Competition between two-photon-resonant three-photon ionization and four-wave mixing in Xe

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Competitive inhibition of a resonance enhanced multiphoton ionization process by a resonant four-wave mixing has been observed in Xe atoms. When an intense IR (1064 nm) laser was applied to a sample of Xe which was also being irradiated by a UV laser tuned to the two-photon absorption line of Xe, the two-photon-resonant three-photon ionization signals decreased with increasing IR laser power. This phenomenon is dependent on the resonant states of Xe and the polarization of the two laser beams. Three $6s$ excited states $[5/2]_2$, $[3/2]_2$, and $[1/2]_0$ were examined. At the $[1/2]_0$ resonant state, the ion signals were not decreased but slightly increased with the increase of the IR laser power. No suppression of the ion signal was observed at the $[5/2]_2$ resonant state, when the polarization directions of the lasers were perpendicular to each other. The result of the polarization dependence reflects the selection rules of four-wave mixing. A simple rate equation analysis including the contribution of two-photon ionization from the $[1/2]_0$ state by the IR laser well represents the IR laser-power dependence of the ion signal.

I. INTRODUCTION

Resonant four-wave mixing (RFWM) [1] is one of the most effective methods to produce coherent vacuum ultraviolet (VUV) radiation since the frequency conversion of the laser light source is quite efficient [2]. In general, a two-photon resonance of atoms or molecules is used as the RFWM scheme. The pump laser frequency (ω_1) is fixed to the two-photon absorption and the probe laser (ω_2) is added to generate the sum ($2\omega_1 + \omega_2$) or difference ($2\omega_1 - \omega_2$) frequency. If the three-photon energy of ω_1 is above the ionization energy, $[2 + 1]$ resonance enhanced multiphoton ionization (REMPI) occurs as the competitive process to the RFWM. Multiphoton ionization is considered to be the main reason for the power saturation of the RFWM efficiency [3]. On the contrary, multiphoton ionization is interrupted when a RFWM process occurs to compete with REMPI.

Such effect was observed in the three-photon-resonant multiphoton ionization of Xe, where the $[3 + 2]$ REMPI signals via $6s[3/2]_1^o$ state disappeared at pressures above 40 Pa (0.3 Torr) [4]. This anomalous pressure effect turned out to be the apparent competition between two different, but coherent pathways to the $6s$ state [5–8]. Glownia and Sander [9] verified the competition between the third harmonic generation and the ionization in Xe by an experiment using circularly polarized lasers. Recently, Peet [10] reported that the interference effect was defeated in the crossed-beam excitation with different polarizations.

Similar effects were also observed in the two-photon-resonant excitation states of Xe [11]. In that case, the interference effect was observed as the suppression of the ac Stark shifts [12] for the REMPI spectra. Since the RFWM process is strongly dependent on the density of atoms or molecules, the suppression effect was observed at rather high sample pressure conditions and multiphoton ionization dominates in the low pressure conditions.

In the present paper, we observed REMPI spectra of Xe in a supersonic jet condition with UV laser tuned to the two-photon absorption wavelength around 250 nm corresponding to the transition to the $6p$ excited states. Suppression of the ionization signal was observed when an intense IR laser at 1064 nm irradiated simultaneously with the UV laser. The efficiency of suppression depends on the resonant state, and the polarization direction of the two lasers. The competitive inhibition of the REMPI by the RFWM process induced by the additional IR laser is discussed with the results of IR laser-power dependence of the ionization signals.

II. EXPERIMENTAL

Resonance enhanced multiphoton ionization (REMPI) spectra of Xe atoms were measured by a molecular beam chamber equipped with a time-of-flight (TOF) mass spectrometer. A pulsed supersonic jet of Xe was generated by expanding a gas mixture of Xe in He ($\leqslant 0.1\%$) into the vacuum through a pulsed valve (Jordan) with nozzle diameter of 0.5 mm. The stagnation pressure was kept between 100 and 120 kPa. The duration of the pulsed jet was less than 150 μs.

