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Two- and three-photon ionization of rare gases using femtosecond harmonic pulses generated in a gas medium

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The fifth harmonic of a 60-fs 10-Hz terawatt titanium:sapphire laser generated in Xe gas is used to ionize Xe and Kr atoms by nonresonant two-photon absorption and Ar atoms through a quasiresonant three-photon process. At relatively low harmonic yields, the variation of the number of Kr and Xe ions with the number of harmonic photons is quadratic. At high harmonic yields, it deviates from a quadratic behavior, which we attribute to the influence of ionization in the harmonic process distorting the harmonic wave front. The two-photon ionization cross sections in Xe and Kr at 160 nm are found to be comparable.

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Though theoretically predicted in the 1930's at the beginning of quantum mechanics [1], multiphoton processes were not observed experimentally until 30 years later, thanks to the masers in the radio-frequency domain [2], and to the lasers in the optical range [3], which were able to achieve a sufficiently high intensity. It is only 40 years later that the extension of these nonlinear processes to the vacuum and extreme ultraviolet (vuv-xuv) range is becoming experimentally accessible. The development of x-ray lasers, high-order harmonic sources, and self-amplified spontaneous emission free-electron lasers [4] has made considerable progress during the last few years. The demonstrated (or predicted) specifications for the number of photons, pulse duration, and spatial coherence for these advanced light sources now allow the scientific community to tackle the problem of inducing nonlinear processes in the xuv range, in spite of the low cross sections in that spectral region [5].

Among the above-mentioned light sources, high-order harmonic radiation has the advantage of being simple and easily produced by table-top devices, and also to provide short pulse durations, of the order of the pulse duration of the generating laser pulse [6–9], which can be in the few femtosecond range. The number of photons per pulse and per harmonic reaches up to a few 10^9, corresponding to efficiencies (defined as the ratio between the output and input energies) of the order of 10^{-6} [10–12]. In addition, the radiation exhibits good spatial coherence properties [13,14], allowing it to be focused to a small spot [15]. Simple calculations predict that the intensity of the xuv harmonic beam should be sufficient to put low-order nonlinear processes, e.g., two-photon ionization in a gas, within experimental reach [16].

However, the successful attempts to observe nonlinear processes using high-order harmonics have been scarce. Xenakis *et al.* observed resonant $(1+1)$ two-photon ionization in Ar, using the third harmonic (15 eV) of a KrF laser [17]. Watanabe and co-workers report the observation in He of two-photon ionization using the ninth harmonic of a titanium-sapphire (Ti:sapphire) laser and four-photon ionization using the fifth harmonic [8,9]. One difficulty is to obtain a short-pulse duration, a high number of photons, and a small focal spot simultaneously. Another major difficulty is to eliminate the influence of other ionization processes, such as multiphoton ionization due to the fundamental laser field, one-photon ionization due to higher-order harmonics, and ionization processes involving mixing of several harmonic or fundamental frequencies [6].

In this Rapid Communication, we report experimental evidence for nonresonant two-photon ionization in xenon and krypton using the fifth harmonic (7.7 eV) of a Ti:sapphire laser. A quasiresonant three-photon ionization is also observed in argon at the highest harmonic yield. A particular effort is devoted to eliminate unambiguously the influence of the fundamental laser pulse, the third harmonic, as well as of the higher-order harmonics. At moderate harmonic yields, the number of Kr and Xe ions varies quadratically with the number of photons. The deviation from the quadratic dependence at higher harmonic yields is attributed to the influence of ionization in the harmonic generation process affecting the spatial profile of the harmonic pulse.

