Nonsequential double ionization of nonaligned diatomic molecules N_2 and O_2*

Jia Xin-Yan(贾欣燕)[a], Fan Dai-He(樊代和)[a], Li Wei-Dong(李卫东)[b]†, and Chen Jing(陈 京)[c,d]‡

[a] *Quantum Optoelectronics Laboratory, Southwest Jiaotong University, Chengdu* 610031, *China*
[b] *Institute of Theoretical Physics and Department of Physics, Shanxi University, Taiyuan* 030006, *China*
[c] *HEDPS, Center for Applied Physics and Technology, Peking University, Beijing* 100084, *China*
[d] *Institute of Applied Physics and Computational Mathematics, Beijing* 100088, *China*

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Nonsequential double ionization (NSDI) processes of nonaligned diatomic molecules N_2 and O_2 are studied using the *S*-matrix theory. Our results show that the NSDI process significantly depends on the molecular symmetry and structure. The ratio of NSDI rate to single ionization rate as a function of the field intensity is obtained. It is found that N_2 behaves closely with its companion atom Ar in the ratios over the entire intensity range, while O_2 exhibits an obvious suppression effect, which is qualitatively consistent with the experiment.

Keywords: nonsequential double ionization, nonaligned diatomic molecules, *S*-matrix theory, suppression effect

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1. Introduction

Nonsequential double ionization (NSDI) of atoms, as one of the most important multi-electron effects in strong-field physics, has been intensively studied during the last decade.[1–8] Compared with atoms, molecules with higher degrees of freedom exhibit more complex dynamics. In recent years, physics and applications of molecular dynamics in strong laser fields has attracted more and more attention,[9–14] such as tomographic imaging of molecular orbitals,[15] and probing molecular dynamics on an attosecond time scale.[16–19] There is no doubt that the molecular NSDI process has also become an interesting problem worth investigating.[20–30] Rescattering has been commonly accepted to be the dominant mechanism for molecular NSDI:[3] the first active electron is freed by the field, then driven back to its parent ion after the field changes its direction, and finally dislodges the second electron by transferring part of its energy.

Early measurements of ion signals for diatomic molecules in CO_2 lasers indicated that molecules have nearly the same single ionization (SI) signals as its companion atoms.[31–33] More recent studies using Ti:sapphire laser radiation,[20,21] however, have shown that the SI yield of O_2 has an obvious suppression effect compared with that of its companion Xe atom. While for N_2, the SI signal remains comparable to that of its companion Ar atom.[34] Moreover, these studies have been extended to the double ionization and a suppression effect for O_2 in the double ionization process has also been observed experimentally,[20] which indicates that molecular symmetry and structure strongly influence the ionization process of molecules.

In our previous work,[29] it is reported that, when only the parallel aligned N_2 and O_2 are considered, a suppression effect of O_2 in the NSDI process is found. However, the N_2 and O_2 molecules used in the experiment[20] are not aligned. Therefore, in this paper, differently from Ref. [29], we aim to study the NSDI process of nonaligned N_2 and O_2 using the *S*-matrix theory, in which the NSDI rates of N_2 and O_2 are averaged over alignment angles. Our results show that the NSDI rate of nonaligned O_2 is a little lower than that of N_2. On the contrary, Ar has a higher NSDI rate than the nonaligned N_2 and O_2 molecules. This can be interpreted by taking all factors of the NSDI process for N_2 and O_2 at different molecular alignment angles into consideration. The ratios of the NSDI rate to the SI rate are also calculated. We find that N_2 has a similar NSDI/SI ratios to Ar over the entire intensity range, while O_2 shows an obvious suppression effect. These results are qualitatively consistent with the experimental observations.

