Influence of laser intensity on the double-resonance multiphoton ionization process of NO molecule

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The analytic formula of the ionization efficiency in the process of double resonance enhanced multi-photon ionization (DREMPI) is derived from the dynamic rate equation about the interaction of photon and material. Based on this formula, the ionization efficiency and the laser power index versus laser intensity in the DREMPI process of NO molecule, via $A^2\Sigma$ and $S^2\Sigma$ intermediate resonant states, is numerically simulated. It is shown that the ionization efficiency of NO molecule increases with the laser intensity until getting saturation, while the laser power index decreases with the enhancement of the laser intensity and changes to zero at last. The variation of the laser power index with the laser intensity indicates that the ionization efficiency reaches saturation in the one, two, and three excitation steps respectively. It is also found that the narrower the laser pulse duration is, the higher becomes the laser intensity for saturation.

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NO is not only a stable diatomic molecule with unpaired electron outside the nuclear, but also a serious pollutant with some special physical and chemical characteristics. It plays a key role in the formation of acid rain, photochemical smog, and the physiological reaction of human body. Searching for the most suitable method for the study and detection of NO is a fascinating subject for a long time. The technique of resonance enhanced multi-photon ionization (REMPI) spectroscopy, which is based on the coming forth of high power laser, is a practical method for studying the structure of highly excited state. It uses simple apparatus, but with higher detection sensitivity. This provides information about not only molecular states and molecular structures but also the reaction dynamics. One of the advantages of this technique is to study the transitions that are single-photon forbidden. There are many reports about the applications of REMPI spectroscopy[1−7]. How to improving the ionization efficiency by selecting suitable excitation transition pathway and laser parameter is very important for the practical use of this technique. Considering that most of the excited states of NO are Rydberg type[8], the observation of these excited states usually be via multi-photon process when using visible light as excitation source. We have already shown the optimum ionization pathway for detecting NO molecule with the technique of REMPI spectroscopy[6,7]. It is $\mathrm{NO}(X^2\Pi) \xrightarrow{2h\nu} \mathrm{NO}(A^2\Sigma) \xrightarrow{2h\nu} \mathrm{NO}^+$. Because the energy level of NO is very dense in the high electronic states, so in fact it is a (2+1+1) single color double REMPI (DREMPI) process. This makes the ionization efficiency of this process is much higher than the one of other four-photon process.

Considering that the ionization efficiency of multiphoton process depends on the laser characteristic deeply, we deduce the analytic formula of the ionization efficiency in the process of (2+1+1) DREMPI from the dynamic rate equation about the interaction of photon and material. Based on this formula, the ionization efficiency and the laser power index versus laser intensity in the DREMPI process of NO molecule are simulated. The variations of ionization efficiency and laser power index versus the laser parameters are analyzed.

Under the radiation of high power laser, NO molecule is ionized by absorbing photons via two intermediate resonant states. This process can be shown as a model of four energy levels of Fig. 1. The molecules excited to the first resonant state can be de-excitated by the processes of spontaneous radiation, stimulated radiation, and collision relaxation process. The second resonant 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[6−8]. It is much smaller than the period of collision relaxation process. So the collision process can be neglected also in the excitation process. The rate equation of the variation of the molecule number density during the period of laser pulse and molecule interaction can be shown as

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = -\sigma_1 I^2 n_1 + \sigma_1 I^2 n_2 + k_{\mathrm{F}} n_2, \tag{1}$$

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = \sigma_1 I^2 n_1 - (\sigma_1 I^2 + \sigma_2 I + k_{\mathrm{F}}) n_2, \tag{2}$$

$$\frac{\mathrm{d}n_3}{\mathrm{d}t} = \sigma_2 I n_2 - \sigma_{\mathrm{i}} I n_3, \tag{3}$$

$$\frac{\mathrm{d}n_{\mathrm{i}}}{\mathrm{d}t} = \sigma_{\mathrm{i}} I n_3. \tag{4}$$

The initial condition is $n_1 = n_0$, $n_2 = n_3 = n_{\mathrm{i}} = 0$, where n_1, n_2, n_3, and n_{i} are the number densities of the molecule in the ground, the first, the second resonant, and the ionization state respectively, n_0 is the total molecule number density; σ_1, σ_2 are the absorption transition cross section from the ground state to the first resonant one and from the first resonant state to the second one respectively, σ_{i} is the ionization cross section

