Direct detection of enhanced ionization in CO and N₂ in strong fields

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Enhanced ionization (EI) of molecules has been extensively studied over the past two decades as a common process in molecular dissociative ionization in strong laser fields. Direct evidence for EI has been found only in I_2 and H_2 . However, in this work we perform a direct study of EI in CO and N_2 , and find enhanced ionization in an alternate dissociation channel in each of these two molecules following double ionization. Surprisingly, EI does not happen in the commonly seen dissociation channels that were previously assigned undergoing EI. Instead, EI occurs only in the alternate channels seen here with a lower kinetic-energy release.

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When exposed to an intense laser field, a molecule can dissociate following the first electron ionization. Subsequently, enhanced ionization (EI) can occur when the molecular ion reaches a critical internuclear distance, R_c , where the ionization rate is greatly enhanced [1–5]. EI has been extensively studied in the past two decades [1–6], and recent advancements have shown interesting effects of EI related to molecular orbital type dependence [7], carrier envelope phase dependence in asymmetric molecules [8], and EI in atomic clusters [9].

However, direct experimental observation of EI has been more elusive: So far, EI has only been directly found in I₂ and H_2 [10,11], and most other experimental studies only showed EI indirectly [12–16]. Surprisingly, there is no *direct* observation of EI in a number of most commonly studied diatomic molecules, such as N2, O2, and CO, although some indirect experimental studies have been performed with these molecules [12,15,16]. Furthermore, recently ultrashort-pulsed experiments have raised a great amount of controversy over the established framework of EI. For example, the commonly seen $N^+ + N^+$ channel from doubly ionized N_2 was believed to come from EI previously [4,12,16]. However, this channel consistently appears in recent experiments using pulses as short as 7 fs [17], 8 fs [18,19], and 35 fs [18]. Under these conditions, EI should be greatly suppressed since molecular ion N_2^+ does not have time to reach R_c during these short time spans [4]. Therefore, mechanisms other than EI, such as nonsequential double ionization (NSDI) and stepwise sequential transition [17, 19], have been suggested as possible mechanisms producing these channels. Therefore, the role of EI in double ionization of N_2 is unclear [4,17,19].

Given to the apparently conflicting experimental observations, the conflicting view of EI is particularly significant for lower charged states in many commonly studied diatomic molecules [4,12,17]. It was found that the analytical model of EI only matches well with experimental data of higher charged states, where different molecules begin to follow a similar dissociation pattern. On the other hand, dissociation dynamics of lower charged molecules is usually molecule specific [4,12,17]. Again using N₂ as an example, the commonly seen N⁺ + N⁺ channel of doubly ionized N₂ has a kinetic-energy release (KER) of about 7 eV [15,17], and this value is significantly different from the 3.8 eV predicted by the

EI model [4,20]. In fact, most previous experimental studies of EI have been focused on higher charged states [10,14], and EI in lower charged states requires further study.

In this work, we perform a direct experimental study of EI in CO and N_2 . Two sets of experiments are performed, one with shorter 45-fs pulses and one with longer 68-fs pulses. In both sets of experiments, we observe an enhanced ionization in an alternate dissociation channel in each of the two molecules following double ionization. Surprisingly, EI does not happen in the commonly seen dissociation channels that were previously assigned undergoing EI. Instead, EI occurs only in the alternate channels seen here with a lower KER.

Our experimental study of EI is performed with our recently upgraded time-of-flight (TOF) mass spectrometer for studying molecular dissociation dynamics, which provides an improved temporal or energy resolution in distinguishing neighboring channels with small KER and/or flight time differences [21]. The laser used is a Ti:sapphire system that delivers pulses of 1.0–1.2 mJ/pulse at a 1 kHz repetition rate with the central wavelength at 800 nm. By adjusting the bandwidth of the seed pulses and dispersion in the amplifier cavity, we manage to generate two pulse durations at 45 and 68 fs. Both pulse durations are virtually dispersion free with both their second-and third-order dispersions compensated.

