Selection of the magnetic quantum number in resonant ionization of neon using an XUV–IR two-color laser field

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Abstract

A recent experiment (Villeneuve *et al* 2017 *Science* **356** 1150) has shown that two-color photoionization of neon by the combination of an attosecond XUV pulse train and a moderately strong, linearly polarized IR pulse can preferentially produce photoelectrons with orbital angular quantum number $l = 3$ (f-wave) and magnetic quantum number $m = 0$. This result was rationalized by the occurrence of different Stark shifts of $m = 0$ and $|m| = 1$ sub-levels in the IR laser field. Here we perform 3D time-dependent Schrödinger equation calculations with a neon effective potential to identify the mechanism for the selective excitation and ionization of $m = 0$ sub-levels. Calculations of the ionization and excitation yields as a function of the IR intensity and the XUV and IR photon energy reveal that a coupling between two dominant ionization channels involving 3p and 3d intermediate excitations is responsible for the observed m -level selectivity. We compare calculated and measured photoelectron velocity map images and ionization yields over a range of IR intensities and XUV and IR photon energies, and confirm that the $m = 0$ or $|m| = 1$ channel, and thus a single set of the quantum numbers, (J_{ion}, l, m) , can be selected by an appropriate choice of these parameters.

Keywords: attosecond science, high-harmonic generation, intense field-matter interaction

(Some figures may appear in colour only in the online journal)

1. Introduction

Quantum state-selective excitation or ionization by laser fields is one of the major challenges for quantum control in atoms or molecules [1, 2]. In general, single photon excitation or ionization by a weak laser pulse is governed by angular momentum selection rules, preventing the control of optical transitions at will. A one-photon transition from a state with orbital angular momentum l can excite states with $\Delta l = \pm 1$ and $2l + 1$ different magnetic quantum numbers m . Attosecond XUV pulses

combined with infrared laser fields permit greater control over the final state [3–9] by means of their ability to induce quantum interferences between multiple pathways that reach the same final state [10–12]. Using intense laser pulses that permit mixing of energy levels combined with the use of tunable XUV laser pulses opens a new approach toward selective excitation and/or ionization.

Recently [13] it was demonstrated that for certain values of the IR intensity and the XUV photon energies within an attosecond pulse train (APT), an almost pure f-wave $(l, m) = (3, 0)$ can be selectively observed in Ne XUV + IR photoionization. This result was surprising, since it implied the absence

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of $|m| = 1$ contributions. XUV ionization of the $1s^2 2s^2 2p^6$ ground state of Ne removes an electron from one of the 2p valence orbitals. Given that $l = 1$, three degenerate magnetic sub-levels $m = 0, \pm 1$ exist, which are expected to ionize with comparable probabilities. In [13], it was postulated that IR-induced Stark shifts that lift the degeneracy between the $m = 0$ and $|m| = 1$ sub-levels of a 3d intermediate state might open a path toward resonance-enhanced ionization of the $m = 0$ sub-level only, thus creating the possibility to produce an f-wave with $m = 0$ only. This proposal was supported by calculations where the time-dependent Schrödinger equation (TDSE) was solved for Ar (not Ne) and where analogous behavior could be identified.

In the present study, we use three-dimensional, one-electron TDSE calculations to identify the detailed mechanism by means of which the $m = 0$ level is selected in Ne. We furthermore use an analytical two-state model to rationalize the mechanism. In order to achieve satisfactory agreement with the experiment, it proved necessary to consider Rydberg series associated with the $^2P_{3/2}$ and $^2P_{1/2}$ spin-orbit states of the Ne^+ ion core separately, by generating spin-specific effective potentials. We obtain excitation and ionization yields for $l = 1$, $m = 0, \pm 1$ for both Ne^+ spin-orbit sub-states, as a function of the IR intensity, and as a function of the IR and XUV photon energy (which are linked by the fact that the XUV frequency is an odd harmonic of the IR frequency). In doing so, we identify the physical mechanism behind, and the conditions for the selective excitation and ionization of either $m = 0$ or $|m| = 1$.

To compare with the calculated results, we have extended the IR intensity and the XUV photon energy range in our experiments, measuring photoelectron velocity map images (VMI) for two-color XUV + IR ionization. The VMI spectrometer projects the 3D photoelectron momentum onto the detector plane [14]. Extension of the XUV photon energy range was necessary to establish conditions where the $|m| = 1$ state is selectively ionized. We varied the photon energy of H13 from 20.04 to 20.42 eV, thus including all field-free 2p–3d resonance energies [15]. At each photon energy the IR intensity was varied from 0 to 4.7 TW/cm² and VMI images were recorded. Contributions from both $m = 0$ and $|m| = 1$ channels could be identified in the measured photoelectron angular distributions.

