PHYSICAL REVIEW A **73**, 041401(R) (2006)

Holding molecular dications together in strong laser fields

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(Received 13 October 2005; published 3 April 2006)

Metastable channel of doubly ionized carbon monoxide, CO^{2+}, was scantly seen in previous strong-field experiments at the visible wavelength region, but was commonly observed using single high-energy photon or electron excitation. For the first time with near-IR ultrashort-pulse radiation, we observe an abundance of CO^{2+}. We show that CO^{2+} results from nonsequential double ionization, while its dissociation counterpart, $C^{+}+O^{+}$, results from sequential processes, and CO^{2+} can be obtained through either single high-energy photon or electron excitation or multiphoton ionization with ultrashort pulses before a critical internuclear distance is reached. Our study demonstrates the experimental conditions to converge the outcomes from two vastly different regimes, namely, multiphoton excitation and ionization in strong fields and single high-energy photon or electron excitation and ionization in weak fields.

DOI: 10.1103/PhysRevA.73.041401 PACS number(s): 33.80.Rv, 33.80.Wz, 42.50.Hz

The study of doubly charged molecules has attracted much attention in the past two decades as these ions constitute a new class of molecular entity [1]. Among them, carbon monoxide, CO, is of particular interest in both strong-field and weak-field studies. In weak-field spectroscopy studies using single high-energy photons or electrons, there has been much controversy on the origin of the metastable dication CO^{2+} and the dissociation fragment $C^{+}+O^{+}$ [1–5]. The study becomes even more complicated in the strong-field regime, where the laser field is strong enough to ionize many electrons during the short interaction time. In the intensity range of $10^{13}-10^{15}$ W/cm^2, doubly ionized CO has been studied systematically using picosecond laser pulses at wavelengths of 305 and 610 nm [6]. Separately, double ionization of CO was studied using 0.6-ps laser pulses at a wavelength of 600 nm [7]. Both these studies show that doubly ionized CO, once produced, will predominately dissociate to ionic fragments, i.e., $CO^{2+}\rightarrow C^{+}+O^{+}$. A negligible amount of metastable ion CO^{2+}, if at all, is observed in these strong-field experiments [6,7]. This observation is interesting because, as some of the authors noted, a significant amount of doubly ionized metastable ions is seen in other diatomic molecules, such as in N_2 (the isoelectronic counterpart of CO), under similar or identical experimental conditions [6]. It is unclear why metastable CO^{2+} is scantly seen in strong laser fields [6].

A metastable ion CO^{2+} has been more commonly produced by synchrotron radiation or high-energy electron beam impact [1–5,8], where a single high-energy photon or electron is used to overcome the ionization threshold of CO^{2+} ($\sim$41 eV) [1,8]. In comparison, a single photon in the strong-field experiments has only 2-eV photon energy at 610 nm or 4-eV photon energy at a 305-nm wavelength. Thus, it appears that CO^{2+} is more likely produced by a single high-energy photon in weak fields than multiple low-energy photons in strong fields.

In the past, various studies have shown that high-lying energy states that are typically accessible through single high-energy photon or electron excitation may be reached by using ultrashort IR femtosecond laser pulses in the strong-field regime [9]. For example, charge asymmetric dissociation, such as $N_2^{2+}\rightarrow N^{2+}+N$, following doubly ionized small molecules N_2 and O_2 can be produced in UV and soft x-ray radiation, but not in the long-pulse visible radiation (610-nm ps pulses) [10]. Using 30-fs ultrashort pulses, charge asymmetric separation has been shown commonly existing following double ionization in both N_2 and O_2 in even longer wavelengths (800 nm) [9]. It is believed that the critical internuclear separation, R_c, plays a key role in the process, where electron localization and enhanced ionization occur due to the nature of the double-well potential of a diatomic molecule [11]. Charge symmetric dissociation (e.g., $N_2^{2+}\rightarrow N^{+}+N^{+}$) appears to dominate the dissociation process once R_c is reached [9,12]. By freezing the internuclear separation in its initial distance using the ultrashort laser pulses, charge asymmetric dissociation is seen in the near-IR radiation [9,12].

Motivated by the study of charge asymmetric dissociation, we set out to study the double ionization of CO using 55-fs laser pulses at 800 nm in the same intensity range as the previous strong-field experiments, $10^{13}-10^{15}$ W/cm^2 [6,7]. For the first time with near-IR radiation, we observe an abundance of metastable CO^{2+} before the molecule reaches its critical internuclear separation. We show that CO^{2+} results from nonsequential double ionization, while $C^{+}+O^{+}$ results from sequential double ionization.

