Coherent Microwave Rayleigh Scattering from Resonance-Enhanced Multiphoton Ionization in Argon

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Multiphoton ionization and electron recombination processes are studied in argon using coherent microwave Rayleigh scattering from a localized, resonance-enhanced multiphoton ionization produced plasma. A time dependent one-dimensional plasma dynamic model is developed to predict the time evolution of the microwave scattering from the plasma. Experimental results of the argon ionization spectrum and electron recombination rates are in good agreement with the model predictions.

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Multiphoton ionization (MPI) has been intensively studied since the invention of the giant pulsed laser and is an important mechanism in the formation of laser generated plasmas. Multiphoton ionization is greatly enhanced if an intermediate state is single or multiphoton resonant with the laser, and by using these resonances, it can become an accurate spectroscopic method for measuring trace species or pollutants [1,2]. This is called resonance-enhanced multiphoton ionization (REMPI). Common detection methods for the MPI or REMPI signal are electrical probes or electrodes [1,2] and time of flight (TOF) mass spectroscopy [2]. Both methods require that the electrons or ions be extracted from the ionization region, so neither method directly measures all the free electrons that are generated and neither can follow the electron recombination process with high accuracy.

In this Letter, we demonstrate that microwave scattering from a REMPI produced plasma provides a new means for the direct, time accurate observation of the free electrons and thus a new method for high sensitivity REMPI spectroscopy of a gas and a new method for the measurement of electron formation and loss processes. The REMPI plasma acts as a coherent microwave scatterer, with the scattering electric field amplitude proportional to the number of electrons. Since the size of the REMPI plasma is small compared to the microwave wavelength, the scattering falls into the Rayleigh regime [3,4]. No local probes are required and the electrons do not have to be extracted from the REMPI region to be detected. The absence of a probe or mass spectrometer allows this approach to be used for nonlocal measurements, such as in combusting environments or at long distances for pollution and threat gas detection. Measurements can also be made at high pressure, since even though the lifetime of the free electrons may be short, the high bandwidth capability of microwave detection allows them to be measured. Common microwave diagnostics for plasmas, including microwave absorption [5,6] and microwave interferometry [6], are not suitable for the measurement of these REMPI plasmas because the volumes are small compared to the microwave wavelength. Furthermore, the use of scattering rather than transmission avoids the need for a detector located on the opposite side of the sample volume.

The multiphoton ionization of argon is used here as an example. In argon the first step of the 3 + 1 REMPI process is three-photon excitation to an excited state ($3p^5 3d[5/2]$, $J = 3$) by three circularly polarized 261.27 nm photons. The second step is one-photon ionization to the continuum state. Including the laser linewidth, natural, and pressure broadening effects, the three-photon excitation rate to the intermediate state (in s^{-1}) can be written as [7,8]

$$\overline{W_{f,g}^{(3)}} = (2\pi\alpha F\omega)^3 \left| \sum_{|2\rangle} \sum_{|1\rangle} \langle f|r|2\rangle \frac{\langle 2|r|1\rangle}{\sqrt{(\omega_{2,g} - 2\omega_L)^2 + \gamma_2^2/4}} \frac{\langle 1|r|g\rangle}{\sqrt{(\omega_{1,g} - \omega_L)^2 + \gamma_1^2/4}} \right|^2 \mathcal{G}(\omega_L), \quad (1)$$

where g and f denote the ground state ($3p^6 1S$) and the excited state ($3p^5 3d[5/2]$, $J = 3$) of the argon atom, respectively. The circular polarization of the photons leads to $\Delta J = \pm 3$, $\Delta M = \pm 3$ selection rules, which uniquely select the $3p^5 3d[5/2]$, $J = 3$ state from among the various states that fall within the tuning range of the laser. The summations are over dipole allowed off resonant transitions to intermediate states, ω_{2g} is the frequency difference between states $|2\rangle$ and $|g\rangle$, ω_{1g} is the frequency difference between states $|1\rangle$ and $|g\rangle$, α is the fine-structure constant (1/137.036), $F(r, t) = I(r, t)/\hbar\omega_L$ is the total photon flux measured in number of photons per unit area per second, $I(r, t) = I_0(t)\exp(-r^2/r_b^2)$ is the laser intensity which has a Gaussian profile, where r_b is the radius of laser focus, ω_L is the angular frequency of the exciting incident laser, and $\langle|r|\rangle$ are the dipole transition matrix elements, connecting the ground state, intermediate states, and excited state g, 1, 2, and f. γ_i is the linewidth of the ith intermediate states. $\mathcal{G}$ is a generalized line shape scale factor, which is the convolution of level Lorentz broadening, Doppler broadening, and laser broadening. $\mathcal{G}$ is strongly peaked at $\omega_{3,g} = \omega_L$, the three-photon resonance condition. The general three-