Figure 1 illustrates the relevant energy levels of Ne. For the IR wavelengths used in the experiment ($\lambda_{\text{IR}} = 790\text{--}805$ nm), harmonic 15 can directly photo-ionize the Ne atoms, whereas harmonic H13 is nearly resonant with the Ne(3d) manifold. Absorption of a single IR photon ($\hbar\omega \approx 1.5$ eV) is sufficient to transfer 3d population to the continuum, resulting in photoelectron angular distributions characterized by p and f partial waves. Within the aforementioned IR wavelength range, the energy difference between the Stark-shifted 3p and 3d manifolds is close to the IR photon energy. As we will show with both an analytical model and the TDSE calculations, a strong near-resonant coupling is induced between the 3p and 3d levels, which leads to the existence of two dominant ionization pathways, exploiting resonance with the 3d manifold and the $3p + 1\omega$ level (which borrows intensity from the 3d manifold), respectively. Our calculations reveal that in each of these

Figure 1. Energy diagram for Ne. Harmonic H13 (tuned from 20.04–20.42 eV) is approximately resonant with the 2p–3d transition. The IR laser field induces a coupling between the 3p and 3d states, $\Delta E \approx 1.4$ eV (dashed green line). The blue bands represent the approximate range of XUV frequencies produced by the high harmonic source.

Figure 2. (a) Measured high-harmonic spectra as a function of the distance between the compressor gratings. (b) Peak positions of the 13th harmonic. The red lines indicate the range over which VMI images were measured.

pathways, differences in the precise energy position of the $m = 0$ and $|m| = 1$ magnetic sub-levels originate from differences in the effective polarizabilities of these levels for $m = 0$ and $|m| = 1$.

It is well-known that the energy levels of atoms and molecules can be significantly altered by an intense infrared laser field. Non-resonant, laser-induced energy level shifts explain channel-closing [16], and the occurrence of Freeman resonances in strong-field ionization [17], while strong resonant coupling of pairs of energy levels explains the formation of Autler–Townes doublets [18], with accompanying intensity-dependent energy splittings. The present case is more complicated, since it combines the non-resonant response to the laser field that all levels experience with a near resonant coupling of the 3p and 3d states.

Table 1. Parameters of the effective potential in neon atom. The potential is in the form: $-r^{-1}(1 + a_1 \exp(-a_2 r) + a_3 r \exp(-a_4 r) + a_5 \exp(-a_6 r) + a_7 r^2 \exp(-a_8 r))$ [22].

Core	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$J_{\text{ion}} = 3/2$	8.0731	2.0833	-3.5921	1.980 51	0.898 27	0.719 19	-0.026 825	0.674 24
$J_{\text{ion}} = 1/2$	8.0854	2.0374	-3.5867	1.928 89	0.870 84	0.795 50	-0.023 105	0.732 10

2. Method of experiments

We used the same experimental set-up reported in [13]. An XUV attosecond pulse train was generated by focusing ~ 790 nm, ~ 35 fs, 1 kHz, fundamental (IR) laser pulses onto an argon gas jet. Both the XUV pulse and a part of the IR are focused onto a pulsed neon gas jet injected into a VMI spectrometer, by using a toroidal mirror (ARW Optical Corporation). The photoelectrons produced by both pulses are accelerated toward a 2D micro-channel plate (MCP) by a DC field and the velocity distribution of the photoelectrons is imaged on the MCP. In addition, the XUV pulses are dispersed after the VMI detector by a flat-field grating to record the XUV spectrum.

The XUV photon energy of the attosecond pulse trains was varied by changing the distance between the compressor gratings of our Ti:sapphire amplifier system (Komodo-Dragon, KMLabs). Although the mechanism of the XUV spectral shift by the introduction of higher-order dispersion in the IR pulse is not fully clear, this results in a continuous change of the high-harmonic frequency in the XUV pulse by ~ 0.4 eV as shown in figures 2(a) and (b). The central frequency of the fundamental pulse was not measured. As a cross-check, we measured the above threshold ionization (ATI) photoelectron spectra using the fundamental pulse. We confirmed that the ATI spectrum shifts as the distance between the compressor grating is changed. For simplicity, in our TDSE calculation, we assume that the IR pulse has no chirp and the central IR frequency is determined from the high-harmonic photon energy.

3. Method of calculations

3.1. TDSE calculations

All calculations were performed using a one-electron atomic TDSE code described in reference [19]. A variable-density grid contained 50 uniformly-spaced points near the origin, followed by 129 points at coordinates $2.0 \times 1.02^{n-1}$ Bohr ($n = 1 \dots 129$). The remaining 13 821 points were uniformly spaced by 0.5 Bohr. The radial grid extended to 6935.7 Bohr, with the last 131.1 Bohr taken by a transmission-free absorbing boundary [20]. In all simulations reported here, the photoelectron wavefunction did not reach the absorber. The angular grid extended to $L_{\text{max}} = 15$. A uniform time step of 0.005 atomic units of time was used in all calculations. A truncated Gaussian envelope ($T_{\text{FWHM}} = 35$ fs, baseline duration 112 fs) was used for both XUV and IR, which were chosen to overlap perfectly. The XUV and IR central frequency was fixed at a ratio of 13:1. The IR intensity was varied in 0.25 TW/cm²

Table 2. Experimental and calculated ionization energies for the centers of mass of atomic multiplets in neon, in electron-volts.

