Theoretical analysis on the efficiency of optical-optical double-color double-resonance multiphoton ionization

Guiyin Zhang (张贵银)* and Yidong Jin (靳一东)

School of Mathematics and Physics, North China Electric Power University, Baoding 071003, China

**E-mail: gyzhang65@yahoo.com.cn*

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Analytic formula of the efficiency of optical-optical double-color double-resonance multi-photon ionization (OODR-MPI) is derived from the dynamic rate equation about the interaction of photon and material. Based on this formula, the influence of characteristic of the pump and probe laser on the ionization efficiency of (1+2+1) OODR-MPI process is simulated theoretically. It is shown that the pump laser will affect the ionization efficiency by the number control of the molecules excited to the first resonance state. The ionization efficiency is decided by the probe laser directly. Both of the excited molecules and ionization efficiency increase with the intensity and pulse duration of the laser until saturation. It is also found that the longer the delay time of the probe laser to the pump one is, the lower the ionization efficiency would be. The delay time ought to be smaller than the lifetime of the excited molecule in the practical use of the OODR-MPI technique.

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The technique of multi-photon ionization (MPI) is an effective method for detecting trace elements and observing the high energy electronic states of atoms and molecules[1−5]. It provides information about not only the molecular states and molecular structures, but also the reaction dynamics of the correlating energy levels. Investigations show that when this technique is used to observe the high energy levels of the molecule, the molecule is ionized usually via multi-resonance states due to the dense rovibronic energy levels. This makes the obtained spectrum very complex. Sometimes it is difficult to assign the spectral lines. To overcome this defect, the technique of optical-optical double-resonance MPI (OODR-MPI) is coming into use. In this method, the pump laser excites the molecules to the first resonance electronic state, and the probe laser makes the excited molecules be ionized via the second resonance state. The characteristic of the second resonance state is observed by scanning the probe laser. The step for the spectral transition turns into the first resonance state by the effect of the pump laser. So the structure of the spectrum is simplified. This is suitable for the investigation of the higher energy levels[6−11]. Because the technique of OODR-MPI is based on the detection of the ions, so how to increase the ionization efficiency is a main topic for its practical use. In view of that the dynamic rate equation about the interaction of photon and material is simple, the concept is clear. The analytic formula of the ionization efficiency in the process of OODR-MPI is derived from the rate equation. Use this formula, the influence of characteristic of the pump and probe laser together with the delay time of the probe laser to the pump one on the ionization efficiency is numerically simulated.

In the process of OODR-MPI, the molecule is ionized by absorbing pump and probe photons and via two intermediate resonance states. This process can be shown as a model of four energy levels of Fig. 1. Usually, there is a time delay of the probe laser to the pump one during the OODR-MPI experiment. The delay time is longer than the pulse duration of the pump laser, but shorter than the relaxation time of the excited molecules in the first resonance state. So this double-resonance process can be thought as composed of two steps. The first one is the molecules excited to the first resonance state 2> by absorbing pump photons. The second is that the excited molecules ionized by absorbing probe photons and via the second resonance state 3>. The molecules excited to the first resonance state can de-excited by the process of spontaneous radiation, stimulated radiation, and collision relaxation process. When observing the characteristic of the high electronic states with the technique of double-resonance, the second resonance state is Rydberg one usually. Radiation from the molecules of the Rydberg state can be neglected due to the small transition probability. The laser pulse duration is 35 ps[5−7]. It is much smaller than the period of the collision relaxation process. So the collision process can also be neglected in the excitation process.

The rate equation of the variation of molecule number density during the first step can be described as

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -\sigma_1 I_1^m n_1 + \sigma_1 I_1^m n_2 + k_F n_2, \tag{1}$$

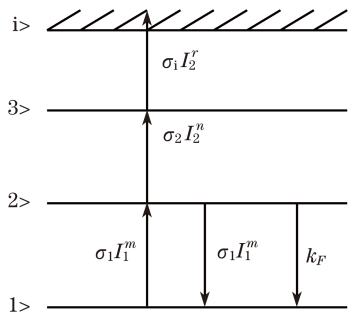

Fig. 1. Dynamic model of the double-resonance multiphoton ionization.

