

# Suppression effect in the nonsequential double ionization of molecules by an intense laser field

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The  $S$ -matrix theory is developed to study the nonsequential double ionization (NSDI) of diatomic molecules  $N_2$  and  $O_2$  in an intense field. It is shown that electronic structures influence the NSDI process of molecules. Compared to  $N_2$ , a suppression effect of NSDI of molecule  $O_2$  is found and it can be explained by the difference between the angular distributions of the first ionized photoelectrons of  $N_2$  and  $O_2$ . The ratios of the NSDI rate to the single-ionization rate are also obtained and compared with experimental observations.

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## I. INTRODUCTION

Since it was discovered in 1983 [1], nonsequential double ionization (NSDI) has attracted continuous interest over the past two decades [2–14]. The rescattering picture that was established to correctly describe atomic NSDI was also applied to explain the molecular NSDI process [15–25]. However, the latter one, possessing more degrees-of-freedom, exhibits a more complicated ionization dynamic. Theoretical studies were first conducted with the simplest diatomic molecule  $H_2(D_2)$  [22,24,26–28]. Very recently, a semiclassical theory has been developed to investigate the NSDI of  $N_2$  and gives results that are consistent with experimental observations [29,30]. For the  $O_2$  molecule, however, the theory gives results which differ significantly from the experimental ones [31]. In an attempt to resolve this problem, in this paper we present a developed  $S$ -matrix theory for the NSDI of molecules and apply it to study the NSDI of  $N_2$  and  $O_2$ .

The  $S$ -matrix theory has gained great success when applied to explain the atomic NSDI process [5,12]. From the semiclassical point of view, it gives the same “rescattering” picture of atomic NSDI as the semiclassical model. Moreover, it has also succeeded in a description of the single ionization of molecules—e.g., an explanation of the abnormal “suppression” effect in a comparative study of  $O_2$  versus Xe and  $N_2$  versus Ar [32], where  $N_2$  and  $O_2$  are also the diatomic molecules of interest to the current study of the double-ionization process. Those closely related successful experiences have encouraged us to extend the  $S$ -matrix theory to study molecular NSDI.

The present paper is organized as follows. In Sec. II a quantum-mechanical  $S$ -matrix theory for diatomic molecules is presented from which an analytical formula for the NSDI rate is derived. In Sec. III we apply this theory to the diatomic molecules  $N_2$  and  $O_2$ . We find that there is also a suppression effect of the NSDI rate for the molecule  $O_2$

compared to  $N_2$ , and then we explain this effect by investigating the angle distributions of the first ionized photoelectrons of  $N_2$  and  $O_2$ . The ratios of the NSDI rate to the single-ionization rate are calculated and are also compared with available experiment data. The conclusion is given in Sec. IV.

## II. THEORY

It is well known that single ionization and high harmonic generation of atoms and molecules can be well described within the single-active-electron (SAE) approximation where only the outmost electron is assumed to be active and affected by the external field. It is interesting to note that the interaction between electrons of atoms and molecules is neglected in this picture. However, it will lead in the absence of interelectron interactions to sequential double ionization, which was disproved by experiments [1,3,4]. Therefore one should study the double-ionization process within the two-active-electron (TAE) approximation involving the correlation between the two ionized electrons [33]. In the TAE approximation, the influence of other electrons—e.g., the remaining 14 electrons of the  $O_2$  molecule—is approximately considered by choosing the adequate effective charge of the nuclei in the Hamiltonian [34]. Hence under the TAE approximation, the Schrödinger equation for a homonuclear diatomic molecule system in an intense laser field is given in the dipole approximation and velocity gauge by (atomic units are used through this paper unless specified)

$$i\frac{\partial}{\partial t}\Psi = [H_0 + V_A(t) + V_B]\Psi, \quad (1)$$

where  $H_0$  is the unperturbed Hamiltonian,  $V_A(t)$  is the laser-electrons interaction, and  $V_B$  represents the interaction potential between the two ionized electrons as follows:

$$H_0 = \sum_{j=1,2} \frac{\hat{p}_{nj}^2}{2} + \frac{Z^2}{R} + \sum_{i=1,2} \frac{\hat{p}_i^2}{2} - \sum_{ij} \frac{Z}{R_{ij}},$$