Multiplet	Reference		Calculated	
	$J_{\text{ion}} = 3/2$	$J_{\text{ion}} = 1/2$	$J_{\text{ion}} = 3/2$	$J_{\text{ion}} = 1/2$
1s	870.2	870.2	869.1	870.5
2s	48.474	48.474	44.106	44.045
3s	4.893	4.812	4.891	4.810
4s	1.875	1.881	1.880	1.867
5s	0.993	0.998	0.997	0.992
6s	0.614	0.617	0.617	0.615
7s	0.417	0.419	0.419	0.418
2p	21.564	21.660	21.564	21.658
3p	2.951	2.934	2.952	2.933
4p	1.353	1.291	1.362	1.356
5p	0.751	0.758	0.784	0.782
6p	0.506	0.509	0.509	0.508
7p	0.355	0.346	0.358	0.357
3d	1.523	1.521	1.518	1.518
4d	0.855	0.855	0.856	0.855
5d	0.546	0.546	0.548	0.547
6d	0.379	0.379	0.380	0.380
7d	0.278	0.278	0.279	0.279
4f	0.852	0.850	0.849	0.850
5f	0.544	0.544	0.543	0.544
6f	0.377	0.377	0.378	0.378
7f	0.277	0.277	0.277	0.278

increments (1 TW/cm² above 5 TW/cm²). The XUV intensity was fixed at 0.1 TW/cm². The total two-photon ionization probability due to non-linear XUV absorption remained well below 10^{-6} , much below the probability of any IR-assisted processes of interest. Energy- and angle-resolved photoelectron spectra were calculated by resolving the wavefunction in asymptotic field-free scattering solutions [21]. The uniform photoelectron momentum grid contained 1000 points, up to $k_{\text{max}} = 1$ (maximum resolved photoelectron energy of 13.6 eV).

Preliminary calculations using a published neon effective potential [22] indicated that 4s, 3p, and 3d excited manifolds are important under the experimental conditions of interest. Unfortunately, the absolute Rydberg energy levels in this effective potential are in error by up to 230 meV (3p)—well in excess of the IR and XUV pulses bandwidth (50 meV). Furthermore, the separation of the sublevels due to the spin-orbit coupling (100 meV for the 2p level; 20 meV for 3p) is comparable to the IR pulse bandwidth. The combination of these two factors precludes a quantitative description of the experiment with the published effective potential [22].

We have therefore generated a new effective potential for the neon atom, by requiring that the field-free energy levels

Figure 3. Measured and calculated VMI images for photoionization of neon with an XUV + IR two-color laser field. (a)–(c) are measured VMI images at three different IR intensities for an IR wavelength of 800.5 nm, corresponding to an H13 photon energy of 20.14 eV. The IR intensities are (a) 3.5, (b) 1.5, (c) 1.0 TW/cm², respectively. The polarization axis of both the XUV and the IR laser is vertical. (d)–(f) are calculated VMI images for an XUV photon energy of 20.26 eV, and an IR intensity of (d) 3.5, (e) 1.5, and (f) 1.0 TW/cm², respectively. The bottom row shows hydrogenic wavefunctions for $l = 3$, $m = 0$ and $l = 3$, $m = 1$. Note that, for $m = 0$, there is a horizontal nodal plane, whereas for $m = 1$ a maximum occurs.

reproduce the centre-of-mass positions of the atomic multiplets, up to $L_{\max} = 3$ (f-wave) and $N_{\max} = 7$. The fit was performed separately for the multiplets associated with the two spin–orbit sublevels ($J_{\text{ion}} = 1/2, 3/2$) of the ^2P ground state of Ne^+ . The atomic data were obtained from [15]. The core-level energies were adopted from [23]. The final fit parameters are collected in table 1. The calculated energy levels are compared to the experimental multiplet positions in table 2.

3.2. Volume averaging

In order to compare the experiments to calculated VMI images, we take into account the XUV and IR intensity distribution within the ionization volume. Volume averaging requires detailed knowledge of the configuration of the interaction region, including focal-spot parameters of both the XUV and IR beams, gas-jet profile, and their relative positions. As a first approximation, we first assume that the gas jet is larger than the confocal parameters and beam waists of the two beams. If

the XUV and IR beams have similar diameters, then because of its longer wavelength, the IR will have a much shorter Rayleigh range than the XUV. (The XUV beam diameter in the generating gas jet is somewhat smaller than the IR, but due to wavefront curvature in the HHG process, the XUV will be somewhat out of focus in the neon gas jet.) Under these assumptions, it is sufficient to average over the IR intensity distribution only, and treat the XUV and the medium as uniform. We follow the approach of Zimmermann *et al* [24], based on the principles discussed by Kielpinski [25]. Under the above assumptions, the volume V containing intensities greater than I is given by:

$$V = V_0 (y^3 + 6y - 6\text{atan}(y)) \quad (1)$$

$$V_0 = \frac{2}{9} \pi w_0^2 Z_r$$

$$y = \sqrt{\frac{I_0}{I} - 1}$$

Figure 4. Experimental VMI images produced by photoionization of neon, as a function of the XUV photon energy (horizontal) and the IR intensity (vertical). The transition from dominant $m = 0$ ionization to dominant $|m| = 1$ ionization can be seen when increasing the XUV photon energy or reducing the IR intensity. Raw images are shown without correction for the high-harmonic intensity. The ‘f’ along the top is the factor by which the image intensity was divided to give a color scale range of 0–1.

where I_0 is the peak intensity, w_0 is beam waist, and Z_r is the Rayleigh range. The constant factor V_0 only affects the overall normalization of the result, and was set to unity. The factor y , and therefore V/V_0 , tend to infinity as $I \rightarrow 0$, strongly biasing the average toward zero IR intensity. We have therefore subtracted the XUV-only photoelectron yield from the average, calculating the volume average as:

$$\bar{Y} = \int (Y(I) - Y(0)) \frac{dV(I)}{dI} dI \quad (2)$$

where $Y(I)$ is the desired observable (e.g. total yield or VMI signal) at a given, fixed peak intensity I . The integral (2) was evaluated using the trapezoidal rule. For the experiments, we have subtracted the photoelectron yield obtained by the XUV pulse alone from that obtained by both XUV and IR pulses together.