For the REMPI excitation light source from 245 to 260 nm, a frequency-doubled output of a dye laser (Continuum ND6000) pumped by a Nd:YAG laser (Continuum PL8000) was used. Typical output power of the UV laser is around 500 μJ/pulse. Fundamental output of a Nd:YAG laser (Spectron SL803G) was used as the probe IR (1064 nm) light source. Pulse duration of the UV pump (ω_1) and IR probe (ω_2) lasers are 5 ns and 15 ns, respectively. Both lasers are linearly polarized. In order to observe the polarization effect, a quartz half-wave plate was employed to rotate the polarization direction of ω_2. The IR laser was operated at the maximum output power of 150 mJ/pulse. On the measurement of ω_2 laser-power dependence, a polarization filter was placed after the half-wave plate to reduce the output power by rotating the polarization direction. The two laser beams were overlapped in the copropagating direction by using a dichroic mirror. Then the laser beams were focused by a quartz lens with 300-mm

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focal length to the sample jet at 150 mm downstream from the pulsed valve. The pulsed valve and the two lasers were operated at repetition rate of 10 Hz. They were triggered by a pulse delay generator (Stanford DG535) to adjust the timing of the pulse sequence. The delay between the pulsed valve and the pump laser (ω_1) operation was set to observe the early part of the pulsed jet in order to avoid the effect of cluster formation of the Xe atoms.

The TOF mass spectrometer used to detect the Xe ions is a linear type and the flight tube length is 500 mm. It has Wiley-McLaren-type electrodes [13] made of three mesh plates. The ionization point was located at the center of the repeller and extractor electrodes. The Xe ions were accelerated by two electric fields of Wiley-McLaren-type electrodes with total acceleration energy of 3 keV. The ratio between the two electric fields was set to the space focusing [13] condition. The ions were detected by a multichannel plate mounted at the end of the flight tube. No electric lens and diffractors were required to increase the detection sensitivity. The ion signals were accumulated by a digital oscilloscope (Tektronics TDS3012B) and transferred to a personal computer for further analysis.

III. RESULTS AND DISCUSSIONS

A typical TOF mass spectrum of Xe is shown in Fig. 1(a). This spectrum was measured with an UV laser (252.48 nm) only. The laser wavelength is two-photon-resonant to the $[3/2]_2$ excited state. The REMPI excitation scheme is also shown in Fig. 1(a). Since the isotope shift of Xe [14] is within the laser bandwidth (0.3 cm^{-1}), all the seven isotopes of Xe are observed in the mass spectrum. The intensity pattern of the mass spectrum reflects the natural abundances of the Xe isotopes. The laser-power dependence showed no saturation effect in the two-photon absorption at the experimental condition below 500 μJ/pulse.

When the IR laser was applied, the ion signal decreased to almost a factor of 10 as shown in Fig. 1(b). The depression of the ion signal is the effect of competitive inhibition of the REMPI process by RFWM. The situation is that a weak UV laser resonant to the two-photon absorption of Xe and a very intense but off-resonant IR laser simultaneously irradiate the Xe atoms. This is exactly the same condition for the RFWM to generate sum ($2\omega_1 + \omega_2$) or difference ($2\omega_1 - \omega_2$) frequency. Sum-frequency mixing requires the dispersion of the medium to be negative for tightly focused beams. This restricts the available tuning range [15] to be rather narrow. In the present case, the sum frequency $2\omega_1 + \omega_2$ corresponding to 112.85 nm is out of the tuning range. Therefore, only difference-frequency mixing which is possible, either positive or negative dispersion, contributes to the RFWM process. The difference-frequency mixing scheme is illustrated in Fig. 1(b).

The depression of the ion signal was not observed if the delay time between the two laser pulses was not zero. If any multiphoton absorption by the IR laser (ω_2) occurs to excite the ground state Xe to another excited state, the REMPI process is also prevented. However, such effect is also observable when ω_2 pulse arrives just before ω_1 that is not consistent with the experimental result. We also investigated the possibility of accidental resonance by the two lasers, such as $\omega_1 + \omega_2$, $\omega_1 + 2\omega_2, \ldots, \omega_1 + n\omega_2$, but no excited states were found in the atomic spectral database [16].