The laser used in the experiment is a Ti:sapphire system running at a 1 kHz repetition rate, producing about 1.6 mJ/pulse in 55-fs pulses with a center wavelength of 800 nm. The details of our experimental setup have been described elsewhere [13,14]. Briefly, the ion fragments are analyzed with a standard time-of-flight (TOF) mass spectrometer. The signal is either integrated with a boxcar to produce ion yields or sent to an ultrahigh resolution (100 ps) time digitizer to generate TOF mass spectra. Using a technique described in Ref. [13], 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 at different intensities across the delay range corresponding to the metastable

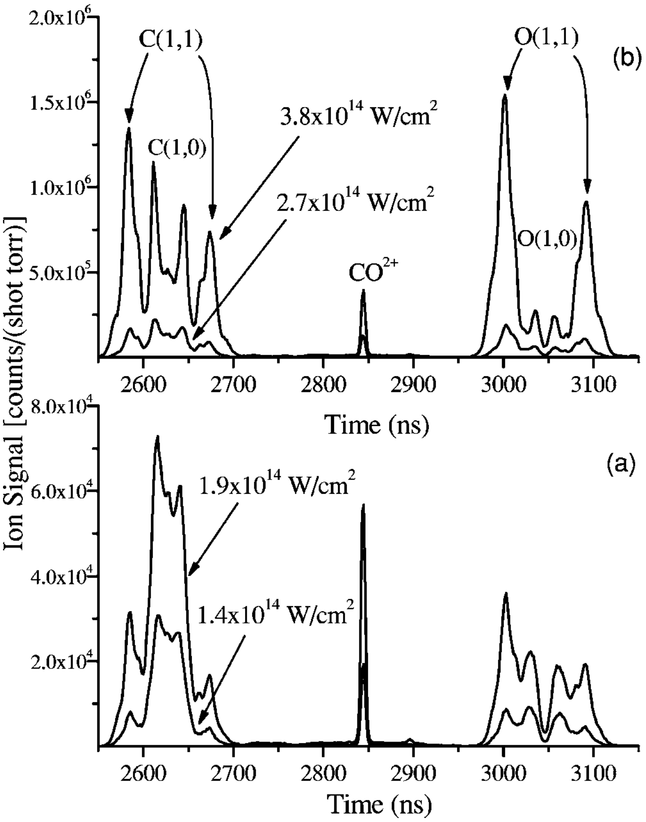

FIG. 1. TOF data show CO^{2+}, C^+, and O^+ signals with linearly polarized light at various intensities. The laser intensity increases by a constant ratio of 1.4. C(1,1) and O(1,1) denote the C^+ and O^+ signals, respectively, from the $C^+ + O^+$ dissociation channel. C(1,0) denotes the C^+ signal from the $C^+ + O$ channel, while O(1,0) denotes the O^+ signal from the $C + O^+$ channel.

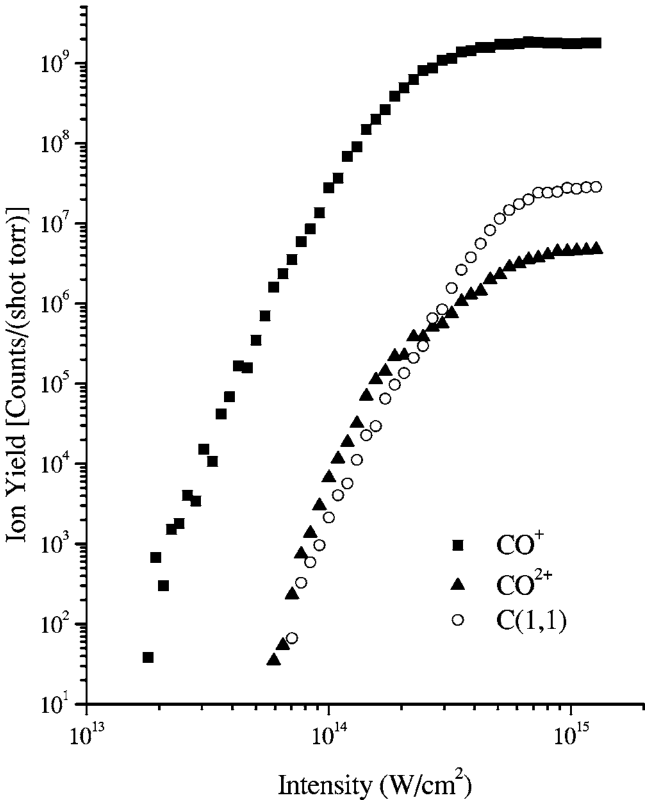

FIG. 2. Ionization yields of CO^+, CO^{2+}, and C(1,1) with linearly polarized light.