4. Results and discussion

4.1. Experimental and calculated VMI images

Figures 3(a)–(c) shows experimental VMI images for low energy electrons resulting from two-color ionization by H13 and a single IR photon (denoted as H13 + 1ω), for an IR wavelength of 800.5 nm ($\hbar\omega = 1.55$ eV) and for three different IR intensities. At the highest IR intensity (a), a six-fold

structure with a nodal plane perpendicular to the laser polarization axis is observed, as reported in our earlier work [13], and demonstrating that dominant ($l = 3, m = 0$) outgoing photoelectron partial waves can be created by a correct choice of the XUV frequency and IR intensity. At lower intensities, the $|m| = 1$ channel becomes dominant, revealed by the fact that the nodal plane perpendicular to the laser polarization axis is replaced by local maxima in the photoelectron angular distribution. In figure 3(d)–(f), we show calculated VMI images that can be compared to the experimental images. The experimental VMI images closely mirror the simulated VMI images from the TDSE calculations, which show the same transition from dominant $m = 0$ ionization to dominant $|m| = 1$ ionization. For comparison, the bottom of figure 3 shows the hydrogenic wavefunctions corresponding to $l = 3, m = 0$, and $l = 3, |m| = 1$.

In figures 4–6, we present measured and calculated VMI images over the full accessed range of IR intensity and XUV photon energy. The switching from dominant $m = 0$ ionization to dominant $|m| = 1$ ionization is seen in both the calculated and measured images. As shown in figures 5 and 6, volume averaging of the simulated VMI images causes a slight shift of the photon energy at which the $|m| = 1$ ionization become dominant over $m = 0$ ionization.

Figure 7 shows a detailed comparison between the experimental (a)–(d) and calculated (e)–(h) VMI images for an IR

Figure 5. Calculated VMI images without focal volume averaging. As the XUV photon energy increases while keeping the same IR intensity, e.g., $I = 2 \text{ TW/cm}^2$, the six-fold structure corresponding to $m = 0$ ionization diminishes, while the structure corresponding to $|m| = 1$ ionization becomes significant. At lower IR intensities, the XUV photon energy where the structure $|m| = 1$ appears decreases. In conclusion, a transition from the $m = 0$ to $|m| = 1$ ionization is clearly seen.

intensity of 3.1 (experiments) and 3.0 (calculations) TW/cm^2 for four different H13 harmonic photon energies. We separately chose XUV photon energies for the experiment and the simulation where the VMI images resemble the measured images, while keeping almost same IR intensity. With increasing photon energy, the six-fold structure becomes less prominent and the angular distribution for $|m| = 1$ ionization becomes dominant in both the experiments and the calculations. Although the radial extent of the calculated images is slightly smaller than that of the measured VMI images, the VMI structure is well reproduced. A possible explanation for the discrepancy in the photon energy between the experiments and calculations is that volume averaging may shift the XUV photon energy where the $m = 0$ resp. $|m| = 1$ contributions are dominant.

4.2. Comparison of the ionization yields

The total ionization yield, Y , can be written as a sum over four channels:

$$Y = \frac{2}{3} [I_{1/2}^{m=0}] + \frac{4}{3} [I_{3/2}^{m=0}] + \frac{4}{3} [I_{1/2}^{m=1}] + \frac{8}{3} [I_{3/2}^{m=1}] \quad (3)$$

where the superscript indicates the involvement of $m = 0$ or $|m| = 1$, and the subscripts indicate whether the ionization forms the $J_{\text{ion}} = 3/2$ ionic state ($^2\text{P}_{3/2}$) or the $J_{\text{ion}} = 1/2$ ionic state ($^2\text{P}_{1/2}$). The weights sum up to the number of electrons in the 2p shell, i.e. 6, and reflect the fact that in the neutral ground

state there are two orbitals with $|m| = 1$ as opposed to a single orbital with $m = 0$, whereas the $J_{\text{ion}} = 3/2$ ionic state has four magnetic sub-levels, while the $J_{\text{ion}} = 1/2$ ionic state has only two.

Figures 8(a) and (b) shows the calculated H13 + 1ω ionization yield, starting from either $m = 0$ (a) or $|m| = 1$ (b), and includes contributions for ionization producing both the $J_{\text{ion}} = 1/2$ and $J_{\text{ion}} = 3/2$ cores.