2. Theory

Strong-field phenomena, such as the NSDI, are successfully described within the strong-field approximation (SFA), which assumes that the electron in the initial state of an atom or molecule is unaffected by the laser field, and the electron in the continuum does not feel the presence of the binding po-

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†Corresponding author. E-mail: wdli@sxu.edu.cn
‡Corresponding author. E-mail: chen_jing@iapcm.ac.cn

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tential. Using the S-matrix theory, one obtains the transition amplitudes of the NSDI process caused by the laser-assisted inelastic rescattering within the two-active-electron (TAE) approximation as[29,30,35]

$$A_{\rm fi} = -{\rm i}\int_{-\infty}^{\infty}{\rm d}t_2\int_{-\infty}^{t_2}{\rm d}t_1\langle\Psi_{\rm Af}(t_2)| \times V_{\rm B}G_0(t_2,t_1)V_{\rm A}(t_1)|\Psi_{\rm Bi}(t_1)\rangle, \quad (1)$$

where $G_0(t_2,t_1) = -{\rm i}\theta(t_2-t_1)\sum_j|\Psi_{{\rm A}j}(t_2)\rangle\langle\Psi_{{\rm A}j}(t_1)|$ represents the intermediate two-electron Green's function, and $V_{\rm A}(t)$ and $V_{\rm B}$ denote the laser–electron interaction in the velocity gauge and the electron–electron interaction, respectively. The wave functions of the initial, intermediate, and final state of the system can be written as

$$\begin{aligned}\Psi_{\rm Bi}(t) &= {\rm e}^{-{\rm i}W_{n_1n_2\upsilon}t}\Phi_{n_1n_2\upsilon}(R)\psi_{n_2}(\boldsymbol{r}_2,\boldsymbol{R})\psi_{n_1}(\boldsymbol{r}_1,\boldsymbol{R}),\\ \Psi_{{\rm A}j}(t) &= {\rm e}^{-{\rm i}W_{n_2'\upsilon'}t}\Phi_{n_2'\upsilon'}(R)\psi_{n_2'}(\boldsymbol{r}_2,\boldsymbol{R})\phi_{\rm A}(\boldsymbol{r}_1,\boldsymbol{p},t),\\ \Psi_{\rm Bf}(t) &= {\rm e}^{-{\rm i}W_{n''\upsilon''}t}\Phi_{n''\upsilon''}(R)\phi(\boldsymbol{r}_2,\boldsymbol{p}_2,t)\phi(\boldsymbol{r}_1,\boldsymbol{p}_1,t),\end{aligned} \quad (2)$$

according to Born–Oppenheimer approximation, where $W_{n_1n_2\upsilon}$, $W_{n_2'\upsilon'}$, and $W_{n''\upsilon''}$ denote the binding energies of X_2, X_2^+, and X_2^{2+}, respectively. Additionally, $\Phi_{n_1n_2\upsilon}(R)$, $\Phi_{n_2'\upsilon'}(R)$, and $\Phi_{n''\upsilon''}(R)$ are the wavefunctions of the corresponding nuclei, with υ, υ', and υ'' being the vibration state's quantum numbers, $n_{1,2}$ and n_2' the electronic quantum numbers. The summation over j in $G_0(t_2,t_1)$ representing all the quantum numbers which define the state, includes the integration over momentum $\boldsymbol{p}$ and summation over n_2' and υ'. The rescattering picture can be read from Eq. (1): both of the two active electrons, denoted by $\psi_{n_1}(\boldsymbol{r}_1,\boldsymbol{R})$ and $\psi_{n_2}(\boldsymbol{r}_2,\boldsymbol{R})$, are initially in the molecular bound states; subsequently one of them is ionized by the external field to the virtual Volkov state, which can be expressed as

$$\phi_{\rm A}(\boldsymbol{r},\boldsymbol{p},t) = \phi(\boldsymbol{r},\boldsymbol{p})\exp\left(-\frac{\rm i}{2}\int^t{\rm d}\tau(\boldsymbol{p}-\boldsymbol{A}(\tau))^2\right), \quad (3)$$