There are two other $6s$ excited states in the vicinity of $[3/2]_2$ which are two-photon allowed from the ground state. They are $[1/2]_0$ and $[5/2]_2$ states of which the two-photon absorption wavelengths are 249.63 nm and 256.01 nm, respectively. We carried out the same measurements at these two resonant states. Polarization effects were also observed by changing the polarization direction of the IR laser. The results are summarized in Fig. 2. At each resonant state, three TOF mass spectra were measured by UV laser only; UV and IR lasers
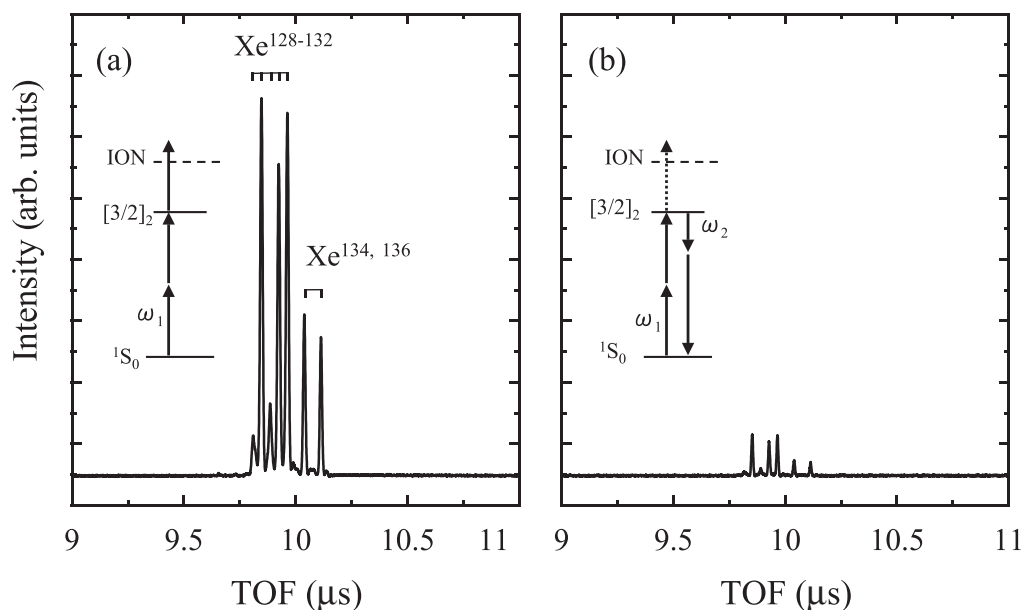

FIG. 1. TOF mass spectra of Xe ionized through $6p$ $[3/2]_2$ resonant state. (a) With UV pump laser only. (b) With UV pump (ω_1) and IR probe (ω_2) lasers.
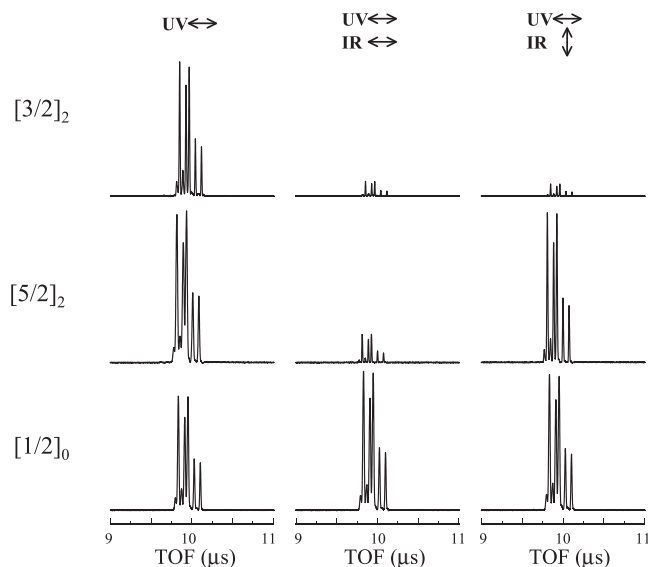
FIG. 2. Laser polarization dependence of the REMPI TOF spectra of Xe for the three resonant states $[3/2]_2$ (top), $[5/2]_2$ (middle), and $[1/2]_0$ (bottom). The spectra were measured by UV laser only (left), UV and IR lasers with parallel polarization direction (middle), and UV and IR lasers with perpendicular polarization direction (right).

with parallel and perpendicular polarization conditions are shown in Fig. 2. Depressions of the ion signal by the IR laser were observed except in the $[1/2]_0$ state. No depression was observed in the perpendicular polarization condition at $[5/2]_2$ state. This polarization effect can be explained by the selection rule of the RFWM on the magnetic quantum number m. In the RFWM process by linearly polarized lights, the total change of m must be zero. If the two-photon transition [17] to the resonant state by the pump laser is $\Delta m = \pm 2$, the polarization direction of the probe laser must be parallel to the pump laser. The results observed at $[5/2]_2$ state reflect this selection rule. As the two-photon transition to this state is $\Delta m = \pm 2$, no RFWM process occurs when the polarization directions of the two lasers are perpendicular to each other. In fact the TOF spectrum measured at this state in the perpendicular condition does not change from that measured by UV laser only. Depressions of the ion signals are observed in both parallel and perpendicular conditions at $[3/2]_2$ state because $\Delta m = 0$ transition is allowed for the two-photon transition to this state.