As we will demonstrate, within the range of experimental conditions accessed within this work, the two-color ionization of Ne $m = 0$ and $|m| = 1$ states benefits from resonance enhancements whose nature is very different for the two magnetic sub-levels (predominantly via the 3d branch of the 3d–3p system in the case of $m = 0$, and via a dressed 3p + 1ω branch in the case of $|m| = 1$). Accordingly, as can be recognized in both the experimental and numerical results shown in figures 3–7, the photoelectron kinetic energies accompanying $m = 0$ and $|m| = 1$ ionization are *different*, implying that the relative yields of the $m = 0$ and $|m| = 1$ photoelectrons can be extracted from the VMI images by integrating the center part and the outer part of the VMI images, respectively. Figures 8(g)–(j) show the two regions of integration. Accordingly, the ionization yields starting from $m = 0$ and $|m| = 1$ are plotted as a function of the IR intensity and the XUV photon energy in figures 8(c) and (d) for the computational results, and (e) and (f) for the experiments, respectively. Figures 8(c) and (d) differ from figures 8(a)

Figure 6. Calculated VMI images including focal volume averaging. The change in the VMI images from the $m = 0$ ionization to the $|m| = 1$ ionization upon changing the XUV photon energy is clearly observed. ‘f’ is a scaling factor and is the factor by which the signal was divided in order to yield a color scale range of 0–1. The volume averaging assumes a cell geometry, with the XUV-only signal subtracted.

and (b) in that they are calculated in the same way as the experimental VMI images were treated: the calculated volume-averaged VMI images are integrated over a range of radii, and the integrals are then plotted in figures 8(c) and (d). Note that the calculations in (a) and (b) cover a broader range of parameters than the other figures, denoted by the boxes in (a) and (b).

The experiment and the calculations agree that, as the IR intensity is increased, a higher XUV photon energy is required to maximize ionization. Moreover, the yield in the $|m| = 1$ channel maximizes at a higher XUV frequency than the yield in the $m = 0$ channel. This observation supports the conclusion that the $m = 0$ channel can be isolated from the $|m| = 1$ channel by a proper choice of the XUV frequency and the IR intensity.

4.3. Analytical two-state model

We now focus on the mechanism by which this quantum state selectivity is achieved. To this end, figure 9 shows the combined excitation yield to all excited states calculated for the $J_{\text{ion}} = 1/2$ core with (a) $m = 0$ and (b) $|m| = 1$, as a function of the IR intensity and the XUV photon energy. The results for the $J_{\text{ion}} = 3/2$ core shown in (c) and (d) are qualitatively

similar, but are shifted to lower XUV photon energies. This is because in the absence of the dressing IR field excitations in the spin–orbit excited $J_{\text{ion}} = 1/2$ channel are found at higher XUV photon energies. Dominant features in the excited state populations are labeled as A, B and C. Line A corresponds to excitation of the 4s level. It is necessarily only observed for $m = 0$, and is resonantly populated at lower XUV photon energies. Line A intercepts the XUV photon energy axis at the field-free energy of the 4s state, i.e., at 19.78 eV for $J_{\text{ion}} = 1/2$ and 19.68 eV for $J_{\text{ion}} = 3/2$, respectively. The linear intensity dependence of this line matches the expected pondermotive shift U_p of an isolated Rydberg state. In atomic units, $U_p = I_0 / (4\omega_{\text{IR}}^2)$, where the intensity $I_0 = F_0^2$ is the square of the electric field amplitude (1 atomic unit of intensity is $\approx 3.51 \times 10^4$ TW/cm²). The effective cycle-averaged polarizability $\alpha = -4U_p / F^2 = -1/\omega_{\text{IR}}^2$ coincides with the free-electron value (-300 au for an 800 nm driving field). Away from resonances, all Rydberg states in intense IR fields are expected to exhibit cycle-averaged polarizability close to the free-electron value [26]. At higher IR intensities along feature A, the 3s state is also populated through a two-photon resonance with the 4s level, mediated by the 3p state.

Figure 7. Detailed structure of the VMI images recorded at H13 harmonic energies of (a) 20.07 eV, (b) 20.14 eV, (c) 20.21 eV, and (d) 20.38 eV, respectively. The IR intensity is kept at 3.1 TW/cm². For comparison, the calculated, volume-averaged VMI images are shown in (e) to (h). The H13 harmonic photon energy used in the simulations is (e) 20.18 eV, (f) 20.20 eV, (g) 20.26 eV, and (h) 20.38 eV, respectively, and the IR intensity is kept at 3.0 TW/cm². The signal appearing near zero momentum (i.e. the center of the image) in (d) is caused by background photoelectrons.

The other two main features of the excitation map in figure 9 exhibit a more complex intensity dependence, and cannot be attributed to isolated, non-resonantly Stark-shifted Rydberg states. Their behavior can be qualitatively understood by considering the 3p and 3d excited states within a two-state model that includes polarizability, with a Hamiltonian matrix given by:

$$H = \begin{pmatrix} \epsilon_1 - \frac{1}{2}\alpha_1 F^2 & -dF \\ -dF & \epsilon_2 - \frac{1}{2}\alpha_2 F^2 \end{pmatrix} \quad (4)$$

where the laser field $F = \frac{1}{2}F_0 (e^{i\omega_{\text{IR}}t} + e^{-i\omega_{\text{IR}}t})$. The quantities $\epsilon_{1,2}$, $\alpha_{1,2}$, and d are respectively the field-free state energies, the adiabatic polarizabilities, and the dipole coupling matrix element between the two states, where state 1 is the 3p-level and state 2 is the 3d-level. In the Hamiltonian (4), the diagonal terms account for the adiabatic, non-resonant polarization of each state, leading to the standard quadratic Stark shift with laser field strength (i.e. a linear shift of the level with laser intensity). The off-diagonal terms represent resonant coupling between the two levels. Within the present experiment, the two levels are nearly in a one-photon resonance, so that the detuning $\delta = \epsilon_2 - \epsilon_1 - \omega_{\text{IR}}$ is small.