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$$V_A(t) = \sum_{i=1,2} \left( -\hat{p}_i \cdot \mathbf{A}(t) + \frac{A(t)^2}{2} \right),$$

$$V_B = \frac{1}{r_{12}}, \quad (2)$$

where  $\mathbf{A}(t)$  is the vector potential of the external field,  $\hat{p}_{nj}$  and  $\hat{p}_i$  are the canonical momenta of the  $j$ th nucleus and  $i$ th electron of the molecules and  $\frac{Z}{R}$ ,  $\frac{Z}{R_{ij}}$ , and  $\frac{1}{r_{12}}$  represent the long-ranged nucleus-nucleus ( $Z$  is the effective nuclear charge), nucleus-electron, and electron-electron Coulomb interactions, respectively. Here  $R_{ij}$  is the distance between the nuclei and electrons in which  $i=1,2$  refers to the electrons and  $j=1,2$  refers to the nuclei. It is worth pointing out here that the interaction between the nuclei and the external field is neglected in Eq. (2) since in the Born-Oppenheimer approximation (BOA) (adopted in our calculation as to be shown below), in which the motion of the nuclei and electrons is separable, the influence of the external field on the nuclei can be neglected for molecules [35].

We have the solution vectors  $\Psi_A$  and  $\Psi_B$  of the Schrödinger equations

$$\left( i \frac{\partial}{\partial t} - H_0 - V_A(t) \right) \Psi_A = 0, \quad (3)$$

$$\left( i \frac{\partial}{\partial t} - H_0 - V_B \right) \Psi_B = 0. \quad (4)$$

Equation (3) describes a molecular system in an external field in the absence of the electron-electron Coulomb interaction, while Eq. (4) depicts an isolated molecular system considering the interaction between the electrons. The corresponding Green's functions are defined by

$$\left( i \frac{\partial}{\partial t} - H_0 - V_A(t) \right) G_A(t, t') = \delta(t - t'), \quad (5)$$

$$\left( i \frac{\partial}{\partial t} - H_0 - V_B \right) G_B(t, t') = \delta(t - t'). \quad (6)$$

The advanced Green's function solution of Eq. (5) can be explicitly written as

$$G_A^{(-)}(t, t') = i\theta(t' - t) \sum_j |\Psi_{Aj}(t)\rangle \langle \Psi_{Aj}(t')|, \quad (7)$$

where  $\Psi_{Aj}(t)$  is the solution of Eq. (3) with quantum number  $j$ . The solutions of the Schrödinger equation (1) can be written in terms of the Green's functions

$$\Psi^{(-)}(t) = \Psi_A(t) + \int dt' G_A^{(-)}(t, t') V_B(t') \Psi^{(-)}(t'),$$

$$\Psi^{(-)}(t) = \Psi_B(t) + \int dt' G_B^{(-)}(t, t') V_A(t') \Psi^{(-)}(t'). \quad (8)$$

The transition  $S$  matrix to describe the ionization may be expressed as

$$S_{fi} = \lim_{t \rightarrow -\infty} \langle \Psi_f^{(-)}(t) | \Psi_{Bi}(t) \rangle, \quad (9)$$

where the subscripts  $i$  and  $f$  represent initial and final conditions, respectively. According to Eq. (8) we have

$$\Psi_f^{(-)}(t) = \Psi_{Bf}(t) + \int dt' G_B^{(-)}(t, t') V_A(t') \Psi_f^{(-)}(t'),$$

$$\Psi_f^{(-)}(t') = \Psi_{Af}(t') + \int dt'' G_A^{(-)}(t', t'') V_B(t'') \Psi_f^{(-)}(t''). \quad (10)$$