Our experimental setup, which resembles that of Sekikawa *et al.* [9] is shown in Fig. 1. The laser is an amplified Ti:sapphire 10-Hz system delivering 60-fs pulses around 800 nm with an energy up to 200 mJ. Most of the results presented here are obtained with only a fraction of this energy, 20 mJ. Furthermore, the beam is apertured down by an 11-mm-diameter diaphragm, so that only about 3-mJ infrared energy is actually sent into our experimental setup. The beam is focused by a 2-m focal-length lens into a windowless Xe gas cell. The Xe gas is injected into the cell through a 10-Hz-pulsed nozzle. The interaction length is estimated to be about 3 mm (1 mm inside the cell and 1 mm on each side). The gas cell is placed 4 cm before the laser focus in order to obtain a high photon number. A 500-μm-thick high-quality uv-grade fused silica plate is used to absorb harmonics higher than fifth order. Its transmission is measured to be 0.6 for the fifth harmonic, below 10^{-6} for the seventh harmonic, and drops very rapidly for higher harmonic orders. Used with a 45° incidence angle in *p*-polarization, the fused silica plate reflects 1% of the beam into an xuv spectrometer. This spectrometer, operated without entrance slit and with a wide (6-mm) exit slit, records the fifth harmonic flux without cutting part of the beam. Using a more conventional vuv-spectrometer with narrow entrance and exit slits, we also measure the spectral width of the fifth harmonic to be 1.4 nm full width at half maximum.

The fundamental field is eliminated by two beam splitters

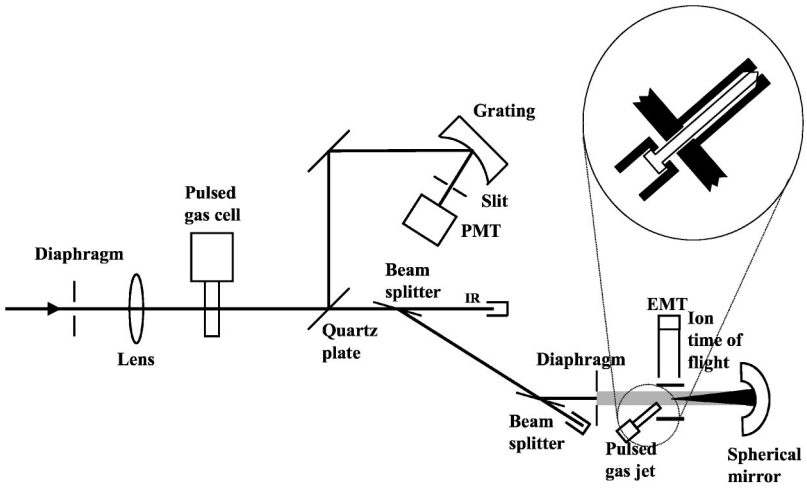

FIG. 1. Experimental setup.

used in *s*-polarization at an incidence angle of 70° [18]. These beam splitters are antireflection coated at 800 nm, with a reflectivity less than 1% at the fundamental wavelength and about 40% at the fifth harmonic frequency. A second diaphragm (8 mm diameter), 2.2 m after the source allows us to further reduce the remaining fundamental beam, without affecting the less divergent harmonic beam. The harmonic beam is focused by a normal incidence 10-cm focal-length spherical mirror, with MgF_2-protected aluminum coating. The Al-MgF_2 coating ensures a high reflectivity ($R=75\%$) at 160 nm (fifth harmonic). The gas medium in the interaction region is provided by a pulsed gas jet, equipped with a 3.5-mm-thick and 3-cm-long capillary, filled to 1 bar backing pressure (see inset, Fig. 1). The valve mechanism is placed at the end of the capillary to ensure high pressure at the ouput. We estimate the atomic density in the interaction region to about 10^{14} atoms/cm^3. The produced ions are detected in a time-of-flight spectrometer: They are extracted between two plates providing a homogeneous electrostatic field of 500 V/m, are separated in time in a 30-cm-long field-free region, and finally recorded by an electron multiplier tube. Since the gas-jet capillary is placed between the two time-of-flight plates it is equipped with a conducting layer and biased with a voltage adjusted to minimize its influence on the homogeneous extraction field. The dispersion of the thin fused silica plate introduces a positive frequency modulation (chirp) of the fifth harmonic. In Fig. 2, we show the number of fifth harmonic photons, as well as the number of Kr ions as a function of the distance between the gratings of the laser compressor (varying this distance allows us to induce a chirp in the laser pulse, and hence in the harmonic pulse). We also indicate the corresponding pulse duration of the fundamental pulse. As expected, the number of fifth harmonic photons reaches a maximum at the shortest pulse duration (60 fs). The number of ions, however, reaches its maximum when the fundamental pulse is slightly negatively chirped. This induces a negative chirp also in the fifth harmonic pulse, which is needed to compensate the positive chirp due to group velocity dispersion in the fused silica plate. We see no evidence for a large intrinsic dipole chirp of the fifth harmonic [9].

