12], developed from the pioneering work of Walker *et al.*[13] and analogous to the tomographic technique of Goodworth *et al.*[4], we circumvent this hindrance. By softly focusing a high-energy ultrafast laser pulse into a tightly apertured photoion detector, only those ionization states generated within a narrow spatial (and therefore intensity) window are detected. By translating the focusing optic, this restricted range of observed laser intensities may be accurately manipulated.

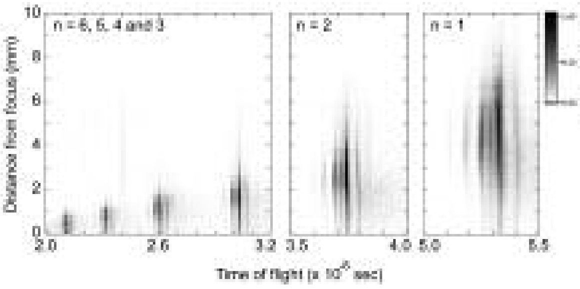

Figure 1. Intensity selective scan ion yield matrix for Kr^{n+} ($n = 1$ to 6) generated at the focus of a 50 fs 790 nm circularly polarized laser pulse. The 2000-laser shot average ion yield is recorded with an apertured time-of-flight mass spectrometer as the focusing optic is translated parallel to the direction of propagation.

Up to six-fold ionization of krypton saturates at intensities less than 100 PWcm^{-2}, and the 30 mJ 790 nm 50 fs laser pulses generated by the ASTRA Laser Facility (UK) need only be softly focussed (*f* /11 optics) to generate a peak intensity in excess of 100 PWcm^{-2}. Indeed the active range of the focused ASTRA beam extends over tens of millimetres. By limiting the spatial acceptance of our ion time-of-flight mass spectrometer to 250 microns, the ion yield is strongly dependent on the position of the optical focus with respect to the spectrometer. By recording the relative ion yield of Kr^{n+} ($n = 1$ to 6) while translating the focusing optic in 125 micron steps, the intensity selective scan presented in figure 1 is measured.

At this point, we wish to stress the importance of identifying background contaminants in the ISS data. In previous studies on argon[2], such an encumbrance is not present, as argon has three naturally occurring isotopes ^{36}Ar, ^{38}Ar and ^{40}Ar with abundances of 0.33%, 0.06% and 99.60 % respectively, which do not suffer from significant charge-to-mass degeneracy with any possible atmospheric contaminants (greater than 0.1% yield). Krypton however has six main isotopes ^{78}Kr, ^{80}Kr, ^{82}Kr, ^{83}Kr, ^{84}Kr and ^{86}Kr, with natural abundances 0.35%, 2.28%, 11.58%, 11.49%, 57.00% and 17.30% respectively. The high charge-to-mass ratio resolution of our spectrometer allows selective ion yield integration over those isotopes not degenerate with background contaminants. An example is the Kr^{3+} peak in figure 1: $^{84}Kr^{3+}$ is degenerate with N_2^+. Ionization to N_2^+ requires a far lower intensity than $^{84}Kr^{3+}$, apparent in figure 1 as the faint ion yield extending to large distances from the focus. To recover the probability of ionization, the non-degenerate isotopes (78, 80, 82 and 86) are integrated with respect to flight time, thus the spatial dependence of the ion yield is measured.