photon excitation cross section is defined as $\overline{W_{f,g}^{(3)}} = \sigma_{(3)}F^3$. Equation (1) gives the peak three-photon excitation cross section $\sigma_{(3)} \approx 2.81 \times 10^{-92}\ \mathrm{m}^6 \cdot \mathrm{s}^2$.

A quantum-defect approximation is used for the one-photon ionization from the excited bound state of an atom, which is exact for hydrogenic atom and quite good for Rydberg states of rare gases [9].

$$\sigma_{\mathrm{Pi}} = \frac{8 \times 10^{-22}}{Z(U_I/R)^{1/2}(\hbar\omega_L/U_I)^3}[\mathrm{m}^2], \tag{2}$$

where Z is net charge on the ion, U_I is the ionization potential for the atom at the excited state, R is Rydberg constant, and $\hbar\omega_L$ is the photon energy. This gives $\sigma_{\mathrm{Pi}} = 7.77 \times 10^{-23}\ \mathrm{m}^2$. Note that the kinetic energy of the free electrons generated by the ionization process is $\varepsilon_{\mathrm{ph}} = \hbar\omega_L - U_I \approx 3.2$ eV. As a comparison, the direct multiphoton ionization rate using Keldysh theory [10] is about 3 orders of magnitude lower than that of the resonance-enhanced multiphoton ionization.

Microwave scattering from the plasma generated by REMPI can be calculated by following [3,4]

$$E_{\mathrm{peak}} \propto E_{m0}N, \tag{3}$$

where E_{peak} is the time dependent electric field of the scattering signal, E_{m0} is the incident microwave electric field, and N is the time varying number of electrons inside the plasma generated by REMPI. Note that the microwave scattering field strength is proportional to the total electron number inside the plasma when skin layer thickness is greater than the size of the plasma. By measuring the peak electric field of the microwave scattering as a function of the laser wavelength, the REMPI spectrum can be obtained.

The rate equation for the local density of argon atoms in the excited state ($3p^5 3d[5/2]$, $J = 3$) can be written as

$$\frac{\partial N^*}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD^*\frac{\partial N^*}{\partial r}\right) + N_g\sigma_{(3)}F^3 - N^*\sigma_{Pi}F - (1/\tau + k_1N_g + k_3N_g^2 + k_en_e)N^* \tag{4}$$

with the initial condition, $N^*(t = 0) = 0$.

$N_g = N_g(r, t) = N_g(0) - N^*(r, t) - n_+(r, t)$, N^*, and n_+ are number densities of the ground state argon atom, of the excited state, and of the atomic ions (Ar^+). D^* is the diffusion coefficient of the argon atom in the excited state. $\tau \approx 6.66 \times 10^{-8}$ s is the spontaneous relaxation time of the excited state. k_1, k_3, and k_e are the quenching collision coefficient of two-body and three-body collisions between ground state atoms and excited atoms, and the quenching collision coefficient between excited atoms and electrons, respectively.

Because of the long relaxation time of the electrons, the plasma is nonequilibrium, $T_g = T_0 = T_+ \neq T_e$. Since the plasma is generated in the laser focal volume which has an extended elliptical shape, it is assumed that the plasma region has cylindrical shape. This symmetry allows the plasma to be modeled with time dependent one-dimensional codes. Electrons and ions remain near the laser focal region, so the rate equations for the electron number density n_e and the ion number density n_+ can then be written as

$$\frac{\partial n_e}{\partial t} + \frac{1}{r}\frac{\partial r\Gamma_e}{\partial r} = N^*\sigma_{\mathrm{Pi}}F - \beta n_e n_+ \tag{5}$$

$$\frac{\partial n_+}{\partial t} + \frac{1}{r}\frac{\partial r\Gamma_+}{\partial r} = N^*\sigma_{\mathrm{Pi}}F - \beta n_e n_+, \tag{6}$$

where β is the effective recombination rate including the three-body and radiative recombination rates between electrons and atomic ions [11].