Substituting Eq. (10) into Eq. (9) and using Eq. (7) we have

$$\begin{aligned} S_{fi} &= \lim_{t \rightarrow -\infty} \langle \Psi_{Bf}(t) | \Psi_{Bi}(t) \rangle + \lim_{t \rightarrow -\infty} \int dt' \langle G_B^{(-)}(t, t') V_A(t') \Psi_f^{(-)}(t') | \Psi_{Bi}(t) \rangle \\ &= \delta_{fi} + \lim_{t \rightarrow -\infty} \int dt' \langle \Psi_f^{(-)}(t') | V_A(t') G_B^{(+)}(t', t) \Psi_{Bi}(t) \rangle \\ &= \delta_{fi} - i \int dt' \langle \Psi_{Af}(t') | V_A(t') | \Psi_{Bi}(t') \rangle - \sum_j \int \int dt'' dt' \langle \Psi_f^{(-)}(t'') | V_B(t'') | \Psi_{Aj}(t'') \rangle \langle \Psi_{Aj}(t') | V_A(t') | \Psi_{Bi}(t') \rangle \theta(t'' - t'). \end{aligned}$$

Above, we have considered the infinite-time limit [ $\lim_{t \rightarrow -\infty} \theta(t' - t) = 1$ ] and the properties of the Green's functions [ $G_B^{(+)}(t', t) \Psi_{Bi}(t) = -i\theta(t' - t) \Psi_{Bi}(t')$  and  $G_B^{(-)}(t, t') = G_B^{(+)\dagger}(t', t)$ ]. Finally, we obtain

$$(S - 1)_{fi} = -i \int dt' \langle \Psi_{Af}(t') | V_A(t') | \Psi_{Bi}(t') \rangle - \sum_j \int \int dt'' dt' \langle \Psi_f^{(-)}(t'') | V_B(t'') | \Psi_{Aj}(t'') \rangle \langle \Psi_{Aj}(t') | V_A(t') | \Psi_{Bi}(t') \rangle \theta(t'' - t'). \quad (11)$$

As pointed out in [12], the first term describes the shake-off process and the second term describes the NSDI process.

According to the BOA in which the complete wave function of a molecule can be obtained through the wave functions of the electrons with the nuclei in a fixed configuration and the wave function of the nuclei alone, the initial, intermediate, and final wave functions of the system can be expressed as

$$\Psi_{Bi}(t) = \exp(-iW_{n_1n_2\nu}t)\Phi_{n_1n_2\nu}(R)\psi_{n_2}(\vec{r}_2,R)\psi_{n_1}(\vec{r}_1,R),$$

$$\Psi_{Aj}(t) = \sum_{n'_2\nu'} \exp(-iW_{n'_2\nu'}t)\Phi_{n'_2\nu'}(R)\psi_{n'_2}(\vec{r}_2,R)\phi_A(\vec{r}_1,\vec{p},t),$$

$$\Psi_{Bf}(t) = \exp(-iW_{n''\nu''}t)\Phi_{n''\nu''}(R)\phi(\vec{r}_2,\vec{p}_2,t)\phi(\vec{r}_1,\vec{p}_1,t). \quad (12)$$

Here we assume that the laser field is turned off in the final state.  $W_{n_1n_2\nu}$ ,  $W_{n'_2\nu'}$ , and  $W_{n''\nu''}$  are the binding energies of molecule  $X_2$ , molecular ion  $X_2^+$ , and molecular ion  $X_2^{2+}$ , respectively. The wave functions of the nuclei of molecule  $X_2$ , molecular ion  $X_2^+$ , and molecular ion  $X_2^{2+}$  are described by  $\Phi_{n_1n_2\nu}(R)$ ,  $\Phi_{n'_2\nu'}(R)$ , and  $\Phi_{n''\nu''}(R)$ , respectively.  $\nu$ ,  $\nu'$ , and  $\nu''$  are quantum numbers of the vibration states of the corresponding systems, respectively. In the initial state  $\Psi_{Bi}$ , both electrons are in the ground state of the molecule and are denoted by  $\psi_{n_1}(\vec{r}_1,R)$  and  $\psi_{n_2}(\vec{r}_2,R)$ . In the intermediate

state, one electron has been ionized by the external field to the virtual Volkov state

$$\phi_A(\vec{r},\vec{p},t) = \phi(\vec{r},\vec{p})\exp\left(-i\frac{p^2}{2}t - i\int^t V_A(\vec{p},\tau)d\tau\right), \quad (13)$$

where  $V_A(\vec{p},t) = -\vec{p}\cdot\mathbf{A}(t) + \frac{A(t)^2}{2}$  and another electron is in the bound state  $\psi_{n'_2}(\vec{r}_2,R)$  of the residual molecular ion  $X_2^+$ . In the final state, both electrons are ionized to the continuum state. As mentioned above, the laser field is turned off in the final state. So the wave functions of the electrons are free plane waves:

$$\phi(\vec{r},\vec{p},t) = \phi(\vec{r},\vec{p})\exp\left(-i\frac{p^2}{2}t\right). \quad (14)$$