As pointed out previously, it is important to eliminate other ionization processes: these are (i) multiphoton ionization due to the remaining fundamental field; (ii) one-photon ionization due to higher-order harmonics; (iii) mixing processes involving harmonic and fundamental fields; and (iv) multiphoton ionization due to the third harmonic. (i) The fundamental field is eliminated essentially by the two beam splitters which decrease the infrared intensity by at least a factor 10^4. To confirm that the remaining laser pulse does not perturb our measurements, we checked that there is no ion signal without harmonics, by inserting an absorbing glass plate in the vuv-beam path or alternatively by emptying the gas cell used to generate harmonics. In addition, we measured 8×10^{11} photons per pulse at 800 nm after the beam splitters, using a calibrated photodiode in the same conditions as for the fifth harmonic (see below). Assuming a diffraction-limited beam, we obtain an upper limit for the intensity of 10^{12} W/cm^2, which is not high enough to induce significant multiphoton ionization for a 60-fs 800-nm pulse [19]. (ii) The higher-order harmonics are absorbed by the thin fused silica plate, which has a huge absorption coefficient for wavelengths shorter than 160 nm. (iii) The group-velocity dispersion in the fused silica plate allows us to sepa-

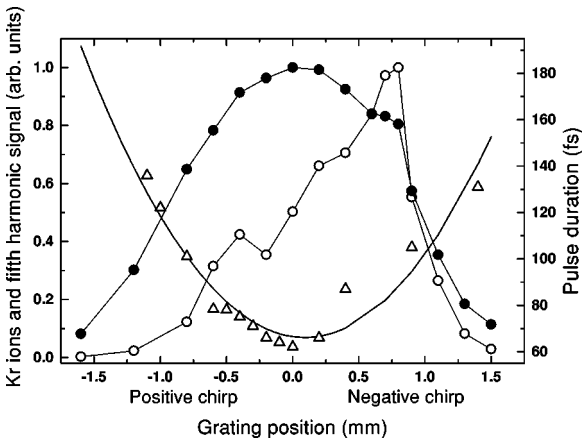

FIG. 2. Number of fifth harmonic photons (closed circles) and number of Kr ions (open circles) as a function of the grating position of the compressor. The pulse duration of the fundamental is indicated in open triangles together with a parabolic fit (solid line).

