

Nonsequential double ionization of triatomic molecules in strong laser fields

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(Received 16 March 2010; published 10 August 2010)

In this paper, we extend strong-field double ionization from diatomic molecules to triatomic molecules. Strong-field double ionization of CO_2 is studied here with both linear and circular polarizations. A clear nonsequential signature is seen in doubly ionized CO_2 . We also compare nonsequential double ionization behaviors of CO_2 to those of the well-studied diatomic molecules, and the difference is attributed to the detailed electronic structures in molecules.

DOI: [10.1103/PhysRevA.82.021401](https://doi.org/10.1103/PhysRevA.82.021401)

PACS number(s): 33.80.Rv, 33.80.Wz, 42.50.Hz

Multielectron effects are a challenging question when studying atoms and molecules in high-intensity ultra-short pulsed laser radiation. Among various problems related to multielectron effects, nonsequential double ionization (NSDI) is an interesting example [1–10]. Most studies on NSDI are based on rare-gas atoms, which all have similar closed-shell electronic structures [1–9]. Molecules can potentially provide important tests of strong-field phenomena as even easily studied diatomic molecules have a greater diversity of electronic structures [11–14]. Recently, we have extended the study of NSDI to both homonuclear and heteronuclear diatomic molecules [11–14]. We found that electronic structures play a key role in NSDI for diatomic molecules [11–14].

In this work, we extend our study of double ionization to a more complex form of molecular systems, i.e., triatomic molecules. We start by considering a relatively simple triatomic molecule, carbon dioxide (CO_2). Our study shows that CO_2 has a NSDI rate higher than that of O_2 but lower than that of N_2 , and the difference is attributed to the detailed electronic structures in molecules.

The laser used in the experiment is a Ti:sapphire laser system with a mode-locked oscillator and a two-stage chirped pulsed amplifier (a regenerative amplifier and a multipass amplifier). After final compression, the system produces 65-fs pulses of about 1.5 mJ per pulse at a 1-kHz repetition rate with the central wavelength at 800 nm. A thin lens of 30-cm focal length is used to focus the laser beam into a vacuum chamber. The detailed setup has been described in some of our previous papers [13,14]. In brief, a standard time-of-flight (TOF) mass spectrometer is used for ion collection and detection. The base pressure of the vacuum chamber is below 5×10^{-10} torr. The pure carbon dioxide is introduced into the chamber by a leak valve. The extraction and acceleration plates in our TOF spectrometer each have a 2.5-mm-diameter pinhole to allow ions passing through. Ions are collected by a pair of stacked multichannel plates (MCPs). The signal from MCPs is preamplified and recorded by either a boxcar gate integrator or a time digitizer card. The time digitizer used in our experiments (ORTEC model 9353) provides an ultrahigh flight time resolution of 100 ps. Both linear and circular polarizations (LP and CP, respectively) are used in the experiment with the linear polarization being parallel to the TOF axis. High-precision ionization yield measurements of

different molecular species are essential in order to compare different channels. Using a technique described in Ref. [12], we are able to accurately determine the flight time and width of a certain species and isolate it from contamination from adjacent peaks.

Figure 1 shows the TOF mass spectra of CO_2 ions with both LP and CP at an intensity of 2.2×10^{14} W/cm². From the figure, we see singly and doubly ionized molecular ions, CO_2^+ and CO_2^{2+} , as well as various fragment channels, including CO^+ , O^+ , C^+ , O^{2+} , C^{2+} , C^{3+} and O^{3+} . The ion signals produced by LP are stronger than those produced by CP for all the observed ions. Among all the peaks observed, CO_2^{2+} shows a particularly strong polarization dependence: CO_2^{2+} is extremely low with CP but grows significantly with LP compared to other fragment ions. For example, comparing CO_2^{2+} to a nearby O^+ peak on its left, CO_2^{2+} is much smaller than the O^+ signal with CP but grows to a comparable amount with LP at the intensity of 2.2×10^{14} W/cm².

Figure 2 shows ion yield curves of CO_2^+ and CO_2^{2+} for both LP and CP over an intensity range of 1×10^{13} to 6×10^{14} W/cm². We can see that the CO_2^+ ion yields have a similar dependence on intensity between LP and CP, except a shift of a factor of 1.5 along the intensity axis reflecting the peak intensity difference between LP and CP [15,16]. However, the CO_2^{2+} ion curves show a very different behavior between LP and CP, with the LP signal being significantly higher than that of CP for intensities below 2×10^{14} W/cm² and exhibiting a clear knee structure commonly seen for NSDI. Ionization data of CO_2 have been taken in the past [17]; however, the physical mechanism of double ionization in CO_2 has not been studied.