We solve the time-dependent Schrödinger equation (TDSE) with the Hamiltonian given by equation (4). We are looking for solutions of the form:

$$\Psi = \begin{pmatrix} a_1(t) e^{-i\epsilon_1 t} \\ a_2(t) e^{-i\epsilon_2 t} \end{pmatrix}. \quad (5)$$

The amplitudes $a_{1,2}(t)$ satisfy the equations:

$$\begin{aligned} \dot{a}_1 &= \frac{-\alpha_1 F_0^2}{8} (2 + e^{2i\omega_{\text{IR}}t} + e^{-2i\omega_{\text{IR}}t}) a_1 \\ &\quad - \frac{dF_0}{2} (e^{i\omega_{\text{IR}}t} + e^{-i\omega_{\text{IR}}t}) a_2 e^{-i(\epsilon_2 - \epsilon_1)t} \\ i\dot{a}_2 &= \frac{-\alpha_2 F_0^2}{8} (2 + e^{2i\omega_{\text{IR}}t} + e^{-2i\omega_{\text{IR}}t}) a_2 \\ &\quad - \frac{dF_0}{2} (e^{i\omega_{\text{IR}}t} + e^{-i\omega_{\text{IR}}t}) a_1 e^{+i(\epsilon_2 - \epsilon_1)t} \end{aligned} \quad (6)$$

where we have dropped the time argument of $a_{1,2}(t)$ for compactness. For the laser field parameters relevant for this work, the IR field detuning $\delta = \epsilon_2 - \epsilon_1 - \omega_{\text{IR}}$ is small. Performing the rotating wave approximation that neglects the high-frequency, sub-cycle contributions on the right-hand side of equation (6), we obtain:

$$\begin{aligned} i\dot{a}_1 &= \frac{-\alpha_1 F_0^2}{4} a_1 - \frac{dF_0}{2} a_2 e^{-i\delta t} \\ i\dot{a}_2 &= \frac{-\alpha_2 F_0^2}{4} a_2 - \frac{dF_0}{2} a_1 e^{+i\delta t} \end{aligned} \quad (7)$$

We seek solutions of equation (7) in the form:

$$a_2 = e^{-i\Delta t}, \quad (8)$$

where Δ is the desired correction to the ϵ_2 energy level. Substituting equation (8) into equation (7) and rearranging terms, we obtain the quadratic equation:

$$\left(\Delta + \frac{\alpha_2 I_0}{4}\right) \left(\Delta + \delta + \frac{\alpha_1 I_0}{4}\right) - \frac{d^2}{4} I_0 = 0, \quad (9)$$

Figure 8. Calculated ionization yields as a function of the XUV photon energy and the IR intensity for (a) $m = 0$, and (b) $|m| = 1$, with both the contributions of the $J_{\text{ion}} = 1/2$ and $J_{\text{ion}} = 3/2$ ionic states included. The calculated yields are given as a fraction of the initially-present neon atoms. To compare the model and the experiment, the VMI images including volume integration and the measured VMI images are integrated over the two momentum regions bracketed by green dotted circles, as shown in (g), (h) for the case of the calculations, and in (i), (j) for the case of the experiments. Figures (c) and (d) are obtained by separately integrating the calculated, focal volume-averaged VMI images (see figure 6) for the $m = 0$ (c) and $|m| = 1$ (d) channels. Figures (e) and (f) show the result of applying the same procedure to the experimental VMI images, exploiting the fact that $m = 0$ ionization and $|m| = 1$ ionization yield slightly different photoelectron kinetic energies (see figure 4). (c)–(f) are each normalized to the highest values that occur within the plot. Note that figures (a) and (b) cover a larger range of photon energy and IR intensity than the other figures, whose range is indicated by the dashed box.

where $I_0 = F_0^2$ is the laser field intensity. Solving equation (9) for $\Delta = \lambda_{\pm} - \epsilon_2$, we obtain the effective field-dressed energy levels,

$$\lambda_{\pm} = \epsilon_2 - \left(\frac{\delta}{2} + \frac{\alpha_1 + \alpha_2}{8} I_0 \right) \pm \frac{\delta}{|\delta|} \left(\frac{1}{4} d^2 I_0 + \left(\frac{\delta}{2} + \frac{\alpha_2 - \alpha_1}{8} I_0 \right)^2 \right)^{1/2}. \quad (10)$$

As the IR intensity $I_0 \rightarrow 0$, the lower level λ_+ correlates to ϵ_2 , shown as line B in figure 9. The upper level λ_- converges to the $1\omega_{\text{IR}}$ Floquet satellite of state 1 (i.e. the 3p-level), namely $\epsilon_1 + \omega_{\text{IR}}$, curve C. Thus, we should expect to observe two separate branches in the $\Omega - I_0$ excitation map. These two branches are indeed seen in figure 9. For zero IR intensity, the C (λ_-) branch originates at an XUV photon energy of $\lambda_- = \epsilon_2 - \delta = (\epsilon_{3p} - \epsilon_{2p}) + \omega_{\text{IR}}$ (20.29 eV for $J_{\text{ion}} = 1/2$ and 20.16 eV for $J_{\text{ion}} = 3/2$; because $\Omega = 13\omega_{\text{IR}}$, this condition is equivalent to $\epsilon_{3p} - \epsilon_{2p} = 12\omega_{\text{IR}}$). The complementary B (λ_+) branch originates at the $\epsilon_{3d} - \epsilon_{2p}$ transition energy (20.14 eV for $J_{\text{ion}} = 1/2$ and 20.05 eV for $J_{\text{ion}} = 3/2$).