and the other one remains in the bound state of the residual ion $\psi_{n_2'}(\boldsymbol{r}_2,\boldsymbol{R})$; finally, both of them are emitted to the continuum states $\phi(\boldsymbol{r}_1,\boldsymbol{p}_1,t)$ and $\phi(\boldsymbol{r}_2,\boldsymbol{p}_2,t)$ via the electron–electron interaction $V_{\rm B}$. It is noteworthy that the laser field is turned off in the final state, and thus the electrons are free plane waves

$$\phi(\boldsymbol{r},\boldsymbol{p},t) = \phi(\boldsymbol{r},\boldsymbol{p})\exp\left(-{\rm i}\frac{p^2}{2}t\right), \quad (4)$$

where $\phi(\boldsymbol{r},\boldsymbol{p}) = \exp({\rm i}\boldsymbol{p}\cdot\boldsymbol{r})/V^{1/2}$, and V is the normalization volume.

We will consider the case of a linear monochromatic field $\boldsymbol{A}(t) = A_0\boldsymbol{e}_z\cos(\omega t)$ with the ponderomotive energy $U_{\rm p} = \langle\boldsymbol{A}^2(t)\rangle_t/2 = A_0^2/4$, where A_0 is the amplitude, and $\boldsymbol{e}_z$ and ω are the unit polarization vector and the frequency of the field, respectively. The Volkov wavefunction can be expanded using the Jacobi–Anger formula, so that we can perform the two-fold time integrations over t_1 and t_2 exactly. Then we have the total NSDI rate

$$W = \frac{V^2}{(2\pi)^6}\int\int{\rm d}\boldsymbol{p}_1\,{\rm d}\boldsymbol{p}_2 w, \quad (5)$$

with the differential double ionization rate by absorption of N photons

$$w = 2\pi\sum_{N=N_0}|T^{(N)}(\boldsymbol{p}_1,\boldsymbol{p}_2)|^2 \times\delta\left(\frac{p_1^2}{2}+\frac{p_2^2}{2}+I_{\rm p1}+I_{\rm p2}-N\omega\right), \quad (6)$$

where

$$\begin{aligned}&T^{(N)}(\boldsymbol{p}_1,\boldsymbol{p}_2)\\ &= \frac{V}{(2\pi)^3}\sum_{m=m_0}\sum_{n_2'}\int{\rm d}\boldsymbol{p}\,(U_{\rm p}-m\omega)\\ &\times\langle\phi(\boldsymbol{r}_2,\boldsymbol{p}_2)\phi(\boldsymbol{r}_1,\boldsymbol{p}_1)|V_{\rm B}|\psi_{n_2'}(\boldsymbol{r}_2,\boldsymbol{R})\phi(\boldsymbol{r}_1,\boldsymbol{p})\rangle\\ &\times\langle\psi_{n_2'}(\boldsymbol{r}_2,\boldsymbol{R})\phi(\boldsymbol{r}_1,\boldsymbol{p})|\psi_{n_2}(\boldsymbol{r}_2,\boldsymbol{R})\psi_{n_1}(\boldsymbol{r}_1,\boldsymbol{R})\rangle\\ &\times\frac{J_{m-N}(\boldsymbol{\alpha}\cdot\boldsymbol{p},\eta)J_m(\boldsymbol{\alpha}\cdot\boldsymbol{p},\eta)}{p^2/2+I_{\rm p_1}+U_{\rm p}-m\omega}.\end{aligned} \quad (7)$$

Here, N_0 and m_0 are the minimum numbers of photons needed to be absorbed for the emission of the electrons and the first electron, respectively. The parameters $I_{\rm p_1}$ and $I_{\rm p_2}$ are the ionization potentials of the two ionized electrons. The ${\rm J}_N(a;b)$ is a generalized Bessel function of two arguments: $\eta = U_{\rm p}/2\omega$ and $\boldsymbol{\alpha} = (A_0/\omega)\boldsymbol{e}_z$. Contribution from the ionic ground state of the sum over n_2' is considered, since it is found to dominate over the contribution from any high excited state by some orders of magnitude.[6,7] We adopted "freezing nuclei approximation" to obtain Eq. (7), where the nuclei are fixed during the whole ionization process. Therefore, it is applicable to calculate the ionization process of heavy molecules, such as nitrogen and oxygen.