CO^{2+} and dissociation C^+ and O^+ channels. Various dissociation channels of C^+ and O^+ all have a double peak structure corresponding to the ions with initial velocity toward and away from the microchannel plate detector at the end of the TOF drift tube. Ion signals from different dissociation channels can be distinguished from their flight time. For example, a C^+ signal dissociated through $CO^{2+} \rightarrow C^+ + O^+$ has a different flight time from that through $CO^+ \rightarrow C^+ + O$. To identify different dissociation channels, an ion-ion correlation technique is used, as described in detail in Ref. [13]. In contrast to the previous observation in strong fields that the metastable CO^{2+} state is largely missing in the intensity range of $10^{13}-10^{15}$ W/cm^2 [6,7], we see a clear peak corresponding to the metastable ion CO^{2+} in our TOF spectra over the same intensity range. Figure 1(a) shows that, at lower intensities, the metastable CO^{2+} channel has an even higher signal strength than the dissociation channel, $C^+ + O^+$. The signal strength of the metastable and the dissociation channels of doubly ionized CO becomes comparable at around 2.7×10^{14} W/cm^2. Above this intensity, $C^+ + O^+$ is higher than CO^{2+}.

The relative signal strength between the metastable and dissociation channels following double ionization of CO can be seen more clearly in ion yield measurements. Figure 2 shows high-precision ion yield measurements on CO^+, CO^{2+}, and C^+ from the $C^+ + O^+$ channel over 8 orders of magnitude of dynamic range with linearly polarized light. Note, throughout this Rapid Communication we will label C^+ from the dissociation channel $C^+ + O^+$ as C(1,1). We can see that the ion yields for CO^{2+} and C(1,1) are indeed comparable with CO^{2+} slightly higher over the intensity range between 6×10^{13} and 3×10^{14} W/cm^2. Below the intensity of 6×10^{13} W/cm^2, we reach the collection limit of our TOF setup for doubly ionized CO. Dissociative double ionization of CO is also seen in an even lower intensity range with different techniques, although the metastable CO^{2+} channel is not studied there [15]. For laser intensities above 3×10^{14} W/cm^2, however, C(1,1) yield surpasses that of CO^{2+}. Interestingly, this turning point intensity of 3×10^{14} W/cm^2 also precisely coincides with the saturation intensity of CO^+. At the highest intensity end, C(1,1) is about one order of magnitude higher than CO^{2+}. The obvious explanation for this observation is that C(1,1) is predominately produced through sequential ionization, because as all the neutral CO molecules are ionized to CO^+, sequential double ionization should dominate further ionization processes. In comparison, CO^{2+} signal saturates strongly at higher intensities, suggesting that the precursor of CO^{2+} is not CO^+, i.e., CO^{2+} is most likely produced directly from CO through nonsequential double ionization (NSDI).

The above-speculated ionization dynamics of CO^{2+} and C(1,1) can be more quantitatively examined by a well-established technique based on the intensity dependence of ratio X^{2+}/X^+ [13,14,16], where X^+ and X^{2+} are the yields for single and double ionization of some atom or molecule,

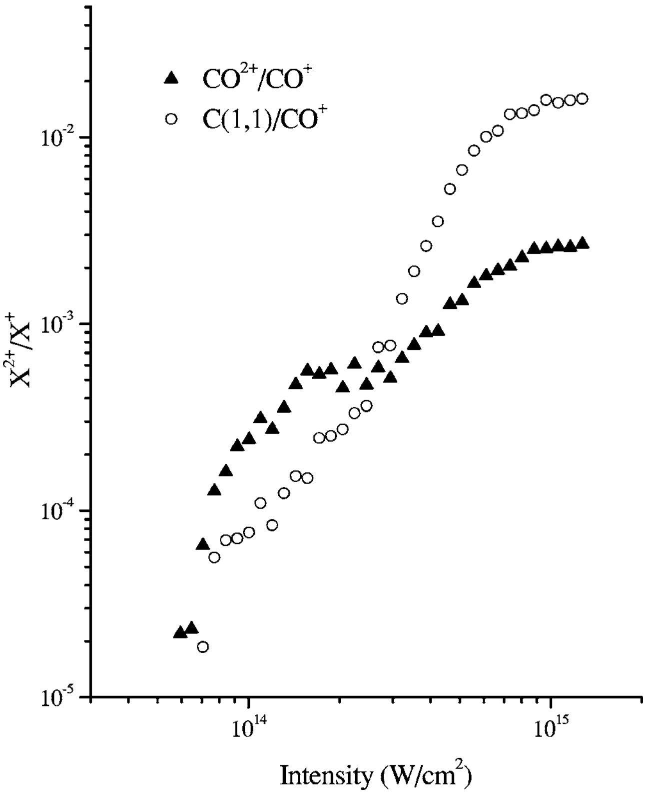

FIG. 3. Ratio curves of X^{2+}/X^{+} for CO^{2+} and C(1,1) with linearly polarized light.