Figure 1 shows the TOF spectra of C^+ ions obtained with (a) 45-fs and (b) 68-fs pulses. By comparing the two spectra, we can see that most of the spectra look identical, except that two peaks are clearly visible in the 68-fs spectrum but unclear in the 45-fs spectrum. To identify these peaks, an ion-ion correlation experiment as described in Ref. [22] is performed with the 68-fs pulses on the two peaks that are most visible at this pulse duration, and the correlation results are shown in Fig. 2(a). We can see that the two peaks come from the same parent molecular ion, i.e., $CO^{2+} \rightarrow$ $C^+ + O^+$. However, this $C^+ + O^+$ channel is different from the commonly seen $C^+ + O^+$ channel since it has a distinctly lower KER [see Fig. 2(b) and description later]. Throughout this Rapid Communication, we label C^+ and O^+ from the $C^+ + O^+$ channel as C(1,1) and O(1,1), while $(C^+ + O^+)$ represents the entire $\mathrm{C}^+ + \mathrm{O}^+$ channel. We label the fast $C^{+} + O^{+}$ channel with a higher KER as $(C^{+} + O^{+})_{fast}$, and label the slow $C^+ + O^+$ channel with a lower KER as $(C^+ + O^+)_{slow}$. Similarly, C(1,0) and O(1,0) represent C⁺ and O^+ from the $C^+ + O$ and $C + O^+$ channels, respectively. We

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FIG. 1. (Color online) TOF spectra of C^+ obtained with (a) 45-fs and (b) 68-fs pulses. The $C(1,1)_{slow}$ channel is clearly visible in 68-fs pulses but unclear in 45-fs pulses.

plot all the O⁺ fragments from various dissociation channels as a function of total KER, shown in Fig. 2(b). The KER is determined to be 3.6 eV for $(C^+ + O^+)_{slow}$, and 6.3 eV for $(C^+ + O^+)_{fast}$. A C⁺ + O⁺ channel with a similar low KER has been seen in the past using single high-energy photon



FIG. 2. (Color online) (a) Ion-ion correlation spectra for $(C^+ + O^+)_{slow}$ using 68-fs pulses. The solid lines are the spectra averaged from all the laser shots, while the dashed lines show the data averaged from only the laser shots containing a backward C⁺ ion of the enhanced C⁺ peak. (b) KER spectrum of all the O⁺ fragments. Five identified channels, $O(1,0)_{slow}$, $O(1,0)_{fast}$, $O(1,1)_{slow}$, $O(1,1)_{fast}$, and O(1,2) are marked.

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excitation, and that channel is believed to come from an excited ${}^{3}\Pi$ state of CO²⁺ after a vertical single-photon transition from neutral CO [23]. However, in the strong fields, here we observe the (C⁺ + O⁺)_{slow} with a KER of 3.6 eV.

To understand why the $(C^+ + O^+)_{slow}$ channel is more pronounced in the long 68-fs pulses, we perform a timeresolved study of CO using both 45-fs and 68-fs pulses. Our time-resolved experiment is as follows. A molecule CO is first ionized by a pump pulse producing the CO⁺ molecular ion, followed by dissociation leading to either $C^+ + O$ or $C + O^+$. As the molecular ion expands, a temporally delayed probe pulse arrives and further ionizes the dissociating fragments, producing a $C^+ + O^+$ channel. By measuring the ionization rate of various dissociating channels from CO⁺ and CO²⁺ as a function of delay time, we can determine the dynamics of the formation of the $C^+ + O^+$ channels. The time-resolved study is performed with a pump-probe setup consisting of a Mach-Zehnder arrangement. The delay stage has a 0.1- μ m resolution that gives a 0.67-fs temporal step. The two beams are both linearly polarized with polarizations parallel to the TOF axis and propagate collinearly into the chamber. At small delays, an ion signal will be selected and analyzed under similar transient pump-probe overlapping intensities to avoid interference-induced intensity fluctuation.

In Fig. 3, the pump-probe TOF spectra of C^+ and O^+ fragments are obtained with (a) 45-fs pulses and (b) 68-fs



FIG. 3. (Color online) TOF spectra of C⁺ and O⁺ ion fragments at different probe delays in the pump-probe experiment with (a) 45-fs pulses (forward ions shown here) and (b) 68-fs pulses (backward ions shown here). In (a), the dashed curve superimposed is the spectrum at the -25 fs delay. In (b), the dashed curve superimposed is the spectrum at the 76 fs delay.

pulses at different time delays. Figure 3(a) shows the details of the forward ions at delays of -25, 23, 42, 54, and 67 fs. The two prominent C^+ peaks are from $C(1,1)_{fast}$ and C(1,0), while the two prominent O^+ peaks are from $O(1,1)_{\text{fast}}$ and $O(1,0)_{slow}$ [see Fig. 2(b)], as identified in Ref. [24]. To see the signal change of the various channels, we superimpose the TOF spectrum obtained from -25 fs to all other spectra, shown as the dashed curves in Fig. 3(a). The 23-fs delay curve is nearly identical to the -25-fs curve reflecting the reverse order of the pump and probe pulses. However, in the 42-fs delay curve, we see a clear enhancement at the flight time around 5.09 μ s compared to the baseline. At the same time, there is also an enhancement around 5.91 μ s. These enhancement peaks are the $(C^+ + O^+)_{slow}$ channel according to the correlation results in Fig. 2(a). Similar enhancements can be seen at the 54 fs delay. At longer delays after 67 fs, the enhancements are reduced. Figure 3(b) shows the time-resolved CO spectra obtained with 68-fs pulses; here the backward ions are shown. The TOF spectrum at a long delay of 76 fs is used as a baseline. Similar signal enhancements in $(C^+ + O^+)_{slow}$ can be seen in the 28, 44, and 52-fs delay curves around the flight times of 5.25 and 6.06 μ s, as marked by arrows. At longer delays, the enhancements from these two peaks disappear. The time-dependent enhancement is a strong indication of $(C^+ + O^+)_{slow}$ coming from EI.