In this paper, we focus our attention on the NSDI process of nonaligned diatomic molecules N_2 and O_2. The wavefunctions of the ground states for N_2, O_2, and their ions are derived within the linear combination of the atomic orbital and molecular orbital (LCAO-MO) method.[36,37] The wavefunction of the n-th molecular valence shell is approximately considered as a SAE two-centered MO, which is chosen as a linear superposition of predominantly contributing (j-th) one-centered one-electron atomic orbitals

$$\begin{aligned}\psi_n(\boldsymbol{r};\boldsymbol{R}) &= \psi_n(\boldsymbol{r}+\boldsymbol{R}/2;\boldsymbol{r}-\boldsymbol{R}/2)\\ &= \sum_j[\phi_j^{(n)}(\boldsymbol{r}+\boldsymbol{R}/2)\\ &\quad\pm\phi_j^{(n)}(\boldsymbol{r}-\boldsymbol{R}/2)]/\sqrt{2(1\pm S_j^{(n)}(R))},\end{aligned} \quad (8)$$

where

$$S_j^{(n)}(R) = \int{\rm d}\boldsymbol{r}\phi_j^{(n)}(\boldsymbol{r}+\boldsymbol{R}/2)\phi_j^{(n)}(\boldsymbol{r}-\boldsymbol{R}/2) \quad (9)$$

is the respective atomic orbital overlap integral with the internuclear distance $\boldsymbol{R}$. It is well known that the highest occupied molecular orbitals (HOMO) for N_2 and N_2^+ belong to two kinds of orbital symmetries, namely, bonding $3\sigma_g$ and $1\pi_u$, with binding energies of 0.5728 and 0.9993 a.u., respectively. The HOMO for O_2 and O_2^+ are both anti-bonding $1\pi_g$ orbitals, with binding energies of 0.4438 a.u. and 0.8875 a.u. For simplicity, one can approximate the two-centered one-electron molecular wave functions for bonding $3\sigma_g$ or $1\pi_u$ valence shells in N_2 by composing from antisymmetric or symmetric superposition of one-electron hydrogen-like 2pz or 2px orbitals.[29,36] Similarly, for O_2, the two-centered one-electron molecular wave function of the anti-bonding $1\pi_g$ orbital can be composed of antisymmetric superposition of one-electron hydrogen-like 2px orbitals.