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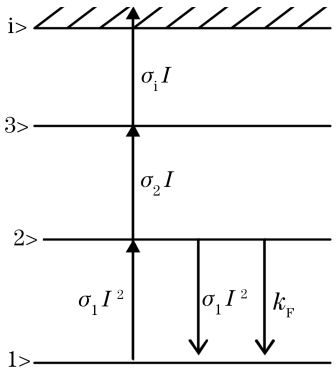

Fig. 1. Dynamic model of DREMPI process.

from the second resonant state; I is the laser intensity; $k_{\rm F}$ is the rate coefficient of the spontaneous radiation.

The Laplace transformations of Eqs. (1)—(4) are

$$sF_1 - n_0 = -\sigma_1 I^2 F_1 + (\sigma_1 I^2 + k_{\rm F})F_2, \tag{5}$$

$$sF_2 = \sigma_1 I^2 F_1 - (\sigma_1 I^2 + \sigma_2 I + k_{\rm F})F_2, \tag{6}$$

$$sF_3 = \sigma_2 I F_2 - \sigma_{\rm i} I F_3, \tag{7}$$

$$sF_{\rm i} = \sigma_{\rm i} I F_3. \tag{8}$$

Solving Eqs. (5)—(8), we can obtain

$$F_{\rm i} = \frac{\sigma_1\sigma_2\sigma_{\rm i} I^4 n_0}{s(s+\sigma_{\rm i} I)(s^2+Ps+Q)}, \tag{9}$$

where $P = 2\sigma_1 I^2 + \sigma_2 I + k_{\rm F}$, $Q = \sigma_1\sigma_2 I^3$.

The Laplace inverse transformation of Eq. (9) is

$$n_{\rm i} = \frac{\sigma_1\sigma_2\sigma_{\rm i} I^4 n_0}{(a_2-a_1)(\sigma_{\rm i} I - a_1)(\sigma_{\rm i} I - a_2)} \times \left[(\sigma_{\rm i} I - a_2)\frac{1-{\rm e}^{-a_1 t}}{a_1} - (\sigma_{\rm i} I - a_1)\frac{1-{\rm e}^{-a_2 t}}{a_2} + (a_2 - a_1)\frac{1-{\rm e}^{-\sigma_{\rm i} I t}}{\sigma_{\rm i} I}\right], \tag{10}$$

where $a_1 = \frac{P-\sqrt{P^2-4Q}}{2}$, $a_2 = \frac{P+\sqrt{P^2-4Q}}{2}$.

Equation (10) is the variation of the ionization molecule versus the laser intensity and pulse duration during the period of laser radiation. Supposing the laser pulse is a square wave with duration of τ. Then the number density of the total ionization molecules is

$$n_{\rm i}(\tau) = \frac{\sigma_1\sigma_2\sigma_{\rm i} I^4 n_0}{(a_2-a_1)(\sigma_{\rm i} I - a_1)(\sigma_{\rm i} I - a_2)} \times \left[(\sigma_{\rm i} I - a_2)\frac{1-{\rm e}^{-a_1 \tau}}{a_1} - (\sigma_{\rm i} I - a_1)\frac{1-{\rm e}^{-a_2 \tau}}{a_2} + (a_2 - a_1)\frac{1-{\rm e}^{-\sigma_{\rm i} I \tau}}{\sigma_{\rm i} I}\right]. \tag{11}$$

The ionization efficiency is

$$\eta = \frac{n_{\rm i}(\tau)}{n_0}. \tag{12}$$

From Eq. (11), the efficiency of double resonance ionization is determined mainly by the laser intensity, the pulse duration, and the molecular constants. Because all of σ_1, σ_2, $\sigma_{\rm i}$, and $k_{\rm F}$ are constants to a certain molecule. So the ionization efficiency lies on the laser characteristics.