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = \sigma_1 I_1^m n_1 - (\sigma_1 I_1^m + k_F) n_2, \tag{2}$$

$$n_1 + n_2 = n_0. \tag{3}$$

The initial condition is

$$n_1 = n_0,\ n_2 = 0. \tag{4}$$

The rate equation of the variation of molecule number density during the second step is

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = -\sigma_2 I_2^n n_2 - k_F n_2, \tag{5}$$

$$\frac{\mathrm{d}n_3}{\mathrm{d}t} = \sigma_2 I_2^n n_2 - \sigma_i I_2^r n_3, \tag{6}$$

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \sigma_i I_2^r n_3, \tag{7}$$

$$n_2 + n_3 + n_i = n_{2t_0}. \tag{8}$$

The initial condition of the second step is

$$n_3 = n_i = 0. \tag{9}$$

n_1, n_2, n_3, and n_i are the number densities of molecule in the four energy levels respectively, and n_0 is the total molecule number density. I_1 and I_2 are the photon fluxes of the pump and probe laser respectively. σ_1 and σ_2 are the absorption transition cross sections. σ_i is the ionization cross section from the second resonance state, and k_F is the rate coefficient of the spontaneous radiation of the molecules excited to the first resonance state.

Solving Eqs. (1)–(3) with the initial condition of Eq. (4), we can obtain

$$n_2 = \frac{\sigma_1 I_1^m n_0}{2\sigma_1 I_1^m + k_F}\left[1 - e^{-(2\sigma_1 I_1^m + k_F)t}\right]. \tag{10}$$

Suppose the pulse duration of the pump laser is τ_1, then at the end of the interaction of the pump laser, the number density of the first resonance state is

$$n_2 = \frac{\sigma_1 I_1^m n_0}{2\sigma_1 I_1^m + k_F}\left[1 - e^{-(2\sigma_1 I_1^m + k_F)\tau_1}\right]. \tag{11}$$

Then the excited molecules de-excit in the manner of spontaneous radiation. The variation of the excited molecules in the first resonance state versus time is

$$n_2 = \frac{\sigma_1 I_1^m n_0}{2\sigma_1 I_1^m + k_F}\left[1 - e^{-(2\sigma_1 I_1^m + k_F)\tau_1}\right] e^{-k_F t}. \tag{12}$$

Let the time delay of the probe laser to the pump one be t_0, then in the initial time of the second step, the number density of the first resonance state is

$$n_{2t_0} = \frac{\sigma_1 I_1^m n_0}{2\sigma_1 I_1^m + k_F}\left[1 - e^{-(2\sigma_1 I_1^m + k_F)\tau_1}\right] e^{-k_F\ t_0}. \tag{13}$$

Solving Eqs. (5)–(8) with the initial condition of Eqs. (9) and (13), we can obtain

$$n_i = A\left[\frac{1 - e^{-(\sigma_2 I_2^n + k_F)t}}{\sigma_2 I_2^n + k_F} - \frac{1 - e^{-\sigma_i I_2^r t}}{\sigma_i I_2^r}\right], \tag{14}$$

where

$$A = \frac{\sigma_1\sigma_2\sigma_i I_1^m I_2^{n+r} n_0}{(2\sigma_1 I_1^m + k_F)(\sigma_i I_2^r - \sigma_2 I_2^n - k_F)} \times \left[1 - e^{-(2\sigma_1 I_1^m + k_F)\tau_1}\right] e^{-k_F\ t_0}. \tag{15}$$

Suppose the probe laser is square with pulse duration of τ_2, then at the end of the interaction of the probe laser, the number density of the ionized molecules is

$$n_i = A\left[\frac{1 - e^{-(\sigma_2 I_2^n + k_F)\tau_2}}{\sigma_2 I_2^n + k_F} - \frac{1 - e^{-\sigma_i I_2^r \tau_2}}{\sigma_i I_2^r}\right]. \tag{16}$$

Equations (15) and (16) are the total number density of the ionized molecules after the interaction of the pump and probe laser.

The ionization efficiency is

$$\eta = \frac{n_i(\tau)}{n_0}. \tag{17}$$

From Eqs. (10) and (15), one can find that the ionization efficiency of OODR-MPI depends on the intensity and pulse duration of both of the pump and probe lasers, delay time of the probe laser to the pump one, and the characteristic of the molecules. To a certain molecule, all σ_1, σ_2, σ_i, and k_F are constants. And the ionization efficiency depends on the characteristic of two lasers totally.