3. Results and discussion

In order to investigate how the NSDI process of molecules will be influenced by the molecular symmetry and structure, we adopt a model molecule which has the same electronic structure as O_2, but the ionization potential equal to that of N_2. For simplicity, we still denote it as O_2 in the following. We first calculate the NSDI rates of N_2 and O_2 molecules at each fixed angle β (the angle between the molecular axis and the polarization direction of the field) using Eq. (5), and then average the results over an ensemble of randomly distributed molecules. The results are shown in Fig. 1(a). For comparison, we also plot the NSDI rate of Ar which is the companion atom of N_2. The laser field with a wavelength of $\lambda = 800$ nm and the coulomb screened potential $V_B = e^{-\gamma r_{12}}/r_{12}$ with $\gamma = 0.2$ between the two ionized electrons are adopted throughout. It is shown in Fig. 1(a) that in the low field intensity regime considered ($I < 2.4 \times 10^{14}$ W/cm^2), the NSDI rate of nonaligned O_2 molecules is a little lower than that of N_2, and it is nearly equal to that of N_2 when the intensity increases. However, Ar has a higher NSDI rate than nonaligned N_2 and O_2 molecules. This can be understood by considering the NSDI process of N_2 and O_2 with different angles β. Figures 1(b) and 1(c) show two specific cases of $\beta = 0°$[29] and $\beta = 50°$. Figure 1(b) shows that in parallel alignment ($\beta = 0°$), N_2 behaves closely as its companion atom Ar in NSDI rate, but the NSDI rate of O_2 shows an obvious suppression effect overall, especially in the low intensity regime considered. This can be interpreted by studying the angular distributions of the first ionized photoelectrons for parallel aligned N_2 and O_2:[29] similar to atoms, N_2 has a maximal angular distribution along the direction of the field and decreases rapidly with increasing angle; while for O_2 the distribution is maximal at about 25° and minimal along the direction of the field, as shown in Fig. 2(a).[29] Therefore, the first ionized electron of N_2 is ejected mainly along the direction of the field. However, the first photoelectron of O_2 has a relatively larger transverse velocity when it is ejected from O_2, which will greatly reduce the probability of recollision with the core. Therefore, the NSDI rates for N_2 and O_2 are significantly different. When the angle β increases to 50°, the angular distribution of O_2 reaches its maximum along the direction of the field, which is similar to

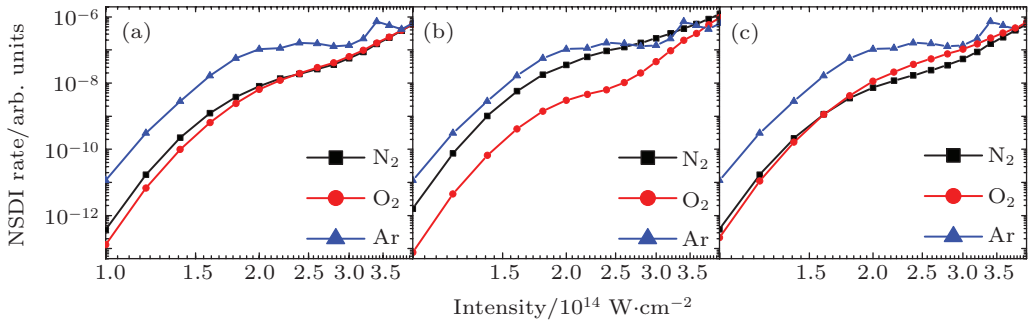


Fig. 1. (color online) NSDI rates of N_2 , O_2 , and Ar as a function of intensity at $\lambda = 800$ nm. The alignment angles of the molecules are (a) averaged, (b) $\beta = 0°$,[29] and (c) $\beta = 50°$.

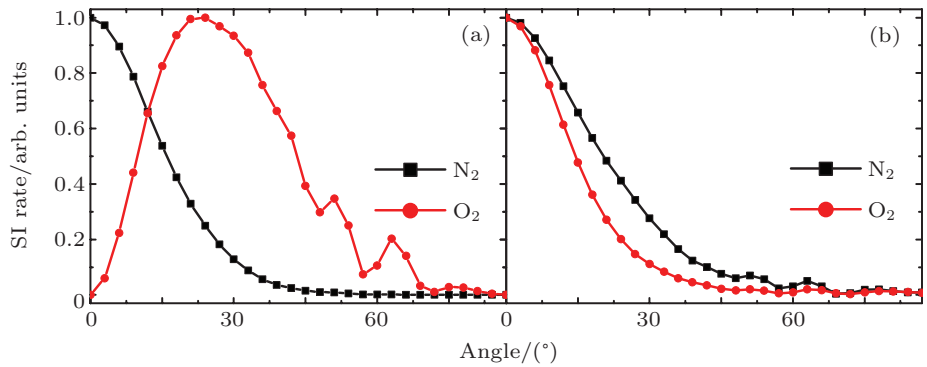


Fig. 2. (color online) Normalized angular distributions of the first ionized electrons from N_2 and O_2 at alignment angles (a) $\beta = 0°$[29] and (b) $\beta = 50°$ at $I = 2 \times 10^{14}$ W/cm^2.