Here  $\phi(\vec{r},\vec{p}) = \exp(i\vec{p}\cdot\vec{r})/V^{1/2}$ , where  $V$  is the normalization volume. Moreover, it should be noted that the interaction between the molecular core and the free electrons is neglected in our calculation as shown in Eqs. (13) and (14).

In this paper we consider a linearly polarized laser field with vector potential

$$\mathbf{A}(t) = A_0\vec{\epsilon}\cos(\omega t), \quad (15)$$

where  $A_0$  is the amplitude,  $\vec{\epsilon}$  is the unit polarization vector, and  $\omega$  is the frequency of the field. After performing the integration over time, one obtains the transition matrix from the second term of Eq. (11) to describe the NSDI process with absorption of  $N$  photons:

$$M^{(N)} = 2\pi i \frac{V}{(2\pi)^3} \int d\vec{p} \sum_m \langle \phi(\vec{r}_2,\vec{p}_2)\phi(\vec{r}_1,\vec{p}_1) | V_B | \psi_{n'_2}(\vec{r}_2,R)\phi(\vec{r}_1,\vec{p}) \rangle \langle \psi_{n'_2}(\vec{r}_2,R)\phi(\vec{r}_1,\vec{p}) | \psi_{n_2}(\vec{r}_2,R)\psi_{n_1}(\vec{r}_1,R) \rangle \frac{J_{m-N}(\vec{\alpha}\cdot\vec{p},\eta)J_m(\vec{\alpha}\cdot\vec{p},\eta)}{\frac{p^2}{2} + U_p + W_{n'_2\nu'} - W_{n_1n_2\nu} - m\omega} \left( W_{n_1n_2\nu} - W_{n'_2\nu'} - \frac{p^2}{2} \right) \delta\left(\frac{p_1^2}{2} + \frac{p_2^2}{2} + W_{n''\nu''} - W_{n_1n_2\nu} - N\omega\right), \quad (16)$$

where the sum over the quantum number  $j$  in Eq. (11) is replaced by the integration over the momentum  $\vec{p}$ . Here  $J_m(\vec{\alpha}\cdot\vec{p},\eta)$  and  $J_{m-N}(\vec{\alpha}\cdot\vec{p},\eta)$  are generalized Bessel functions of two arguments  $\eta = U_p/2\omega$  and  $\vec{\alpha} = \frac{A_0}{\omega}\vec{\epsilon}$ , where  $U_p$  is the pondermotive energy and  $\alpha$  is the quiver radius of the electron along the polarization axis of the laser field. There is an approximation adopted in obtaining Eq. (16): the equilibrium internuclear distances of the neutral molecule and the molecular ion are very close to each other or the mass of the nucleus is very heavy so that  $R$  does not change during the whole process. Therefore the wave functions  $\Phi(R)$  of the nuclei can be integrated and no longer appear in Eq. (16). In other words, this is equivalent to the conjecture that the nuclei are fixed during the whole process, which can be called a ‘‘freezing nuclei’’ approximation. It should be noted that according to this approximation, the above formula (16) is

suitable for calculating the process of heavy molecules such as nitrogen and oxygen, but is not applicable to light molecules such as hydrogen, which has a light nucleus that will move notably during the process. In addition, it is worth noting that we assume that the second electron is in a unique bound state (ground state) in the intermediate state, and therefore the sum over the quantum number  $n'_2$  is neglected as has been done in the atomic treatment [5].