NSDI can be more quantitatively characterized by a well-established technique based on the intensity dependence of ratio X^{2+}/X^+ , where X^+ and X^{2+} are the yields for single and double ionization of carbon dioxide. The weaker intensity dependence indicates a higher NSDI rate, while a strong intensity dependence indicates a weaker NSDI rate [4,11,12]. In Fig. 3, ratio curves of the double ions over single ions for CO_2 are plotted for both LP and CP. We can see that the ratio curves, $\text{CO}_2^{2+}/\text{CO}_2^+$, show a clear weaker dependence on intensity with LP than with CP for intensities below 2×10^{14} W/cm².

Recently, we have studied NSDI extensively in diatomic molecules with different electronic structures [11–14]. We found that electronic structures play a key role in influencing NSDI processes in diatomic molecules [11–14]. For example,

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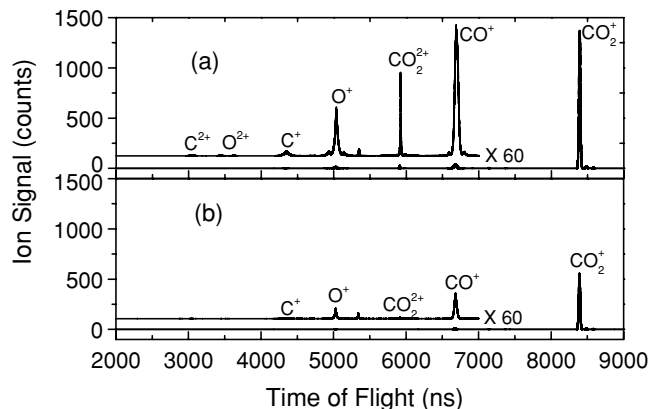


FIG. 1. TOF mass spectra of CO_2 with (a) LP and (b) CP at an intensity of $2.2 \times 10^{14} \text{ W/cm}^2$.

the diatomic molecule N_2 has a higher NSDI rate than O_2 because N_2 has a closed-shell structure with the outermost two electrons responsible for double ionization being in the same orbital $(3\sigma_g)^2$, while O_2 has an open-shell structure with the outermost two electrons being in two different but degenerate $(1\pi_g)^2$ orbitals. The importance of electron structures on NSDI has been further studied and confirmed with heteronuclear diatomic molecules, NO and CO [13,14], demonstrating that electronic structures govern diatomic molecules in different forms. Note, the initial electronic structures of molecules most likely affect the final NSDI behavior through intermediate excitation processes and electron-electron correlation effects. The excitation and electron correlation effects have been recently discussed in studying rare-gas atoms [18,19]. Since all the rare-gas atoms have similar initial electronic structures, the intermediate excitation has to be carefully considered for rare-gas atoms, as there is no correlation between the initial electronic configuration and the final NSDI behavior. In contrast, our systematic studies for molecules in the past have suggested

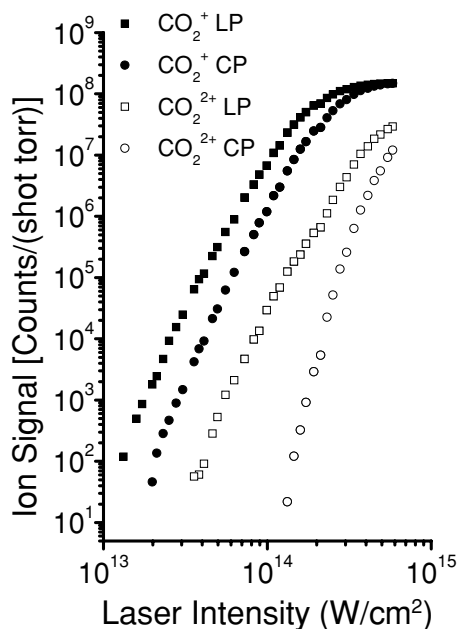


FIG. 2. Ionization yields of CO_2^+ and CO_2^{2+} with LP and CP.