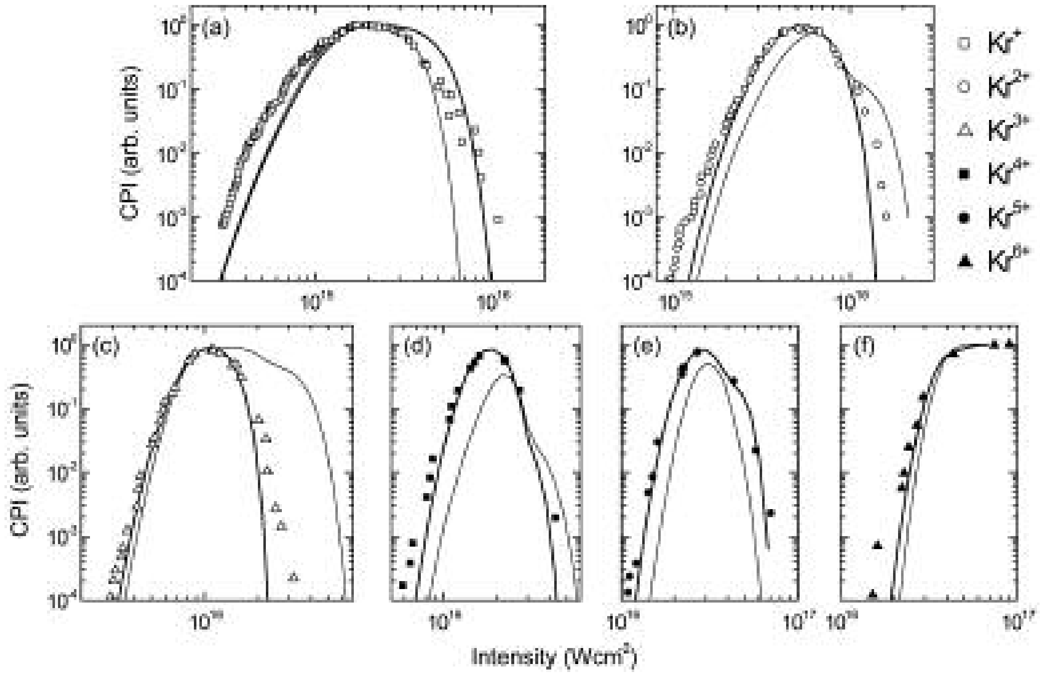

Figure 2. Conserved probability of ionization (CPI) to Kr^{n+} ($n = 1$ to 6) by a 50 fs 790 nm circularly polarized laser pulse. All influence of both the optical or detector geometry has been removed, allowing a direct comparisons with the predictions of Kornev *et al.*[1]. In all frames, the thin line is traditional TI (ADK) prediction, while the thick line is CPI for multi-electron tunnel ionization (METI), including an allowance for excitation to low lying states.

To make the ISS measurements directly comparable with theoretical predictions, we remove the spatial integration through a deconvolution[12,13] or inversion[14] technique, requiring the measured ion yield and theoretical on-axis intensity as a function of focal position as inputs. The quantum efficiency of the detector is also removed, such that the partial probabilities of ionization PPI(n) are now normalized[3]. The break down of the deconvolution routine at intensities greater than saturation can be addressed by conserving the probability of ionization[2,3]. The condition for conserving probability is that the sum of probabilities is less than unity below the saturation of PPI(1) or equal to unity at higher intensities. This definition is extended to an N-electron system in the present work and is only valid following the removal of the quantum efficiency.

Results

A direct comparison between the theoretical predictions of Kornev *et al.*[1] and the present volume-independent conserved probability of ionization (CPI) is presented in figure 2. All experimental curves presented have been universally normalized in intensity to the theoretical data. In all frames of figure 2, the sequential ADK prediction[15] is the thin line, and the multi-electron tunnel ionization (METI) prediction is the thick line. In figure 2(a), neither the ADK or METI predictions represent the Kr^+ CPI: this is due to a contribution from multiphoton ionization (MPI) at sufficiently low intensities to access the perturbative regime[12]. At intensities close to the saturation of Kr^+, it can be seen that both ADK and METI describe the CPI adequately. A similar low intensity response is observed in figure 2(b) (Kr^{2+}), where again around 1 PWcm^{-2} MPI contributes. However, as the intensity increases, the METI prediction is in much better accord with the experimental data, reproducing the CPI far more closely than ADK. The superiority of agreement with METI over ADK is dramatically illustrated for ionization to Kr^{3+}, Kr^{4+} and Kr^{5+}, figure 2(c) to (e), particularly high intensity Kr^{3+} and Kr^{4+} at all intensities. Indeed, at an intensity of around 10 PWcm^{-2}, ADK theory underestimates the CPI of Kr^{4+} by more than an order of magnitude. At the highest intensities discussed in the present work, ionization to Kr^{6+}, figure 2(f) is well described by both ADK and METI, however the latter is still observed to give the better agreement. Throughout figure 2, it is apparent that METI generates an excellent quantification of the CPI of krypton by circularly polarized 50 fs laser pulses. This is a direct consequence of the excitation of the bound valence electrons in the atomic ion. The shake-up mechanism invoked in both the present work is the subject of ongoing interest, see for example the recent review by Becker *et al.*[16]: shaking can only cause excitation at high intensities, as the energy of the departing electron must be sufficient to excite other residual electrons. This is supported by the present work: there is no significant excitation until around 10 PWcm^{-2}. Becker *et al.*[16] predict many orders of magnitude difference between the recollision yield and shake up contribution. However, here the recollision contribution is negligible. In qualitative terms the high degree of agreement between the measured CPI and the METI prediction is a result of (i) the high intensity laser-induced population of low-lying excited states through diabatic shake-up excitation, (ii) the removal of recollision excitation or ionization through the use of circular polarization. Furthermore, this observation would not be possible without the measurement of the geometry-independent PPI and the realization of conservation of probability. The pertinent question raised by the present work is why has this mechanism not been observed before?