The total rate of nonsequential double ionization is

$$W = \frac{V^2}{(2\pi)^6} \int \int d\vec{p}_1 d\vec{p}_2 w, \quad (17)$$

where the differential double-ionization rate is

$$w = \lim_{t \rightarrow \infty} \frac{1}{t} |(S-1)_{fi}|^2 = 2\pi \sum_{N=N_0} \delta\left(\frac{p_1^2}{2} + \frac{p_2^2}{2} + I_{p1} + I_{p2} - N\omega\right) |T^{(N)}(\vec{p}_1, \vec{p}_2)|^2. \quad (18)$$

Here

$$T^{(N)}(p_1, p_2) = \frac{V}{(2\pi)^3} \int d\vec{p} \sum_m \langle \phi(\vec{r}_2, \vec{p}_2) \phi(\vec{r}_1, \vec{p}_1) | V_B | \psi_{n_2'}(\vec{r}_2, R) \phi(\vec{r}_1, \vec{p}) \rangle \\ \times \langle \psi_{n_2'}(\vec{r}_2, R) \phi(\vec{r}_1, \vec{p}) | \psi_{n_2}(\vec{r}_2, R) \psi_{n_1}(\vec{r}_1, R) \rangle \frac{J_{m-N}(\vec{\alpha} \cdot \vec{p}, \eta) J_m(\vec{\alpha} \cdot \vec{p}, \eta)}{\frac{p^2}{2} + U_p + I_{p1} - m\omega} \left(-\frac{p^2}{2} - I_{p1}\right), \quad (19)$$

where  $I_{p1} = W_{n_2'v'} - W_{n_1n_2v}$  and  $I_{p2} = W_{n''v''} - W_{n_2'v'}$  are the ionization potentials of the first and second electrons, respectively.

It is worth emphasizing here that, under the ‘‘freezing nuclei’’ approximation, the developed theory is not only applicable to all kinds of homonuclear diatomic molecules except light molecules [such as H<sub>2</sub> with quite different equilibrium internuclear distances for the molecule (1.4 a.u.) and the molecular ion (2.0 a.u.)], but also to heteronuclear molecules with consideration of the different terms corresponding to the nuclei in Eq. (2). Moreover, Eq. (19) is also available for heteronuclear molecules if the wave functions of two active electrons can be constructed in some way since only the electron states appear in Eq. (19).

### III. RESULT AND DISCUSSION

In this paper, we at first restricted our application of the theory to a study of the NSDI process of diatomic molecules N<sub>2</sub> and O<sub>2</sub>. It is known that N<sub>2</sub> and Ar have similar first and second ionization potentials (N<sub>2</sub>, 15.58 and 27.18 eV; Ar, 15.76 and 27.63 eV) and O<sub>2</sub> has lower ionization potentials (O<sub>2</sub>, 12.07 and 24.14 eV). In addition, the electronic structures of N<sub>2</sub> (N<sub>2</sub><sup>+</sup>) and O<sub>2</sub> (O<sub>2</sub><sup>+</sup>) are quite different. N<sub>2</sub> and N<sub>2</sub><sup>+</sup> have bonding 3σ<sub>g</sub> and bonding 1π<sub>u</sub> outmost orbits, and the outmost orbits of O<sub>2</sub> and O<sub>2</sub><sup>+</sup> are both antibonding 1π<sub>g</sub> orbits. In order to investigate how the molecular structure influences the NSDI rate, we adopt a model molecule which has the electronic structure of O<sub>2</sub>, but first and second ionization potentials equal to those of N<sub>2</sub> (it is still denoted as O<sub>2</sub> for simplicity in the following). Moreover, in our calculation, the wave functions of the ground states of N<sub>2</sub> and O<sub>2</sub> and their ions are constructed using the linear combination of atomic orbital and molecular orbital (LCAO-MO) approximation [36,37] for simplicity instead of using more accurate wave functions as in the atomic case [5]. The wave function of the *n*th molecular valence shell can be approximately regarded as a SAE two-centered MO, which is chosen as a linear superposition of predominantly contributing (*j*th) one-centered one-electron atomic orbitals. In the wave function of the ground state of molecule N<sub>2</sub> of Eq. (19), the first ionized electron has a predominantly contributing bonding 3σ<sub>g</sub> orbital, while O<sub>2</sub> has an antibonding 1π<sub>g</sub> orbit, which can be represented as

$$\psi_{n_1}(\vec{r}_1, R) = \frac{1}{\sqrt{2[1 - s_j^{(n_1)}(R)]}} \left[ \phi_j\left(\vec{r}_1 + \frac{\vec{R}}{2}\right) - \phi_j\left(\vec{r}_1 - \frac{\vec{R}}{2}\right) \right], \quad (20)$$