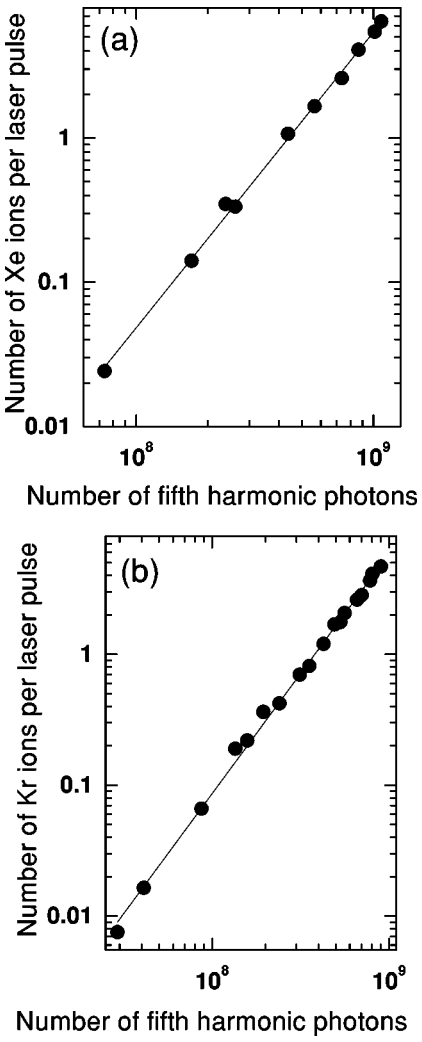

FIG. 3. Number of ions in Xe (a) and Kr (b) as a function of number of fifth harmonic photons.

rate in time the fundamental, third, and fifth harmonic pulses. The fundamental pulse comes first, then after 0.3 ps the third harmonic, and after 1.5 ps the fifth harmonic. This ensures that no mixing processes take place in the interaction region. Even in the case of $2+1$-photon ionization in Ar, the ionization of the excited state can only be from the fifth harmonic. (iv) Finally, ionization with third harmonic photons occurs via absorption of three photons in Xe, and four photons in Kr and Ar. It requires therefore a higher intensity than for two-photon ionization (or quasiresonant three-photon ionization). However, accounting for the higher number of photons at the third harmonic frequency [20], but lower reflectivity on the beam splitters as well as larger focal spot, we estimate the third harmonic intensity in the interaction region to be one order of magnitude less than that of the fifth harmonic, and therefore not high enough to induce a higher-order multiphoton process. In addition, we checked that the ion signal disappears when a (thick) fused silica window, absorbing the fifth harmonic, but not the third, is placed in the beam.

The main result of the present paper is shown in Fig. 3. The number of ions detected in Xe (a) and in Kr (b) is plotted as a function of the number of fifth harmonic photons. (Accounting for the losses in the three grids used in the time-of-flight spectrometer, the number of ions created is approximately a factor of 2 higher). The number of photons is varied by changing the pressure in the gas cell where the harmonics are generated (see Fig. 1), keeping all other experimental parameters constant. We measure a slope of 2.0 ± 0.2 in Xe and 1.8 ± 0.2 in Kr, over more than two orders of magnitude. Each point is obtained by counting all the ions arriving at the detector within a given time gate at each laser shot, for a given harmonic signal (fixed within $\pm15\%$). This technique allows us to detect less than 1 ion per 100 shots. The number of fifth harmonic photons after the two beam splitters is measured by using a LiF prism and a calibrated xuv photodiode. The LiF prism is used to separate the fifth harmonic from the fundamental and third harmonic. We measure 1.2×10^9 photons per pulse at the fifth harmonic frequency, at the highest backing pressure used in these measurements [note that the number of photons really used, indicated as the highest value in Fig. 3(b), is a factor 0.75 less, owing to the reflectivity of the focusing mirror]. Our measurements also show that the cross sections for Xe and Kr are comparable.

These results provide the clearest evidence that the observed signal is due to a two-photon ionization process in Kr and Xe. At higher harmonic yield, we observe also an ion signal in Ar. In this case the harmonic intensity is not simply proportional to the photon number (see below), which prevents us to measure the intensity dependence of the three-photon ionization process. A three-photon ionization process in Ar could occur via a quasiresonance on the $8p$, $9p$, and $7f$ states.