N_2, as shown in Fig. 2(b). Therefore, after the field changes its direction, the photoelectrons have a large probability to be driven back to the core to recollide with it. Thus, the NSDI rate of O_2 at $\beta = 50^\circ$ will be higher than that at $\beta = 0^\circ$ in the whole intensity regime considered. On the other hand, N_2 has a monotonic decreasing SI rate with increasing angle β,[9] which will cause decreasing NSDI rate with increasing β for N_2. With these effects in mind, N_2 and O_2 molecules will have similar NSDI rates after averaging over alignment angle β, and the NSDI rates are apparently lower than that of Ar.

Furthermore, in order to eliminate the influence of the single ionization on the NSDI process, the intensity dependence of ratios of NSDI rate to SI rate for nonaligned molecules N_2 and O_2, together with Ar, are depicted in Fig. 3. It is shown that the ratios of NSDI rate to SI rate for N_2 and Ar are quite similar over the entire intensity range, while the ratios for O_2 are much lower, which means that, after excluding the influence of the single ionization probability, a nonaligned N_2 molecule behaves similarly to Ar and a nonaligned O_2 molecule shows an obvious suppression effect in the NSDI process. Compared with the parallel aligned O_2,[29] the suppression effect of the nonaligned O_2 in the NSDI process still exists, but is weakened. Our results are in qualitative agreement with the experimental observations.[20] Here, it is worth noting that in our calculations above, only the contribution from the outmost valence orbitals in a molecule and ion is involved. According to Ref. [30], the inner valence orbitals in a molecular ion also play an important role in the NSDI process of N_2 since their contribution to the NSDI yield exceeds that from the outmost orbital when the alignment angle is small. Similarly, it is easy to find that for O_2, when the molecular alignment angle is close to $\pi/2$, the contribution from the inner orbitals in a molecular ion can also exceed that from the outmost orbital. However, this effect will not affect the main conclusions of this paper since, according to our calculation, we find that it will increase the NSDI yield of N_2 more obviously than O_2. More details will be given elsewhere.

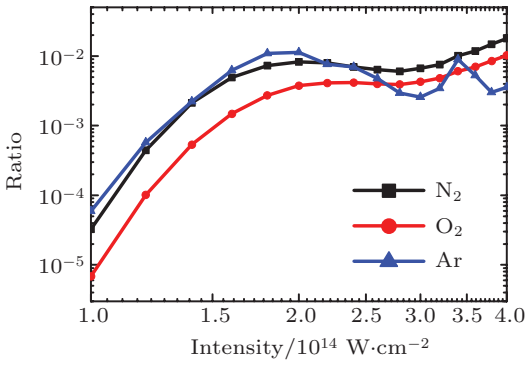


Fig. 3. (colour online) Ratios of NSDI rate to single ionization rate for nonaligned N_2, O_2, and Ar as a function of the field intensity.

4. Conclusions

In summary, the *S*-matrix theory is extended to the molecular case to study the nonsequential double ionization process of nonaligned diatomic molecules N_2 and O_2 in intense laser fields. The results show that the NSDI rate of a nonaligned O_2 molecule is a little lower than that of N_2 in the low intensity regime and is very close to that of N_2 when the intensity increases. However, Ar has a higher NSDI rate than nonaligned molecules N_2 and O_2. This can be understood by studying the NSDI processes for N_2 and O_2 at different molecular alignment angles. The ratios of NSDI rate to SI rate are also obtained. It is shown that compared with Ar, N_2 has a similar NSDI/SI ratio over the entire intensity range. In contrast, O_2 shows an obvious suppression effect. Our calculation is qualitatively consistent with the experimental observations.

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