Solving equation (10) for the IR field intensity at a given XUV photon frequency Ω , we obtain:

$$\begin{aligned} I_0 &= \frac{2d^2}{\alpha_1 \alpha_2} \left(f_1 \pm \sqrt{f_1^2 - f_2} \right) \\ f_1 &= 1 - (\alpha_1 + \alpha_2) \frac{\lambda}{d^2} - \alpha_2 \frac{\delta}{d^2} \\ f_2 &= 4\alpha_1 \alpha_2 \frac{\lambda(\lambda + \delta)}{d^4} \\ \lambda &= \Omega - \epsilon_2 \\ \delta &= (\epsilon_2 - \epsilon_1) - \omega_{\text{IR}} \end{aligned} \quad (11)$$

where (ϵ_1, α_1) are the energy and the adiabatic polarizability of the lower state (3p), and (ϵ_2, α_2) are the energy and polarizability of the upper state (3d). Parameters ϵ_1 and ϵ_2 are fixed by their field-free, spectroscopic line positions. In contrast, α_1 , α_2 , and d summarize complex, non-perturbative interactions of the atom with the IR field, and should be treated as adjustable parameters.

From equation (11), it is clear that no solutions exist below the critical XUV frequency $\Omega = \Omega_{\text{crit}}$, at which the determinant $(f_1^2 - f_2)$ becomes zero. Indeed, in figure 9(a) we observe that the B branch, originating at the 2p–3d transition, has a turning point at 20.11 eV XUV photon energy and 0.5 TW/cm²

Figure 9. Calculated excitation yields as a function of the IR intensity and the XUV photon energy for (a) $m = 0$, $J_{\text{ion}} = 1/2$, (b) $|m| = 1$, $J_{\text{ion}} = 1/2$, (c) $m = 0$, $J_{\text{ion}} = 3/2$, and (d) $|m| = 1$, $J_{\text{ion}} = 3/2$. The dotted lines indicate the field-free energy level of the $3d_{1/2}$ state and the $3p_{1/2}$ state plus one IR photon ($3p_{1/2} + 1\omega$). Line A marks a Stark-shifted transition to the $4s$ manifold. Lines B and C mark transitions to the strongly-driven $3p/3d$ manifold. Note that at IR intensities above $1 \text{ TW}/\text{cm}^2$, the assignment of the dominant transition character is only qualitative.

Figure 10. Influences of the values of the α and d parameters on the position of the features B and C in the model two-level Hamiltonian. (a) At a fixed value of $\alpha = -540$ (a.u.), the value of d is varied as 2.4, 1.8 and 3.0 (a.u.). (b) At a fixed value of $d = 2.4$ (a.u.), the value of α is varied as -540 , -440 , -340 and -240 (a.u.).

IR intensity. No excitation to the coupled $3p$ – $3d$ level system is possible below this photon energy, regardless of the IR

Table 3. Values of the $\alpha_1 = \alpha_2 = \alpha$ and d parameters in the model Hamiltonian. Values of the ϵ_1 and ϵ_2 parameters are fixed at their calculated values (see table 2 and text).

J_{ion}	m	α , au	d , au
1/2	0	−540	2.40
	1	−200	1.92
3/2	0	−520	2.40
	1	−200	2.08

intensity. To the right of the turning point, there are in principle two solutions for the IR intensity for each XUV photon energy.

Comparison of the curves in figure 10 with those simulated by the TDSE calculation (figure 9) indicates that in the $m = 0$ channel, the effective polarizabilities of both the $3p$ and $3d$ levels are somewhat larger than the free-electron value (approx. -500 au vs -300 au expected for the free electron and 800 nm). In the $|m| = 1$ channel, the magnitude of the fitted effective polarizabilities are somewhat below the free-electron value (approx. -200 au). The decrease in the effective dipole coupling between the $3p$ and $3d$ levels in the $|m| = 1$ channel also contributes. We summarize the best-fit parameters in table 3. Please note that the two-level effective model Hamiltonian (equation (4)) affords only a qualitative representation of the rich and complex electron dynamics in this system. The fitted parameters which allow this model to reproduce the essence of these dynamics should not be assigned physical significance of their own. Rather, we consider the fact that the best-fit parameters remain within a factor of two of their field-free (the transition dipole) and free-electron (the effective

Figure 11. Partial wave decomposition of the calculated IR-XUV ionization yield for ionization into the $J_{\text{ion}} = 1/2$ continuum, where $(l, m) =$ (a) (0, 0), (b) (1, 0), (c) (2, 0), (d) (3, 0), (e) (4, 0), (f) (0, 1), (g) (1, 1), (h) (2, 1), (i) (3, 1) and (j) (4, 1), respectively. Not shown is $|m| = 1$ and (0, 0), i.e. formation of an s-wave, because the calculated intensity is zero in all parameter ranges. This is due to the fact that $l = 0$ does not exist in combination with $|m| = 1$. The same color scale is used throughout.

polarizability) values an indication that our model Hamiltonian does capture the essential physics of the process.