where

$$s_j^{(n_1)}(R) = \int d\vec{r}_1 \phi_j\left(\vec{r}_1 + \frac{\vec{R}}{2}\right) \phi_j\left(\vec{r}_1 - \frac{\vec{R}}{2}\right) \quad (21)$$

is the corresponding atomic orbital overlap integral. For molecule N<sub>2</sub>,

$$\phi_j\left(\vec{r}_1 + \frac{\vec{R}}{2}\right) = \phi_{2pz}(\vec{r}_{a1}) = (k_2)^{5/2} \frac{r_{a1}}{\sqrt{\pi}} \exp(-k_2 r_{a1}) \cos(\theta_R), \quad (22)$$

and for molecule O<sub>2</sub>,

$$\phi_j\left(\vec{r}_1 + \frac{\vec{R}}{2}\right) = \phi_{2px}(\vec{r}_{a1}) \\ = (k_2)^{5/2} \frac{r_{a1}}{\sqrt{\pi}} \exp(-k_2 r_{a1}) \sin(\theta_R) \cos(\varphi_R). \quad (23)$$

Here  $r_{a1}$  is the distance between one of the nuclei and the first ionized electron, and  $\theta_R$  and  $\varphi_R$  are the polar and azimuthal angles with respect to the polar axis, which is supposed to be coincident with the internuclear axis, and  $k_2^2/2 = I_{p1}$ , which is the ionization potential of the first ionized electron (here for N<sub>2</sub> and O<sub>2</sub> we choose both ionization potentials of molecule N<sub>2</sub> as stated before). In addition,  $R$  is also chosen to be the equilibrium internuclear distance of molecule N<sub>2</sub> ( $R=2.079$  a.u.) for both N<sub>2</sub> and O<sub>2</sub>. For the ground state of molecule N<sub>2</sub> of Eq. (19), the second ionized electron has a dominating bonding 1π<sub>u</sub> orbital because the ionization potential of this orbital is the lowest one and O<sub>2</sub> has an antibonding 1π<sub>g</sub> orbit, which can be explicitly written as

$$\psi_{n_2}(\vec{r}_2, R) = \frac{1}{\sqrt{2[1 \pm s_l^{(n_2)}(R)]}} \left[ \phi_l\left(\vec{r}_2 + \frac{\vec{R}}{2}\right) \pm \phi_l\left(\vec{r}_2 - \frac{\vec{R}}{2}\right) \right], \quad (24)$$

where  $s_l^{(n_2)}(R)$  is the atomic orbital overlap integral, “+” for molecule  $N_2$  and “-” for  $O_2$ , and

$$\begin{aligned} \phi_l\left(\vec{r}_2 + \frac{\vec{R}}{2}\right) &= \phi_{2p_x}(\vec{r}_{a2}) \\ &= (k_2')^{5/2} \frac{r_{a2}}{\sqrt{\pi}} \exp(-k_2' r_{a2}) \sin(\theta_R) \cos(\varphi_R). \end{aligned} \quad (25)$$

Here  $r_{a2}$  is the distance between one of the nuclei and the second ionized electron. For molecule  $N_2$ ,  $k_2'^2/2 = I_{p1}^{(1\pi_u)} = 17.07$  eV, which is the ionization potential of the bonding  $1\pi_u$  orbital of the ground state of molecule  $N_2$ , while for molecule  $O_2$ ,  $k_2'^2/2 = I_{p1}^{(1\pi_g)}$ , which is the ionization potential of the antibonding  $1\pi_g$  orbital of the ground state of molecule  $O_2$ —i.e.,  $I_{p1}^{(1\pi_g)} = I_{p1}$  and  $k_2' = k_2$ . The wave functions of the ground states of molecular ions  $N_2^+$  and  $O_2^+$  are

$$\psi_{n_2'}(\vec{r}_2, R) = \frac{1}{\sqrt{2(1 \pm s_m^{(n_2')}(R))}} \left[ \phi_m\left(\vec{r}_2 + \frac{\vec{R}}{2}\right) \pm \phi_m\left(\vec{r}_2 - \frac{\vec{R}}{2}\right) \right], \quad (26)$$