The results observed at $[3/2]_2$ and $[5/2]_2$ states support the existence of resonant RFWM competing with the REMPI process. However, depressions of ion signals were not observed at $[1/2]_0$ state in Fig. 2. On the contrary, the ion signals were slightly increased in both parallel and perpendicular conditions. The RFWM process is not forbidden in both conditions because the two-photon transition to this state is $\Delta m = 0$. This means that also the RFWM is competing with the REMPI process; the ionization efficiency is not decreased but slightly increased. The cause of this result is considered to be another multiphoton excitation process contributing ionization by the IR probe laser (ω_2). The level energy of $[1/2]_0$ is the highest among the three excited states. The values of the level energies are 80 118.69, 79 212.47, and 78 119.80 cm^{-1} for $[1/2]_0$, $[3/2]_2$, and $[5/2]_2$, respectively. Since the ionization
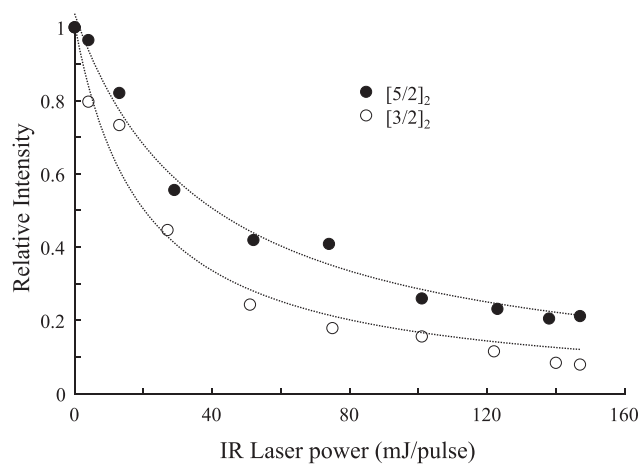

FIG. 3. IR laser-power dependence of the ion intensity measured at $[3/2]_2$ (open circle) and $[5/2]_2$ (filled circle) resonant states. Relative ion intensity of the REMPI TOF mass spectrum is plotted against IR laser power. The ion intensity is normalized to the data measured without IR laser. The curves represent the result of fitting by the rate equation analysis.

energy of Xe is 97 833.787 cm^{-1}, two-photon excitation of $[1/2]_0$ by ω_2 (9398.5 cm^{-1}) is enough for ionization. The two-photon excitation energy of $[3/2]_2$ by ω_2 is also above the ionization energy, but the efficiency seems to be low because the total photon energy ($2\omega_1 + 2\omega_2 = 98\,009.47$ cm^{-1}) is on the edge of the ionization threshold (97 833.787 cm^{-1}).

We measured the IR laser-power dependences of the ion signals. The results are shown in Fig. 3 (for $[3/2]_2$ and $[5/2]_2$) and Fig. 4 (for $[1/2]_0$). At each resonant state, the total ion signal is plotted as a function of the IR laser power. The intensity is normalized by the data measured by the UV laser only. The measurement was carried out in the parallel polarization condition. As shown in Fig. 3, the ionization efficiency via $[3/2]_2$ and $[5/2]_2$ states decreases monotonously with the increase of the IR laser power. On the other hand, the ionization efficiency via $[1/2]_0$ state (Fig. 4) shows rather complicated dependence on the IR laser power.
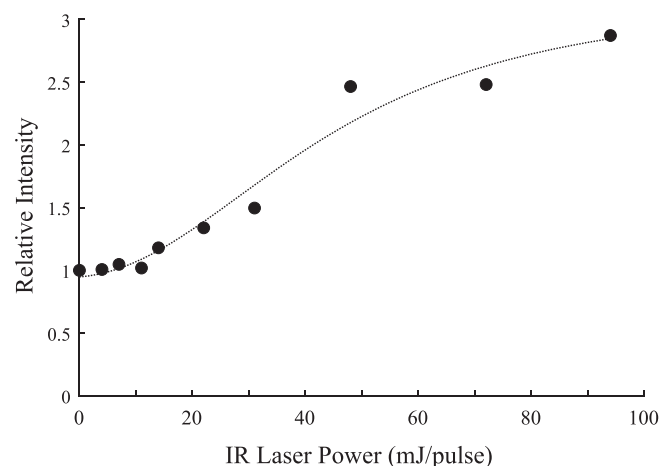

FIG. 4. IR laser-power dependence of the ion intensity measured at $[1/2]_0$ resonant state.
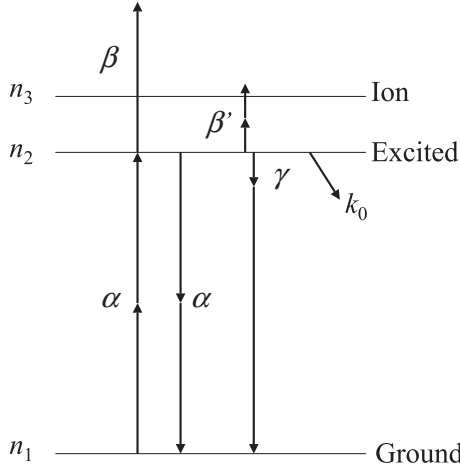
FIG. 5. Diagram of REMPI and four-wave mixing scheme relevant to the rate equation analysis.