X. A weaker intensity dependence of ratio curves indicates a higher NSDI rate [13,14,16]. In Fig. 3, ratio curves of the metastable $[CO^{2+}/CO^{+}]$ and dissociation $[C(1,1)/CO^{+}]$ channels of doubly ionized CO are plotted in linearly polarized light. We can see that the ratio curve of CO^{2+}/CO^{+} clearly shows a weaker dependence on intensity compared to $C(1,1)/CO^{+}$ below the CO^{+} saturation intensity (3×10^{14} W/cm^2). This indicates a higher NSDI component existing in the metastable channel CO^{2+}, confirming our speculation based on the ion yields in Fig. 2.

To understand the different ionization behavior of the metastable vs the dissociation channels of doubly ionized CO, we consider the electronic structure of CO molecules. The electronic configuration of CO is $KK(4\sigma)^2(1\pi)^4(5\sigma)^2$ [1–5,8,17]. Valence electronic bonding of CO has been studied previously [17], and we briefly summarize it as follows. As the first ionization potential implies ($I_p=11.26$ eV for C; $I_p=13.62$ eV for O), the energy level of the atomic orbitals of carbon and oxygen do not match up very well and this leads to some unique electronic bonds in CO compared to, for example, its isoelectronic counterpart N_2. In CO, the outermost orbital $(5\sigma)^2$ is virtually a nonbonding orbital, while the next two orbitals, $(4\sigma)^2$ and $(1\pi)^4$, are strongly bonding orbitals [17]. From the electronic configuration point of view, if we remove the two nonbonding electrons from orbital $(5\sigma)^2$, the remaining strongly bonding electrons should most likely hold the doubly ionized CO in its metastable state, CO^{2+}. However, if we remove one electron from the 5σ orbital but we remove the other electron from an inner strongly bonding orbital (4σ or 1π), the bond between C and O will be less stable and the resulting channel will be most likely the dissociation state, $C^{+}+O^{+}$. This simple analysis from the electronic structure agrees well with the extensive studies based on precision spectroscopy measurements [2,5]. It has been established that the lowest-energy metastable state, $^{1}\Sigma^{+}$(singlet), results from removing a pair of 5σ electrons from CO, while the lowest-energy dissociation state, $^{3}\Pi$ (triplet), results from removing two unpaired electrons, one from the 5σ orbital and the other one from the 1π orbital [2,5]. From this analysis, we can see that the doubly ionized metastable channel CO^{2+} most likely results from removing two electrons from the same orbital, $(5\sigma)^2$, while the dissociation channel, $C^{+}+O^{+}$, most likely results from removing two electrons from two different orbitals, 5σ and 1π.

Recently, we have studied NSDI extensively in diatomic molecules with different electronic structures [9,13,14,18]. We found that the detailed electronic structures play a key role in influencing NSDI processes [13,14,18]. For example, diatomic molecule N_2 has a higher NSDI rate than O_2 due to the fact that 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 [13,18]. In analogy to our findings with O_2, in this Rapid Communication, we expect that if we remove two electrons in CO from two different orbitals (one from 5σ and the other from 1π), there will be a lower NSDI rate and the process will more likely be sequential ionization. As discussed above, two-electron removal in this way leads to the dissociation state C(1,1). Therefore, the dissociation channel C(1,1) most likely results from the sequential double ionization of CO. In contrast, if we remove two electrons in CO from the same closed-shell orbital, $(5\sigma)^2$, we will expect to see a higher NSDI rate, in analogy to our prior findings with N_2. This ionization pathway by removing the two 5σ electrons leads to the metastable channel CO^{2+} (as discussed earlier). Therefore, the metastable channel CO^{2+} most likely results from NSDI of CO. Our analysis through electronic configuration also agrees with previous spectroscopy studies using single high-energy photon or electron excitation, where CO^{2+} is found originating from simultaneous double ionization, while C(1,1) comes from a stepwise ionization process [5,8]. Clearly, the above analysis supports our experimental observation that metastable channel CO^{2+} has a higher NSDI rate than dissociation channel C(1,1) $[C^{+}+O^{+}]$.