It is known that NO molecule can be ionized via $A^2\Sigma$, $S^2\Sigma$ intermediate states by absorbing photons with wavelengths of 429.2 and 452.5 nm when using visible light as excitation source[6,7]. The ionization pathway is

$$\mathrm{NO}(X^2\Pi) \xrightarrow{2h\nu} \mathrm{NO}(A^2\Sigma) \xrightarrow{h\nu} \mathrm{NO}(S^2\Sigma) \xrightarrow{h\nu} \mathrm{NO}^+.$$

To this ionization pathway, $\sigma_1 = 5\times10^{-51}$ cm^{4}s, $\sigma_{\rm i} = 1.7\times10^{-18}$ cm^2, and $k_{\rm F} = 10^7$ s^{-1}[9]. Set $\sigma_2 = 2\times10^{-20}$ cm^2. The ionization efficiency of NO single-color (2+1+1) DREMPI versus the laser intensity and pulse duration can be simulated based on Eq. (11). It is shown in Fig. 2(a).

Firstly, the results show that although the energy of the excitation photon satisfies the resonant condition, but only when the laser intensity is large enough, one can observe ion signal. Assuming that the ion signal can be observed when the ionization efficiency is larger than 2×10^{-6}, it demands the laser intensity at least being 2.2×10^{29}, 4×10^{28}, and 2×10^{28} photon·cm^{-2}·s^{-1} with pulse duration of 3.5, 35, and 100 ps. Secondly, under the condition of certain pulse duration, the ionization efficiency increases with the increase of laser intensity, and gets saturation at last. This is owing to that the ionized molecule in unit time increases with the laser intensity increasing. A saturation phenomenon appears when the molecules are ionized fully. As to the pulse duration

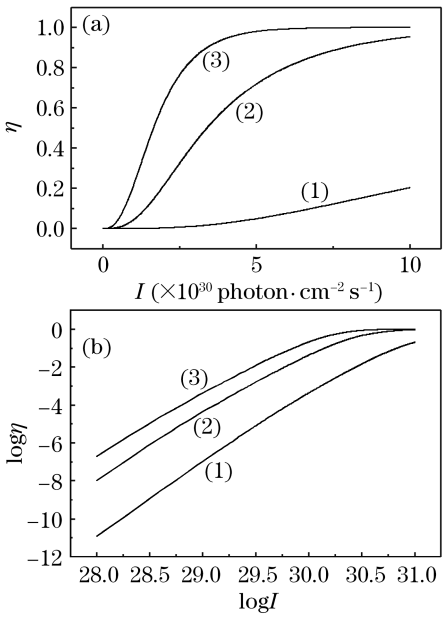

Fig. 2. (a) Ionization efficiency η versus laser intensity I of NO (2+1+1) process with different pulse durations; (b) log-log curve of ionization efficiency η versus laser intensity I. (1) $\tau = 3.5$ ps; (2) $\tau = 35$ ps; (3) $\tau = 100$ ps.

of 3.5, 35, and 100 ps, the laser intensity for saturation is 3.5×10^{32}, 3.6×10^{31}, and 8.0×10^{30} photon·cm^{-2}·s^{-1}, respectively. This indicates that the narrower the laser pulse duration is, the larger becomes the laser intensity for saturation. Thirdly, with a certain laser intensity, the longer the pulse duration is, the higher the ionization efficiency before the phenomenon of saturation appeares. This can be ascribed to the increase of the period of photon-molecule interaction.

Laser power index n is an important parameter for describing the dynamics of multi-photon ionization. It is the slope of the log-log curve of the ion signal versus the laser intensity. Because the saturation effect in multiphoton process will induce the decrease of laser power index, so the index can indicate the characteristic of multiphoton process. The variation of laser power index versus the laser intensity in the process of NO single-color DREMPI can be obtained from Fig. 2(b). It is shown in Fig. 3. Curves (1), (2), and (3) correspond to the pulse duration 3.5, 35, and 100 ps, respectively. The index in the left to point A of curve (1) is 4. This indicates that there is not saturation effect in the three-excitation steps. The fact that the index is 3 at point B indicates that saturation phenomena appear. The region between point A and B is transitional one. The variation of laser intensity in this region is near 10^2. So the saturation must appears in a single-photon transition process[10,11]. We can conclude that the ionization of $S^2\Sigma \rightarrow NO^+$ gets saturation at first by comparing the absorption cross section of each transition.