where “+” for molecular ion  $N_2^+$  and “-” for  $O_2^+$  and

$$\begin{aligned} \phi_m\left(\vec{r}_2 + \frac{\vec{R}}{2}\right) &= \phi_{2p_x}(\vec{r}_{a2}) \\ &= (k_2'')^{5/2} \frac{r_{a2}}{\sqrt{\pi}} \exp(-k_2'' r_{a2}) \sin(\theta_R) \cos(\varphi_R). \end{aligned} \quad (27)$$

and  $k_2''^2/2 = I_{p2}$ , which is the ionization potential of the second ionized electron. Moreover, as stated above, the internuclear distances of the molecular ions are kept the same as those of the molecules.

Assuming that the direction of the polarization of the laser field is parallel to the internuclear axis, we calculate the NSDI rate of molecules  $N_2$  and  $O_2$  using Eq. (17). The results are shown in Fig. 1 together with the NSDI rate of Ar. In Fig. 1(a) and 1(b), the  $\delta$  potential and Coulomb potential between the electrons are adopted, respectively. From Fig. 1 it is easy to find that the NSDI rate of  $O_2$  is lower than that of  $N_2$ , which is much more close to that of Ar, overall, especially in the low-intensity regime considered. Similar to the single ionization of molecules, this can be called a suppression effect in the NSDI of  $O_2$  comparing to  $N_2$ , which shows no obvious suppression compared with its companion atom Ar.

As mentioned above, that the ionization potentials have been set to be the same for  $N_2$  and  $O_2$ , this suppression effect should be mainly due to the difference of the electronic structures of  $N_2$  and  $O_2$ . In the following we study the angular distributions of the first ionized photoelectrons of  $N_2$  and

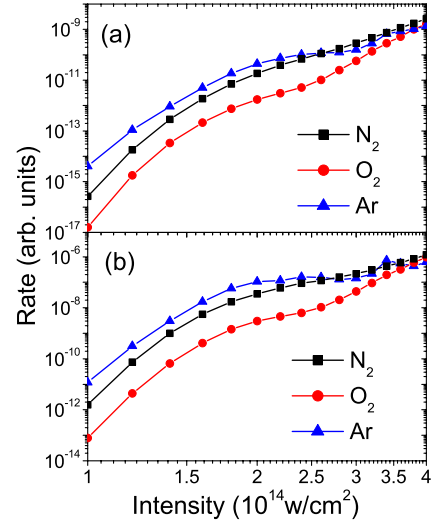


FIG. 1. (Color online) The NSDI rates of  $N_2$  (square),  $O_2$  (circle), and Ar (triangle) as a function of the field intensity.  $\lambda = 800$  nm. The interactions between the electrons are the (a)  $\delta$  potential and (b) Coulomb potential.

$O_2$  with the direction of the polarization of the laser being parallel to the internuclear axis. Here we adopt the Kelysh-Faisal-Reiss (KFR) theory in our calculation [32]. Figure 2 shows the angular distributions of the photoelectrons in the single-ionization process of  $N_2$  and  $O_2$ . It is obvious that the angular distribution of  $N_2$  has a maximum along the polarization direction of the field and decreases rapidly with increasing angle, which is very similar to the atoms. In contrast, a minimum appears along the direction of the field and the distribution reaches the maximum at about  $25^\circ$  for  $O_2$ . For  $N_2$  most of the photoelectrons are ejected along the direction of the field after being ionized. After the direction of the field is changed, it will have a large probability to be driven back to the core to recollide with it. However, the case

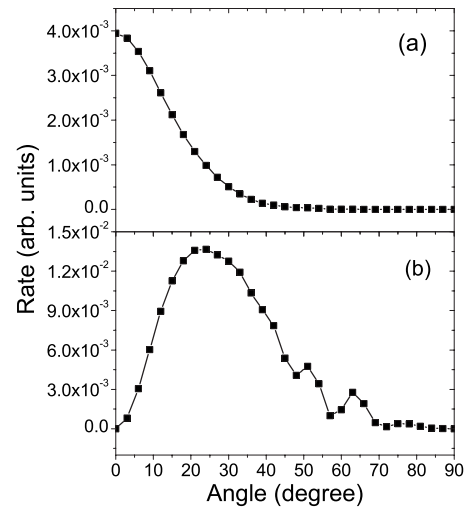


FIG. 2. Angular distributions of the first ionized photoelectrons from (a)  $N_2$  and (b)  $O_2$  with a laser intensity of  $2 \times 10^{14}$  W/cm<sup>2</sup> and  $\lambda = 800$  nm. The direction of the polarization of the laser field is parallel to the internuclear axis.