The curves in Figs. 3 and 4 show the result of fitting by a simple rate equation [18] analysis. The scheme of REMPI and RFWM used to derivate the rate equation is illustrated in Fig. 5. The rate equations for the ground (n_1), excited (n_2), and ionic (n_3) states are

$$dn_1/dt = -\alpha n_1 + (\alpha + \gamma)n_2, \tag{1a}$$

$$dn_2/dt = \alpha n_1 - (\alpha + \gamma + k_0 + \beta + \beta\prime)n_2, \tag{1b}$$

$$dn_3/dt = (\beta + \beta\prime)n_2, \tag{1c}$$

where α denotes the rate constant of the two-photon induced absorption or radiation, and k_0 denotes the rate constant of the fluorescence decay (dipole allowed transition to the $6s$ excited states). β and β' are respectively, the UV one-photon and IR two-photon ionization rate constants. γ is the RFWM rate constant induced by the IR laser. The ionization efficiency is proportional to dn_3/dt. Assuming a steady state for the excited state, $dn_2/dt = 0$, the ion intensity S_{ion} is easily derived from Eq. (1):

$$S_{\text{ion}} = \frac{\alpha(\beta + \beta')}{\alpha + \beta + \beta' + \gamma + k_0}n_1. \tag{2}$$

The rate constants that depend on the IR laser power are β' and γ. They are defined as

$$\beta' \equiv \delta_i I^2, \quad \gamma \equiv \delta_f I, \tag{3}$$

where I denotes the IR laser power and δ_i and δ_f are the cross sections of the two-photon ionization and the RFWM, respectively. Then the power dependence of the ion intensity is represented by the following equation:

$$S_{\text{ion}} = \frac{\alpha(\beta + \delta_i I^2)}{\alpha + \beta + k_0 + \delta_i I^2 + \delta_f I}n_1. \tag{4}$$

If the cross section of the two-photon ionization by the IR laser is very small ($\delta_i \approx 0$), Eq. (4) is simplified to

$$S_{\text{ion}} = \frac{\alpha\beta}{\alpha + \beta + k_0 + \delta_f I}n_1. \tag{5}$$

The fitted curves in Fig. 3 were obtained by using Eq. (5). The ion signals measured at $[3/2]_2$ and $[5/2]_2$ resonant states are in inverse proportion to the IR laser power. As shown in Fig. 4, the power dependence measured at $[1/2]_0$ resonant state is well represented by Eq. (4). The reason why the REMPI signal via this state is not inhibited by the IR probe laser is not the prohibition of the RFWM but the contribution of the two-photon ionization by the IR probe laser. In fact, generation of vacuum ultraviolet radiation by the RFWM with the two-photon resonance at $[1/2]_0$ state was reported [19] to be highly efficient. In that case, the probe laser contributes not only to the two-UV-photon-resonant four-wave mixing, but also to the two-UV-photon-resonant two-IR photon ionization. As the result of the two processes working to decrease and increase the ionization signal, no significant change of the ionization signal intensity was observed.

In conclusion, it is verified that in a certain condition of lasers and the resonant state at the two-photon-resonant state of Xe, resonant four-wave mixing occurs exceedingly to reduce $2 + 1$ REMPI. The conditions necessary for this are as follows: (i) The probe laser (ω_2) has much higher power than the pump laser (ω_1). (ii) The probe laser (ω_2) is not resonant to any allowed transitions from both the ground and excited states. (iii) Contribution of the multiphoton ionization by ω_2 from the excited state is small.

Detecting the mixed output of the RFWM ($2\omega_1 - \omega_2$) can be a sensitive method for two-photon absorption spectroscopy. In principle, RFWM is active for atoms and also molecules that have two-photon absorptions. It can be utilized to a sensitive probe of atoms [20] and molecules. Since the RFWM is a reducible process, it is free from any sample damages such as ionization or decomposition from the excited state in the case of molecules.

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