As to the pulse durations of 35 and 100 ps, curves (2) and (3) show that when the laser intensity is 1×10^{28} photon·cm^{-2}·s^{-1}, the ionization process is already saturation in the last step. The index at point D is 2, which indicates that there are two transition steps getting to saturation. The index is zero in the right to point E, which shows that all the three transition steps reach saturation already. The index in the transitional region of DE becomes from 2 to 0. The variation of corresponding laser intensity is near one magnitude. This shows that the last saturation step is the two-photon process of $X^2\Pi \rightarrow A^2\Sigma$ transition. The index in the transitional region of CD becomes from 3 to 2. The saturation process ought to be the single-photon process of $A^2\Sigma \rightarrow S^2\Sigma$ transition. The unusual phenomena that the variation of corresponding laser intensity is near one magnitude (usually, the variation of the laser intensity corresponding to the saturation transitional region of the single-photon process is near two magnitude[11]) is due to the influence

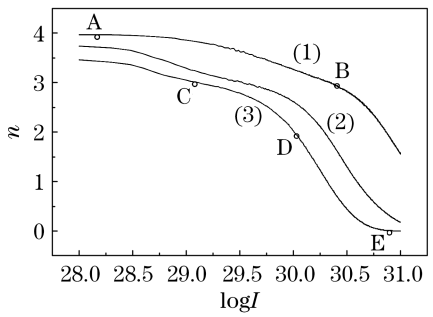

Fig. 3. Variation of laser power index n versus $\log I$. (1) $\tau = 3.5$ ps; (2) $\tau = 35$ ps; (3) $\tau = 100$ ps.

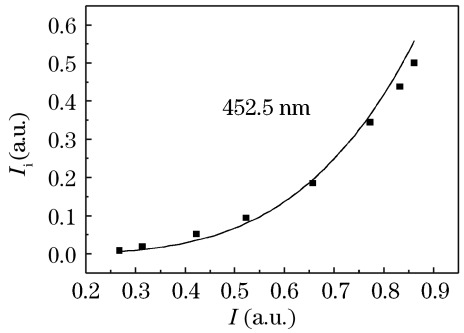

Fig. 4. Variation of ion signal intensity I_i versus laser intensity I.

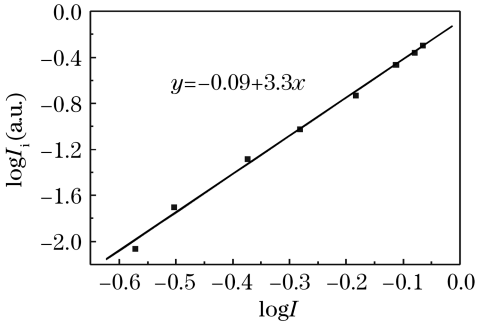

Fig. 5. Log-log curve of ion signal intensity I_i versus laser intensity I.

of $\sigma_1 I^2$.

That presented in Fig. 4 is the experimental result of the ion signal versus the laser intensity under the condition of 266 Pa sample pressure and with the laser of 452.5 nm wavelength as radiation source[6,7]. The laser pulse duration is 35 ps. Figure 5 shows the log-log curve of Fig. 4. It is a straight line with slope of 3.3. The result indicates that when the laser intensity is in the region of $0.5 \times 10^{29} - 3.0 \times 10^{29}$ photon·cm^{-2}·s^{-1}, the ionization process of NO is from instauration of all three steps to saturation of the last one. It is consistent with the result of simulation. The laser power index decreases with the increase of the laser intensity, which was also reported in single REMPI process[12]. So with the help of laser power index, we can analyze the mechanism of multi-photon ionization.

In summary, the ionization efficiency versus laser intensity and pulse duration in the process of NO (2+1+1) DREMPI is simulated. It is found that when NO molecule is ionized with certain pulse duration laser, the ionization efficiency increases with the laser intensity and gets saturation at last. The laser power index decreases with the increase of the laser intensity and becomes to zero at last. In view of that the improvement of the detection limit is based on the saturation excitation and ionization of the system when using REMPI technique detect trace element, we wish that the results can provide a useful reference for selecting optimum laser parameters when use REMPI technique detect NO molecule.

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