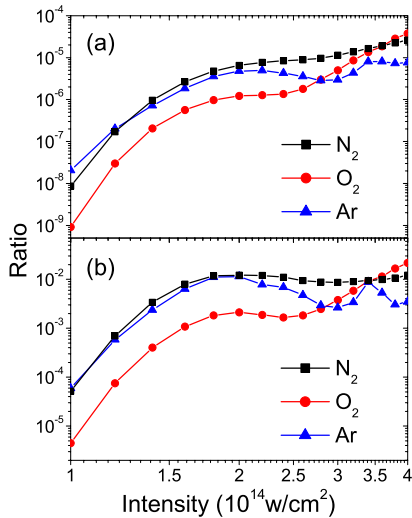


FIG. 3. (Color online) Ratios of nonsequential double-ionization rate to single-ionization rate for  $N_2$  (square),  $O_2$  (circle), and Ar (triangle). The interactions between the electrons are the (a)  $\delta$  potential and (b) Coulomb potential.

is quite different for  $O_2$ . The photoelectron tends to be ejected away from the direction of the field, which means that it has a relatively much larger transverse velocity and will have less probability to recollide with the core when the direction of the field is changed compared with that of  $N_2$ . Consequently, molecular ion  $O_2^+$  will have a lower probability to be ionized by the returned electron, which leads to a suppression effect of the NSDI rate of  $O_2$ . This abnormal angular distribution, which is due to the characteristic of the initial molecular orbital, has been used to explain the mechanism of the unusual dependence of the NSDI and fragmentation of  $C_6H_6$  on the ellipticity of the laser polarization [18]. Furthermore, to get rid of the influence of the single ionization on the NSDI process, the NSDI rate to single-ionization rate ratios of  $O_2^{2+}:O_2^+$ ,  $N_2^{2+}:N_2^+$ , and  $Ar^{2+}:Ar^+$  as a function of the laser intensity are plotted in Fig. 3 considering the  $\delta$  potential [Fig. 3(a)] and Coulomb potential [Fig. 3(b)] between electrons, respectively. Figure 3 clearly shows that

molecule  $N_2$ , showing no suppression in its double-ionization process as in its single-ionization process, behaves very similarly to Ar. Nevertheless, the ratio of  $O_2$  is obvious lower than that of  $N_2$  and shows an obvious suppression effect. It is worth pointing out that our calculation (Fig. 3) is qualitatively consistent with the experimental observation in which the NSDI of  $N_2$  represents no suppression when compared with Ar, while  $O_2$  shows a dramatic suppression (its ratio is even lower than that of  $N_2$  despite their large ionization potential difference) when it is compared with its companion atom Xe ( $I_{p1}=12.13$  eV and  $I_{p2}=21.21$  eV) [15].

#### IV. CONCLUSIONS

In summary, we have developed an  $S$ -matrix theory to study the nonsequential double ionization of molecules in an intense laser field. The NSDI of diatomic molecules  $N_2$  and  $O_2$  is investigated using the theory presented. It is found that, similar to the single-ionization process,  $N_2$  behaves closely to its companion atom Ar in the double-ionization process, but  $O_2$  shows an obvious suppression effect in NSDI. By investigating the angular distributions of the first ionized photoelectrons of  $N_2$  and  $O_2$ , we find that this difference is due to the fact that the first photoelectron of  $N_2$  is ejected mainly along the direction of the field, which is similar to the atoms, but the first ionized electron has a relatively larger transverse velocity when it is ejected from  $O_2$ , which will greatly reduce the probability to recollide with the core when the electron is driven back after the field changes its direction. The NSDI rate to single-ionization rate ratios are also obtained and compared with the experiment.

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