More interestingly, in comparison to previous experiments performed through both weak-field single high-energy photon or electron excitation and strong-field multiphoton excitation, our observation of abundant CO^{2+} is similar to the weak-field spectroscopy experiments, but quite different from those performed using long-pulse strong-field visible radiation in the same intensity range. To further understand these comparisons, we reexamine the TOF spectra in Fig. 1. We note there exist two strong dissociation channels, $C^{+}+O$ and $C+O^{+}$ [labeled as C(1,0) and O(1,0), respectively], following the single ionization of CO, especially at the lower intensity range where CO^{2+} is comparable in strength to $C^{+}+O^{+}$. Therefore, the molecular ion CO^{+} can start to dissociate following single electron removal, and if the internuclear distance reaches the critical value R_c during the presence of a longer laser pulse, the enhanced ionization may occur leading to higher charged dissociative ionization, such as the formation of $C^+ + O^+$ [11]. A simple estimation based on Ref. [19] shows that the time for CO^+ to reach R_c for further double ionization and dissociation is about 65 fs, longer than the pulse duration used in this experiment. In fact, further ionization of CO^+ at R_c requires that the pulse intensity is high enough to first generate CO^+ at the equilibrium internuclear position while remains high throughout the expansion of CO^+ to R_c, and therefore, the time to reach R_c is only a lower limit of the pulse duration if we want to see significant further ionization at R_c. When R_c is reached during a long pulse, the dissociation fragment $C^+ + O^+$ should dominate the final products in double ionization, and we believe that this explains why only $C^+ + O^+$ is mostly seen in the previous long-pulse experiments. Demonstrated both previously in weak fields and here in strong fields, the formation of CO^{2+} requires NSDI [1–5]. Therefore, it is not surprising to see that CO^{2+} can only be obtained through either single high-energy photon or electron ionization or multiphoton ionization with ultrashort pulses before R_c is reached. In the past, studies also showed that charge asymmetric dissociation was also a consequence following ionization before R_c, in both larger diatomic molecules I_2 and smaller molecules N_2 and O_2 [9,12]. We also observe a significant amount of asymmetric dissociation fragments, C^{2+} from $C^{2+} + O$ and O^{2+} from $C + O^{2+}$, confirming that double ionization in our experiment occurs at a very small internuclear separation.

Lastly, the clearly different origin between CO^{2+} and $C^+ + O^+$ (nonsequential vs sequential) accounts for the unique observations in CO in both strong and weak fields. In contrast to CO, doubly charged metastable ions are more commonly seen in other comparable-size diatomic molecules even in long-pulse experiments. For example, following the double ionization of the homonuclear diatomic molecule N_2 (isoelectronic counterpart of CO), both N_2^{2+} and $N^+ + N^+$ have been seen in both long- and short-pulse experiments [6,9,10,13,18]. This has to be due to the fact that N_2 and CO have different electronic configurations and their metastable and dissociation channels come from different origins in each molecule.

In summary, for the first time with near-IR radiation, we observe an abundance of the metastable ion CO^{2+} in the intensity range of $10^{13}-10^{15}$ W/cm^2. At the lower intensity range, the signal strength of CO^{2+} is even higher than the dissociation channel $C^+ + O^+$. This observation is similar to the previous weak-field experiments using single high-energy photons or electrons but is significantly different from the strong-field experiments using longer-pulse visible radiation in the same intensity range. We show that CO^{2+} results from nonsequential double ionization, while $C^+ + O^+$ results from sequential processes, and CO^{2+} can only be obtained through either single high-energy photon excitation or multiphoton ionization with ultrashort pulses before the critical internuclear distance is reached. Our study demonstrates the experimental conditions to converge the outcomes from two vastly different regimes, namely, multiphoton excitation and ionization in strong fields and single high-energy photon or electron excitation and ionization in weak fields. Lastly, we note that the experimental conditions established in this study on either holding a molecular ion together or allowing it to dissociate has a number of important implications. First, the study suggests a possible future high-density energy storage scheme by controlling the conversion of a large amount of potential energy into kinetic energy of fragment ions upon dissociation. Second, dilute multiply charged ions also resemble the underdense plasmas commonly found in interstellar medium, cosmetary halos, and planetary atmospheres. Third, the concept of molecular ionization and dissociation are of significant importance in a broad range of areas, including chemistry, inertial confinement study, laser engineering, and free radical ions in biomedical fields.

The research was supported by the U.S. Air Force Office of Scientific Research.

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