In the process of (1+2+1) OODR-MPI, the first excitation process is a single-photon one. With consideration of transition energy, the molecule ought to be excited to the valance electronic state by absorbing visible photon. For most molecules, the spontaneous radiation lifetime is with μs magnitude usually (for example, NO_2 molecule is 10 – 100 μs[12,13]). Let $k_F = 10^4$ s^{-1}, $\sigma_1 = 1.5\times10^{-18}$ cm^2[13], the number of the molecules excited to the first resonance state via the pump process, versus the intensity and pulse duration of the pump laser can be simulated based on Eq. (14). The result is shown in Fig. 2.

From Fig. 2, it is obvious that the molecules excited to the first resonance state increase with the intensity and pulse duration of the pump laser until saturation. And the number of the excited molecules is half of the total one. It shows further that the narrower the pulse duration is, the larger the laser intensity for saturation

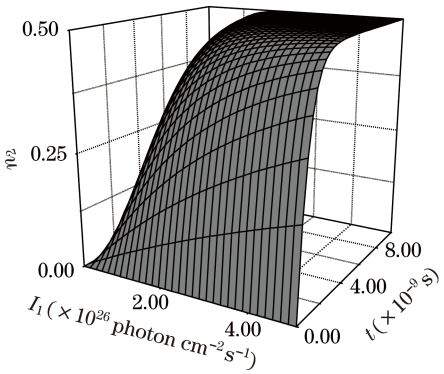

Fig. 2. Number of excited molecules versus intensity and pulse duration of the pump laser ($k_F = 10^4$ s^{-1}, $\sigma_1 = 1.5\times10^{-18}$ cm^2).

is. For example, the laser intensity for saturation is 3.8×10^{28}, 1.1×10^{29}, and 1×10^{30} photon $\mathrm{cm^{-2}s^{-1}}$ when the pulse duration is 100, 35, and 3.5 ps, respectively. Practical use of the technique of OODR-MPI is based on the higher ion yield. We must make more molecules excited to the first resonance state, so that the amount of the ions can be increased. The intensity and pulse duration of the pump laser for saturation in the first excitation step can be selected with the aid of Fig. 2.

Suppose that the molecules excited to the first resonance state is already saturated. That is to say the number of the molecules excited to the first resonance state is half of the total one. The variation of the ionization efficiency versus the intensity and pulse duration of the probe laser can be simulated from Eqs. (14) and (15). Presented in Fig. 3 is the result of the (1+2+1) OODR-MPI process when set $\sigma_2 = 10^{-50}$ $\mathrm{cm^4s}$, $\sigma_i = 1.5\times 10^{-18}$ $\mathrm{cm^2}$[13], and the delay time of probe laser to the pump one $t_0 = 5\times10^{-9}$ s[6]. The results show that to certain pulse duration, the ionization efficiency increases with the enhancement of the probe laser intensity and gets to saturation at last. The ionization efficiency of the molecules pumped to the first resonance state can reach 100%. This can be attributed to the increase of the photon number with the enhancement of the laser intensity. There are more molecules being ionized in unit time. The appearance of saturation appears when the molecules are ionized fully. This is accordance with the anticipation of the theory and the result of the experiment[14,15]. It is also found that the narrower the laser pulse duration is, the higher the laser intensity for saturation would be. Let the pulse duration of the probe laser be 100, 35, and 3.5 ps, then the intensity for saturation is 3.4×10^{30}, 5.8×10^{30}, and 1.9×10^{31} photon $\mathrm{cm^{-2}}$ $\mathrm{s^{-1}}$, respectively. For certain laser intensity, the phenomena of the larger pulse duration on the higher ionization efficiency appears before saturation.