The presence of excitation in previous experiments

In figure 3, we present the PPI(n) to Kr^{n+} for $n = 1$ to 6, where the PPI for each ionization state is scaled by the volume of the laser focus generating the signal. This is easily quantified, as the deconvolution route requires the precise computation of the spatial distribution of intensity. Figure 3 also contains the volume-scaled METI predictions. As is expected, the observations of the previous section are still applicable, however it is now far more difficult to isolate which model applies above saturation.

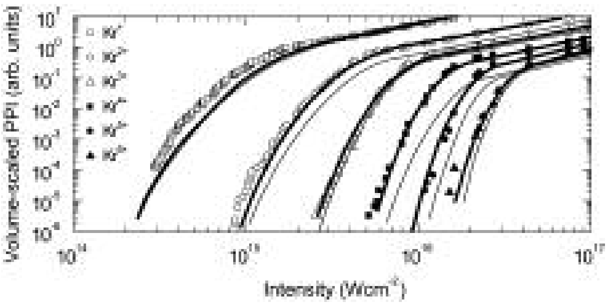

Figure 3. Volume-scaled partial probability of ionization (PPI) to Kr^{n+} (n = 1 to 6) as compared to the volume-scaled predictions of Kornev *et al.*[1], illustrating how diabatic ionization-induced excitation could be more difficult to identify from traditional intensity variation measurements. As in figure 2, the thin line is the ADK prediction, while the thick line is the METI prediction.

Comparing figures 2 and 3, we illustrate how subtle differences between the volume-scaled PPI and either theoretical prediction could be missed in a traditional intensity-variation measurement (equivalent to figure 3, for example see reference 17). If the detector efficiency is unknown, the measurement of which is by no means trivial, the effect of excitation could conceivably be overlooked as a manifestation of detector efficiency or could be ignored if the ADK curves are normalized independently. As apparent from figure 3, excitation is manifest as a major vertical shift in apparent yield, and a minor variation in intensity response. Furthermore, a number of experimental studies have commented on the inadequacy of tunnel theory, specifically the ADK treatment[15], without concrete discussion of why, nor the suggestion of a mechanism by which tunnel theory might be breaking down. It is hoped that the present work allows previous experimental data to be re-examined in terms of the ionization-induced excitation mechanism.

Conclusion

We present strong evidence for the presence of considerable atomic excitation during tunnel ionization of krypton by a 790 nm 50 fs circularly polarized laser pulse focused to intensities in excess of 100 TWcm^{-2}. The polarization of the radiation is such that recollision excitation and ionization are essentially negated. The impressive agreement between the measured conserved probability of ionization and recent theoretical predictions indicate that excitation during ionization need be considered irrespective of recollision processes. Excitation is due to the intense laser field energetically removing valence electrons: during these tunnel ionization events, the wavefunctions of the remaining electrons is impulsively distorted. Such excitation is also expected to occur in a linearly polarized laser field, and, as the results of Kornev *et al.* suggest, is expected to be even more important in a 5 fs laser pulse. This has a major bearing on the emerging field of optical attosecond physics. The influence of initial and transitionary electronic states accessed through intra-pulse excitation must be quantified to accurately predict the energy of the emitted photons.

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