To estimate the fifth harmonic intensity, we measure the diameter of the beam before the spherical mirror, by recording the total pulse energy after a knife edge mounted onto a translation stage. Assuming a Gaussian intensity distribution, the diameter is measured to be 4 mm (at $1/e^2$), leading to a focal spot of 5-μm diameter. The pulse duration of a Fourier-transform limited pulse with a 1.4-nm spectral width at 160 nm is $\tau=30$ fs. This leads to an *upper limit* for the photon flux $F=3\times10^{29}$ photons/(cm^2 s) (i.e., an intensity of 4×10^{11} W/cm^2). Using an atomic density in the interaction region $\rho=10^{14}$ atoms/cm^3, an interaction volume $V=5\times10^{-9}$ cm^3, and $N\approx10$ created ions per pulse, we get an experimental two-photon cross section $\sigma=N/\rho V\tau F^2$ of the order of a few times 10^{-51} cm^4 s. This is about an order of magnitude less than the calculated values [21,22] in krypton or xenon. This probably means that our estimated intensity and/or atomic density in the interaction region are higher than those actually achieved in the experiment.

By increasing further the pressure in the Xe cell, it is possible to increase the ion signal by almost a factor of 3. The number of harmonic photons, however, remains approximately constant. An example of this behavior in Kr is shown in Fig. 4. The dependence of the number of ions on the number of harmonic photons is quadratic up to about 600 mbar. The ion dependence is more rapid at higher backing pressures, where the number of harmonic photons is approximately constant. We attribute this effect to the influence of ionization, introducing a significant defocusing of the laser beam due to the transversal variation of the induced free

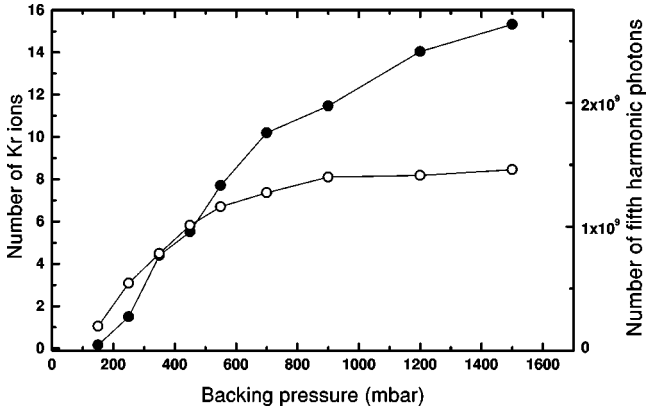

FIG. 4. Number of Kr ions (closed circles) and harmonic photons (open circles) as a function of the backing pressure.

electron density. The diameter of the harmonic beam onto the spherical mirror increases from 4 mm at 400 mbar to 5 mm at 1500 mbar, which leads to a reduced focal spot and hence to an increased harmonic intensity for the same photon number.

Higher ion signals could also be obtained by increasing the laser energy. We detected up to about 60 ions in Kr and in Xe, and 10 in Ar at a laser energy of 40 mJ. However, in these conditions, the fundamental pulse intensity is higher in the Xe gas cell and ionization effects appear at even lower gas pressures. This reduces the region where the intensity depends linearly on the photon number. Another problem is the increase of nonlinear effects occurring during the propagation of the laser beam through air and glass materials, leading to an increase of the bandwidth, a chirp, and a distortion of the fundamental wavefront. In this case, small fluctuations in energy or pulse duration of the fundamental beam strongly affect the harmonic yield making accurate measurements difficult.

In conclusion, we have observed two-photon ionization in Xe and Kr, as well as three-photon ionization in Ar using the fifth harmonic of a Ti:sapphire laser. We have showed that it is possible to obtain a substantial number of ions per shot (120). We believe that it should be possible to multiphoton ionize rare gases also with higher-order harmonics, since the number of photons that can be obtained in the 7th, 9th, or 11th harmonics, for example, are very close to the number of photons in the fifth harmonic [20]. However, the separation of the different ionization processes that can take place during the interaction is more difficult. One way is to use an electron spectrometer to identify these processes.

Our result is of great importance for two reasons: (i) It opens up the field of multiphoton processes and nonlinear optics in general to the vuv and xuv regions. Using higher harmonics, it should be possible, for example, to ionize inner-shell electrons by multiphoton processes. (ii) It provides a way to measure ultrashort, femtosecond, and even attosecond pulse durations in the vuv and xuv regions by autocorrelation.

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