Photoelectron velocity map imaging of single-photon and pump-probe ionization of noble gases using femtosecond high-order harmonics

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High order harmonics are implemented in the study of single-photon and pump-probe ionization experiments on noble gases using velocity map imaging. Anisotropy parameters of photoelectron angular distributions from single-photon ionization of He, Ne, Ar, and Xe are in good agreement with literature values. Pump-probe measurements using the 9th harmonic to excite Ar to the 3d and 5s1P1 states and either 790 or 395 nm pulses to ionize at variable time delays show the temporal resolution of the experiment to be 156 fs and 69.9 fs, respectively.

Keywords: Single-photon; pump-probe ionization.

Se implementan armónicos de alto orden en el estudio de experimentos con monofotones y de ionización bomba-sonda con gases nobles usando mapeo de velocidades. Los parámetros de anisotropía de las distribuciones angulares fotoelectrónicas de la ionización monofotónica de He, Ne, Ar y Xe, corresponden a los reportados en la literatura. Las medidas bomba-sonda usando el 9° armónico para excitar Ar al estado 3d y 5s1P1 y con pulsos de 790 o 395 nm a intervalos de tiempo variables muestran que la resolución temporal del experimento es de 156 fs y de 69.9 fs, respectivamente.

Descriptores: Monofotón; ionización bomba-sonda.

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High order harmonics are implemented in the study of single-photon and pump-probe ionization experiments on noble gases using velocity map imaging. Anisotropy parameters of photoelectron angular distributions from single-photon ionization of He, Ne, Ar, and Xe are in good agreement with literature values. Pump-probe measurements using the 9th harmonic to excite Ar to the 3d and 5s1P1 states and either 790 or 395 nm pulses to ionize at variable time delays show the temporal resolution of the experiment to be 156 fs and 69.9 fs, respectively.

Time-resolved photoelectron angular distributions combined with photoelectron spectroscopy can provide detailed information on the dynamics and ionization properties of atomic and molecular ground and excited states. [1] Using femtosecond pulses ranging from visible to soft x-ray energies allows for valence and core electrons to be investigated on ultrafast time scales. In particular, the measurement of photoelectron angular distributions from single-photon and pump-probe ionization of atoms and molecules investigates properties of the outgoing partial waves.

The photoelectron angular distributions of randomly oriented atoms and molecules from single-photon ionization using linearly polarized light is given by where is the total cross section, is the angle between the laser polarization and electron velocity vectors, and is the anisotropy parameter associated with the second order Legendre polynomial [1]. For atoms, the anisotropy parameter can be described using the equation, where [2]. Here, is the phase shift and is the radial dipole matrix element of the partial wave of angular momentum . For an electron originally in an atomic orbital of angular momentum , the outgoing partial waves will have angular momenta of and the interference pattern of these partial waves results in the observed photoelectron angular distributions. The radial dipole matrix elements and the phase shift differences depend on photoelectron energy and provide information on both the bound and continuum wavefunctions. The anisotropy parameters, therefore, provide detailed information on properties of photoionization.

The experimental setup is similar to those described in previous photoelectron spectroscopy and imaging studies reported by our group [3,4]. The output of an amplified Ti:sapphire laser system producing 2.4 mJ, 790-810 nm, 50 fs pulses with a 1 kHz repetition rate is sent to a variable beam splitter to separate two beams of controllable powers. One beam is focused into an Ar pulsed jet in vacuum resulting in odd order harmonics ranging from approximately 10.9 to 45.0 eV. A home-built EUV monochromator selects and refocuses the harmonic of interest to the interaction region where it intersects with a skinned atomic beam. The high order harmonics either cause single-photon ionization or excitation of the atoms at the interaction region. For pump-probe studies, the second beam from the beam splitter is sent through a retroreflector on a delay stage to control the pump-probe time delay. The second harmonic of the fundamental frequency is generated using a type 1 beta barium borate (BBO) crystal. Either the fundamental or second harmonic probe pulses are focused to the interaction region to overlap with the high harmonic pump pulse at approximately 1.5 degrees causing ionization of the excited atoms. The resulting 3D sphere of expanding photoelectrons is projected by an electrostatic lens to a 2D position-sensitive detector in a velocity map imaging setup [5]. Half wave plates control the polarizations of the
pulses to be parallel to the detector face and to the direction of the atomic beam. The photoelectron angular distributions and energy spectra are recovered from the 2D photoelectron images using the pBASEX inversion method [6].