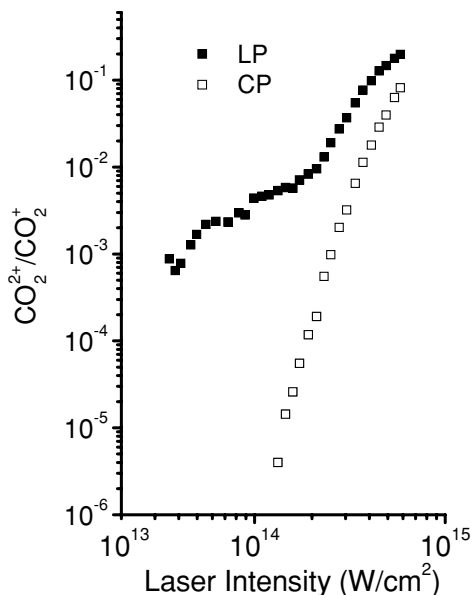


FIG. 3. Ratio curves of $\text{CO}_2^{2+}/\text{CO}_2^+$ with LP and CP.

a clear correlation between the initial electronic structure and the final NSDI behavior [11–14], and, therefore, the intermediate excitation processes do not need to be explicitly discussed for molecules. In this work, we will once again look at electronic structure effects for NSDI for triatomic molecules.

To consider if electronic structures play a key role in affecting triatomic molecules, we first take a look at the detailed electronic structure of CO_2 . CO_2 is a linear molecule with the C core in the center and the two O cores on each side of C. The valence electron orbitals of CO_2 are $\dots(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$ [20]. CO_2 is a closed-shell molecule with the outermost $1\pi_g$ orbital fully occupied with four electrons. The outermost $1\pi_g$ orbitals consist of a pair of degenerate nonbonding orbitals, while the next two orbitals, $3\sigma_u$ and $1\pi_u$, are bonding orbitals. For double ionization of CO_2 , when the two electrons are both removed from the outermost nonbonding $1\pi_g$ orbitals, the bond between the C and O atoms will not break and the double ionization will leave CO_2 in its metastable state CO_2^{2+} . The removal of $1\pi_g$ electrons has two possibilities: first, the two electrons can be both removed from one of the pair of degenerate $1\pi_g$ orbitals; second, the two electrons can each be removed from a separate $1\pi_g$ orbital. When the two electrons are each removed from a different $1\pi_g$ orbital, the doubly ionized CO_2^{2+} is in either the $^3\Sigma_g^-$ or $^1\Delta_g$ state. When the two electrons are both removed from a same $1\pi_g$ orbital, the doubly ionized CO_2^{2+} is in the $^1\Sigma_g^+$ state, and this state is about 2.0 eV above the $^3\Sigma_g^-$ state and 0.8 eV above the $^1\Delta_g$ state [20].

Comparing the CO_2 data to our previous NSDI results in N_2 and O_2 [11,12], the ratio curve of $\text{CO}_2^{2+}/\text{CO}_2^+$ with LP shows a stronger dependence on intensity than $\text{N}_2^{2+}/\text{N}_2^+$ but weaker dependence on intensity than $\text{O}_2^{2+}/\text{O}_2^+$. These results indicate that CO_2 has a higher NSDI rate than O_2 but lower NSDI rate than N_2 , and this can be understood from their detailed electronic structures. First, although O_2 and CO_2 both have a pair of outermost degenerate $1\pi_g$ orbitals, the pair of orbitals are fully filled with four electrons for CO_2 but only half filled for O_2 with each electron occupying one of the pair of

degenerate orbitals. When double ionization occurs, the two outermost electrons are removed from two different orbitals for O_2 , but the two electrons can be either removed from the same orbital or from two different orbitals for CO_2 , as discussed above. Comparing CO_2 and N_2 , they are both closed-shell molecules with the outermost orbitals fully occupied. However, N_2 has only one outermost $3\sigma_g$ orbital, and the removal of the two outermost electrons will have to come from this same orbital, while CO_2 again has two possibilities with two electrons either from the same orbital or from two different orbitals. As we have shown in the past, NSDI is higher when two electrons are removed from the same orbital but lower when two electrons are removed from two different orbitals [11]. Therefore, the NSDI rate of CO_2 should be between that of N_2 and O_2 , and this is consistent with our experimental observations.

In summary, we extend strong-field double ionization from diatomic molecules to triatomic molecules. Strong-field double ionization of CO_2 is studied here with both LP and CP. A clear nonsequential signature is seen in doubly ionized CO_2 . We also compare nonsequential double ionization behaviors of CO_2 to those of the well-studied diatomic molecules, and the difference is attributed to the detailed electronic structures in molecules. This study demonstrates that electronic structures play a key role in understanding strong-field ionization in more complex molecular systems, as we have demonstrated in diatomic molecules [11–14].

This research was supported by the US Air Force Office of Scientific Research.

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