From Eq. (12), the molecules excited to the first resonance state will decay in the manner of index after the pump process. The decrease of the excited molecules will influence the ionization efficiency directly. So the ionization efficiency depends on the delay time of the probe laser to the pump one severely. Figure 4 shows the curve of the ionization efficiency versus the probe laser intensity with different delay time. Where $\tau_1 = \tau_2 = 35$ ps and the pump process is saturation. Comparing the curves in Fig. 4, it can be found that the influence of

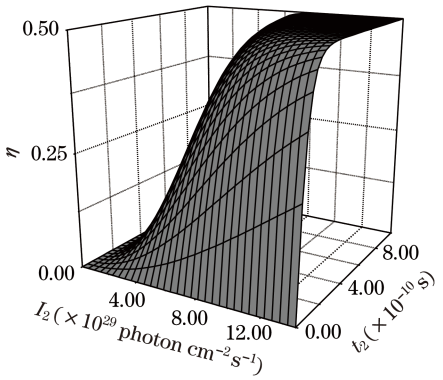

Fig. 3. Ionization efficiency versus intensity and pulse duration of the probe laser ($\sigma_2 = 10^{-50}$ $\mathrm{cm^4}\cdot$ s, $\sigma_1 = 1.5\times10^{-18}$ $\mathrm{cm^2}$, $t_0 = 5\times10^{-9}$ s).

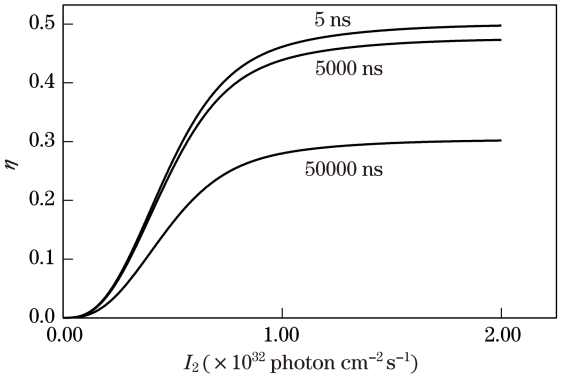

Fig. 4. Curve of ionization efficiency versus laser intensity with different delay times for $\tau_1 = \tau_2 = 35$ ps.

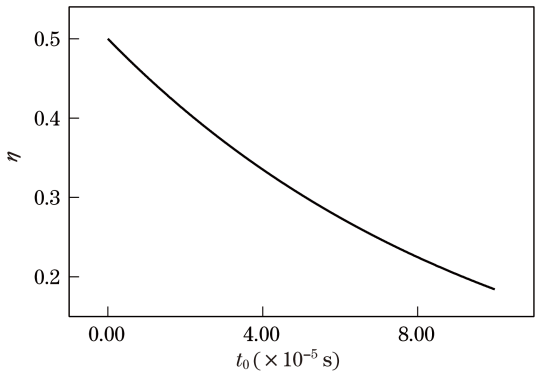

Fig. 5. Curve of ionization efficiency versus delay time for $\tau_1 = \tau_2 = 35$ ps, $I_1 = 2\times10^{28}$, and $I_2 = 4\times10^{28}$ (photon $\mathrm{cm^{-2}s^{-1}}$).

the delay time on the ionization efficiency is not obvious when the delay time is smaller than the spontaneous radiation lifetime of the excited molecules in the first resonance state. While the delay time is similar to the spontaneous radiation lifetime, the ionization efficiency will be reduced obviously. Figure 5 is the simulation result of the variation of the ionization efficiency versus the delay time. It is shown that the ionization efficiency decreases in the manner of index with the increase of the delay time. In the previous literature, most of work did not refer the delay time of the probe laser to the pump one when observing the OODR-MPI process with the theory of rate equation[15,16]. The simulation results show that the delay time of the probe laser to the pump one is an important factor in the process of OODR-MPI. It will influence the ionization efficiency severely.

In conclusion, the ionization efficiency versus the characteristic of the pump and probe laser in the process of (1+2+1) OODR-MPI is simulated. It is shown that the pump laser will influence the ionization efficiency by control the number of the molecules excited to the first resonance state. The ionization efficiency lies on the characteristic of the probe laser directly. It increases with the enhancement of the probe laser intensity and pulse duration. The phenomena of saturation will appear when all of the excited molecules are ionized. In addition, in order to realize the maximum ionization efficiency, the delay time of the probe laser to the pump one ought to be smaller than the relaxation time of the excited molecules. We wish that the results mentioned above can provide useful information for selecting optimum laser parame-

ters when observing molecules or atoms with the technique of OODR-MPI.

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