The electron and ion fluxes are

$$\Gamma_e = -\mu_e n_e E - D_e\frac{\partial n_e}{\partial r} - D_e\frac{n_e}{T_e}\frac{\partial T_e}{\partial r} \tag{7}$$

$$\Gamma_+ = \mu_+ n_+ E - D_+\frac{\partial n_+}{\partial r}, \tag{8}$$

where the mobility of the electron is $\mu_e = e/m(\nu_{en} + \nu_c)$. ν_c and ν_{en} are Coulomb collision frequency and electron-neutral collision frequency, and the diffusion coefficient is $D_e = \mu_e T_e$. For the low pressure we have neglected the conversion $Ar + Ar + Ar^+ \Rightarrow Ar_2^+ + Ar$. The electrical potential is calculated by Poisson equation,

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\phi}{\partial r}\right) = -\frac{e}{\varepsilon_0}(n_+ - n_e) \tag{9}$$

with boundary conditions $\partial\phi/\partial r|_{r=0} = 0$ and $\phi(\infty) = 0$; ε_0 is the permittivity of free space. The field is calculated as

$$E = -\frac{\partial\phi}{\partial r}. \tag{10}$$

We suppose the geometry of the temperature field is spherical because electron heat conductivity is very high. The electron temperature in the plasma thus obeys [12],

$$\frac{\partial}{\partial t}\left(\frac{3}{2}n_e kT_e\right) + \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(5/2\Gamma_e kT_e - \lambda_e\frac{\partial T_e}{\partial r}\right)\right] = J_L + J_{MW} - 3/2n_e k(T_e - T_0)(\nu_{en} + \nu_c)\delta + N^*\sigma_{\mathrm{Pi}}F(\varepsilon_{\mathrm{ph}} - 3/2kT_e) + k_e n_e N^*\varepsilon^*, \tag{11}$$

where $J_L = e^2 n_e I(r,t)(\nu_c + \nu_{en})/\varepsilon_0 c m_e[\omega_L^2 + (\nu_c + \nu_{en})^2]$ and $J_{\mathrm{MW}} = e^2 n_e I_{\mathrm{MW}}(\nu_c + \nu_{en})/\varepsilon_0 c m_e[\omega_{\mathrm{MW}}^2 + (\nu_c + \nu_{en})^2]$ are heating by the laser pulse and the microwave, respectively. The heating by the microwave is considered negligible. k is Boltzmann constant, $\lambda = 5/2kn_e D_e$ is the electron heat conductivity, $\delta = 2m_e/M$ is the collision constant of electrons with neutrals or ions, m_e and M are the mass of electrons and neutrals or ions, and $\varepsilon^* = 14.099$ eV is the energy of the

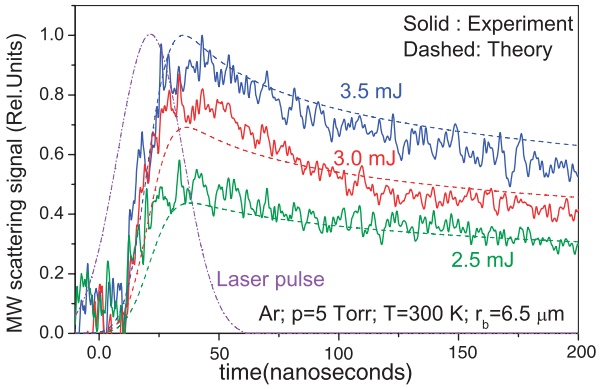

FIG. 1 (color online). Computed and measured microwave scattering signal. Laser has a wavelength of 261.27 nm and an energy of 3.5 mJ/pulse, 3 mJ/pulse, and 2.5 mJ/pulse. The experimental microwave scattering signal has been averaged over 64 laser shots.