Inverted images from single-photon ionizations of He, Ne, Ar, and Xe are shown in Figs. 1a–1d. The anisotropy parameter, $r$, is evaluated at the peak radius for each ring. Using the 17th harmonic (26.5 eV), the values for He and Ne are $2.03 \pm 0.05$ and $0.24 \pm 0.01$, respectively. Using the 13th harmonic (20.2 eV), the values for the ionization of Ar to the $2P_{3/2}$ state and Xe to the $2P_{1/2}$ and $2P_{3/2}$ states are $0.85 \pm 0.06$, $1.59 \pm 0.07$, and $1.72 \pm 0.04$, respectively. For He, there is only one partial wave, the $P$ wave, and the expected value of 2.00 is in agreement with the measurements.

Additional photoelectron images from single photon ionization of Ne, Ar, and Xe were taken with the 11th and 13th harmonics. Using the 11th harmonic (17.1 eV) the values for the ionization of Ar to the $2P_{3/2}$ state and Xe to the $2P_{1/2}$ and $2P_{3/2}$ states are $0.27 \pm 0.05$, $1.05 \pm 0.10$, and $1.45 \pm 0.01$, respectively. Using the 15th harmonic (23.4 eV), the values for the ionization of Ne and Ar are $-0.16 \pm 0.03$ and $1.27 \pm 0.01$, respectively. All reported anisotropy parameters are in excellent agreement with literature values [7-9].

![Figure 1](image1.png)

**Figure 1.** Inverted photoelectron images: (a) He + 17th harmonic, (b) Ne + 17th harmonic, (c) Ar + 13th harmonic, (d) Xe + 13th harmonic, (e) Ar excited with 9th harmonic and ionized with 790 nm, (f) Ar excited with 9th harmonic and ionized with 395 nm.

The inverted images from pump-probe ionization of Ar are shown in Figs. 1e, 1f. In both cases, the 9th harmonic (14.1 eV) of 790 nm excites both the $3d$ and $5s^2 P_1$ states. These excited states are then ionized by either 790 or 395 nm probe pulses. The present experimental energy resolution is not sufficient to distinguish between these two excited states. Pump-probe images using 790 nm show photoelectrons peaked at zero kinetic energy with a maximum kinetic energy of 0.01 eV. Only the most energetic portion of the 790 nm pulse bandwidth is responsible for ionization from the excited states. Pump-probe images using 395 nm show one ring with an energy of 1.49 eV, corresponding to the true pump-probe signal, and additional low energy electrons peaked at 0.09 eV from multiphoton ionization from the 395 nm alone. The signals as a function of pump-probe time delay are shown in Figs. 2a, 2b and are fit to error functions with rise times of 156 fs (790 nm) and 69.9 fs (395 nm), respectively. The rise times give the temporal resolution from the cross correlation of the pump and probe pulses. The rise time is larger when using the 790 nm pump pulse because only a small portion of its bandwidth leads to ionization. Future investigations will analyze angular distributions of the Ar pump-probe signal as well as decay times which may be affected by EUV pulse shaping [10].

![Figure 2](image2.png)

**Figure 2.** Photoelectron signal as a function of temporal delay between the pump and probe pulses demonstrating the temporal resolution of the experiment. The 9th harmonic (14.1 eV) pump pulse excites Ar to the $3d$ and $5s^2 P_1$ states followed by ionization with either (a) 790 nm or (b) 395 nm probe pulses.
Photoelectron velocity map imaging using high order harmonics for single-photon ionization and pump-probe ionization has been demonstrated on He, Ne, Ar and Xe. Single-photon anisotropy parameters are in excellent agreement with literature values. Pump-probe studies of Ar using the 9th harmonic show an experimental temporal resolution of 156 fs and 69.9 fs when ionized with 790 and 395 nm pulses, respectively. Excited state dynamics and properties of photoionization in atoms and molecules will be investigated in the extreme ultraviolet energy range with ultrafast temporal resolution in future studies.

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