From figure 9, it is clear that by simultaneously varying the intensity of the IR dressing field and the XUV photon energy (and thereby the IR photon energy, linked to it through the harmonic ratio), one can selectively address $m = 0, \pm 1$ as

well as 3d and $3p + 1\omega$ levels. As is seen in figure 9, a similar behavior is seen for states with the residual cation core remaining in the $J_{\text{ion}} = 1/2$ spin-orbit excited sub-level of the ground state and for the $J_{\text{ion}} = 3/2$ sub-level spin-orbit ground state. Moreover the 100 meV difference in the field-free line head positions between $J_{\text{ion}} = 1/2$ and $J_{\text{ion}} = 3/2$ transitions

Figure 12. Partial wave decomposition of the calculated IR–XUV ionization yield for ionization into the $J_{\text{ion}} = 3/2$ continuum, where $(l, m) =$ (a) (0, 0), (b) (1, 0), (c) (2, 0), (d) (3, 0), (e) (4, 0), (f) (0, 1), (g) (1, 1), (h) (2, 1), (i) (3, 1) and (j) (4, 1). Not shown is $|m| = 1$ and (0, 0), i.e. formation of an s-wave, because the calculated intensity is zero in all parameter ranges. This is due to the fact that $l = 0$ does exist in combination with $|m| = 1$. The same color scale is used throughout.

permits these features to be addressed individually, at least in principle.

Looking back at the total ionization yield in figure 8(a), we recognize that for $m = 0$ the ionization (near a photon energy of 20.1 eV) is dominated by the pathway due to 3d excitation in the 3p–3d pair. At low intensities, the ionization

yield separately shows two spin–orbit 3d branches, and a shift to higher photon energy with intensity. Beyond 2 TW/cm², the two spin–orbit components broaden and merge. Two-color ionization benefitting from this resonance enhancement will appear as $(l = 3, m = 0)$ in the photoelectron angular distribution. For $|m| = 1$, the dominant pathway originates from the

Figure 13. Experimental photoionization of krypton and xenon atoms by the combination of single photon XUV absorption using H7, H9 or H11, plus or minus one IR photon. Both krypton and xenon have two spin-orbit states corresponding to cores with $J_{\text{ion}} = 1/2$ and $J_{\text{ion}} = 3/2$ (in Kr the splitting is 0.67 eV, and in Xe the splitting is 1.30 eV). Unlike neon, the energy splitting is directly visible in the VMI image, resulting in pairs of rings. In Kr, the inner ring with $J_{\text{ion}} = 1/2$ shows the six-fold structure of the f-wave, but its spin-orbit partner does not.

$3p + 1\omega$ level at >20.2 eV (see figure 8(b)). Ionization as a result of single-photon IR absorption of the dressed $3p + 1\omega$ state lifts the total energy to $3p + 2\omega$ and lifts the orbital angular momentum to $l = 3$, rationalizing the observation of the dominant experimentally observed ($l = 3$, $|m| = 1$) outgoing photoelectron wave.

In figures 11 and 12, we show the partial wave contributions to the yield for ionization into the $J_{\text{ion}} = 1/2$ and $J_{\text{ion}} = 3/2$ continuum. In both cases, the partial wave component with $l = 3$ dominates over the other angular momentum components. The calculated results also suggest that a partial wave with a particular angular momentum component (l, m) may be selected by choosing an appropriate IR intensity and a XUV photon energy.

4.4. Separation of J_{ion} states

In addition to selecting ionization into particular (l, m) partial waves, it may be possible to select the core state J . In rare gas atoms heavier than neon, the spin-orbit splitting between $J_{\text{ion}} = 1/2$ and $J_{\text{ion}} = 3/2$ becomes large enough to resolve them within a VMI image. We have performed preliminary experiments in krypton and xenon (figure 13) in which we can isolate $J_{\text{ion}} = 1/2$, $l = 3$, $m = 0$ partial waves. Although a detailed analysis has not been performed yet, this demonstrates that we can selectively ionize into one spin-orbit state in combination with a dominant f-wave with magnetic quantum number $m = 0$.

5. Summary

Experimentally and theoretically we showed that, by controlling the IR intensity and XUV photon energy, the f-wave photoelectron component of the photoelectron produced by two-color XUV + IR ionization can be switched from $m = 0$ to $|m| = 1$. Within the analysis we employ a two-state model that may be regarded as a general model to estimate how m -selection is possible. This model has general applicability and may also be used to make predictions for other species

or electronic states. The mechanism introduced and explained in the current manuscript extends the way in which quantum control by laser fields can be employed.

Our method is a route toward selection of a quantum state that is characterized by a single set of quantum numbers (J_{ion} , l, m). The experimental result in krypton and xenon is another demonstration of the atomic state selection that is possible using attosecond pulse trains in the presence of infrared dressing fields. For instance, one of the applications of attosecond experiments is to measure the ionization phase of photoelectrons. If a single quantum state is selected, a direct measurement of the phase becomes possible without requiring any further assumption or detailed analysis.

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