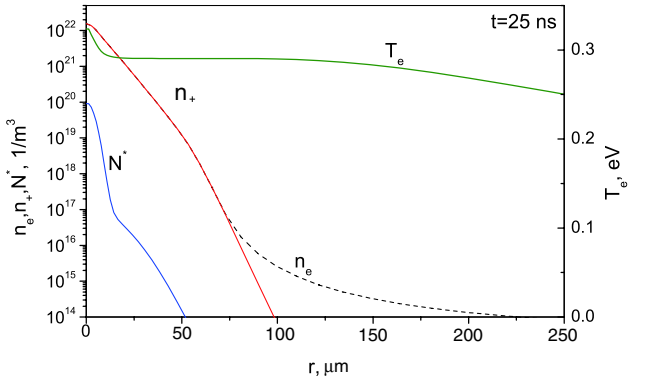

FIG. 2 (color online). Plasma composition of 5 Torr argon at 25 ns after the laser pulse starts. The laser pulse energy is 3.5 mJ; the radius is 6.5 μm in this calculation.

excited state. By solving Eqs. (4)–(11) where constants are found in the literature [13], we can get the time evolution of the excited argon atoms, electrons, and ions. If the plasma dimension is small relative to the microwave wavelength and the electron density is low enough so that skin effects can be neglected (here skin layer thickness is about 110 microns at the peak electron number density, and then increases with electron number density decreasing. Skin layer thickness is always much greater than the size of the plasma), the electric field of microwave scattering is proportional to the total electron number inside the plasma region by Eq. (3), where $N(t) \sim 2\pi \int_0^\infty n_e(r,t) r dr$. For the conditions here, the skin layer thickness is about 110 microns at the peak electron number density and then increases as electron number density decreases, so it is always larger than the physical extent of the plasma. Figure 1 shows computed curves of the time dependent microwave scattering from the plasma generated by REMPI in neutral argon (dotted lines). The rising part is due to the increasing electron number inside the plasma during the ionization by the laser pulse. The decreasing part is due to the recombination losses of electrons. Plasma expansion is followed by ambipolar diffusion. Figure 2 shows an example of the plasma structure at 25 ns after the laser pulse starts.

The experimental setup is shown schematically in Fig. 3. A tunable frequency-tripled Q-switch Ti:sapphire laser was used to generate the ionization. After separation by a prism, the third harmonic of the laser passed through a quarter wave plate and a UV polarization beam splitter to purify the polarization. An advantage of using the combination of the quarter wave plate and polarization beam splitter is that the energy of the REMPI pulse can be changed without changing the laser pumping or upconversion optics. A second quarter wave plate was used to produce circular polarization. Then laser beam was focused by a UV fused silica lens ($f = 7.5$ cm) into the test chamber. The maximum energy of the beam was approximately 4 mJ/pulse, with a pulse length of about 25 ns. Note that the laser pulse length is short enough and the pulse energy is low enough to minimize direct avalanche ionization. The linewidth of this laser is measured to be less than approximately 0.2 nm by using a spectrometer (Acton, PI500Max). The spectrometer has a resolution of 0.03 nm and the wavelength was calibrated by using a commercial mercury lamp line at 253.65 nm. The laser wavelength was monitored by the spectrometer during the experiment.

A 10 mW microwave source at a frequency 12.6 GHz (wavelength 2.3 cm) illuminates the ionization volume from the upper side of the chamber through a microwave horn (WR 75). A microwave receiver was placed perpendicular to the propagation directions of both the laser and the microwave sources. The receiver is located 30 cm away from the plasma. A microwave homodyne receiving system was used for detection and the scattered microwave

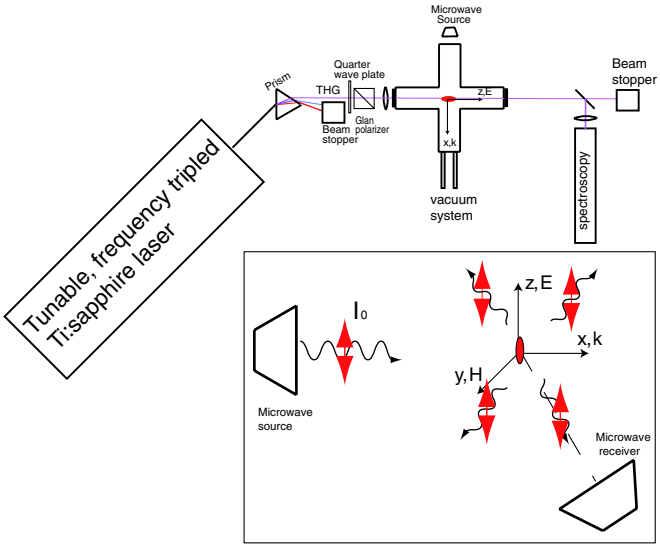

FIG. 3 (color online). Schematic of the microwave scattering experiment used to measure multiphoton ionization in neutral argon: THG, third harmonic generation.

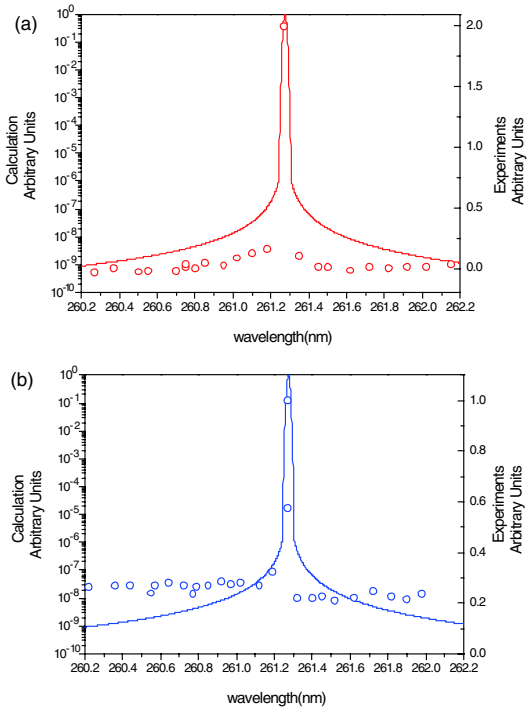

FIG. 4 (color online). REMPI spectrum of neutral argon at 5 Torr. (a) was obtained by microwave scattering method and (b) is by traditional electron-collection electrodes. Both are obtained by using the circularly polarized light. Solid lines are theoretical REMPI calculations by Eqs. (1) and (2). At the wings off the resonance direct multiphoton ionization is about 3 orders of magnitude smaller. Circle marks are experimental results.

signal was amplified by about 90 dB. The vacuum chamber was made of microwave transparent polyvinyl chloride plastic. The inner diameter of the chamber is 8 cm. The cell was purged 3 times before filling with 5 Torr of argon gas. The microwave source was placed in a metal box, and the experiment was covered by microwave absorber to minimize background. Comparisons between the model predictions and experimental results are given in Fig. 1 showing that good agreement with the predicted electron recombination rate has been achieved for three values of laser pulse energy. The residual discrepancies are likely due to the limitations of the two-dimensional model and noise in the detection system.

By measuring the peak intensity of the microwave scattering signal at different wavelengths, REMPI spectra were obtained as shown in Fig. 4(a) where the curve represents the predicted spectrum and the points are measured values. Because of the very low off resonant signal strength, the measured values shown for off resonant points are representative of the background noise in the microwave detection apparatus. The REMPI peak at 261.27 nm matches the empirical value for the circularly polarized light (left- and right-handed circularly polarized lights are equivalent).

To validate the microwave scattering experimental results, a traditional electron-collection method was conducted. The argon sample cell consists of two quartz Brewster-angle windows, a 28 mm inner diameter Pyrex body with 4 pairs of electrodes, and two vacuum valves. The focal length of lens into the cell was 15 cm. The ionization current was monitored through a load resistance of 10 kΩ. A capacitor of 0.01 μF separates the dc current from the ionization current. Finally the measured current pulse was amplified and integrated. The REMPI spectrum taken with circularly polarized light by this method is shown in Fig. 4(b). The spectrum is in good agreement with the one obtained by microwave scattering.

In conclusion, we have used coherent microwave scattering to detect resonance-enhanced multiphoton ionization of neutral argon and to follow the recombination of the free electrons. The time evolution of the recombination process from the ellipsoidal laser produced plasma is modeled with a cylindrical geometry for the electrons, positive ions and excited state argon atoms, and a spherical geometry for the long range electron temperature. Predictions of the time dependent one-dimensional model give good agreement with the measured recombination rates. This nonintrusive detection method provides a method for the time accurate measurement of free electron generation and loss processes and for a high sensitivity detection of the REMPI plasma.

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