In order to inspect the ionization rate change as a function of the delay time, we plot the ion signal branching ratio of $(C^+ + O^+)_{slow}$ over all the single and double ionization and dissociation channels from CO except the highly saturated CO^+ , and these include CO^{2+} , $(C^+ + O^+)_{fast}$, $(C^+ + O^+)_{slow}$, $C^+ + O$, and $C + O^+$. The branching ratio reflects the relative amount of this slow channel produced during each laser shot. In Fig. 4(a), we plot the branching ratio of $(C^+ + O^+)_{slow}$ as a function of probe delays in the pump-probe experiment with 45-fs pulses. We can see that the branching ratio is clearly enhanced in the delay range from 40 to 80 fs and peaks around 50 fs. The branching ratio experiences a jump from 6% at 40 fs to 12% at around 50 fs, and drops significantly at longer time delay to about 9% at 100 fs. This indicates that we produce the highest amount of $(C^+ + O^+)_{slow}$ at a delay time around 50 fs, which is consistent with the observations in Fig. 3(a) that



FIG. 4. (Color online) Ion signal branching ratio curve with error bars of $(C^+ + O^+)_{slow}$ as a function of probe delays with 45-fs pulses at intensities of (a) $1 \times 10^{14} \text{ W/cm}^2$ and (b) $2 \times 10^{14} \text{ W/cm}^2$. The inset in (a) shows the branching ratio curve of $(C^+ + O^+)_{slow}$ in the pump-probe experiment with 68-fs pulses at an intensity of about $1 \times 10^{14} \text{ W/cm}^2$.

 $(C^+ + O^+)_{slow}$ reaches the maximum enhancement at delay time of 42 to 54 fs and then reduces after 67 fs. We also plot the branching ratio of $(C^+ + O^+)_{slow}$ in the pump-probe experiment with 68-fs pulses in the inset of Fig. 4(a). Again, we can see that the branching ratio is clearly enhanced in the delay range from 30 to 65 fs, indicating the highest ionization rate happening at a delay time around 50 fs.

We note that the enhanced peak in $(C^+ + O^+)_{slow}$ is only observed at relatively low intensities (about $1 \times 10^{14} \text{ W/cm}^2$). At a higher intensity, we see a plateau instead of an EI peak, as shown in Fig. 4(b), where the delay dependent ion signal branching ratio of $(C^+ + O^+)_{slow}$ is shown at a higher intensity of $2 \times 10^{14} \,\mathrm{W/cm^2}$. We see that the ratio rapidly increases from 40 to 100 fs and remains nearly a constant after 100 fs. The peaks in Fig. 4(a) at a lower intensity and the plateaus in Fig. 4(b) at a higher intensity are consistent with the theoretical predictions presented in Ref. [4] for molecular dissociation and ionization. From the TOF spectra, we also observed that the $(C^+ + O^+)_{slow}$ peaks shift towards the $O(1,0)_{slow}$ peaks as the delay time increases and eventually move past $O(1,0)_{fast}$ and merge into $O(1,0)_{slow}$ at a sufficiently long delay (>600 fs). We believe this is due to the postdissociation ionization (PDI) [16]. A similar phenomenon has been observed in diatomic molecules N_2 and O_2 [18], in which a much higher-intensity probe pulse $(1.7 \times 10^{15} \,\text{W/cm}^2)$ is used in the pump-probe experiments. The fact that $(C^+ + O^+)_{slow}$ peaks eventually merge into $O(1,0)_{slow}$ suggests that $(C^+ + O^+)_{slow}$ comes from $O(1,0)_{slow}$ at higher intensities, and therefore, we suspect that the enhanced $(C^+ + O^+)_{slow}$ at lower intensities also comes from the $O(1,0)_{slow}$ channel. From Fig. 3, we can see a simultaneous depletion of $O(1,0)_{slow}$ along with an enhancement in $(C^+ + O^+)_{slow}$ at the delay time around 50 fs, and this is particularly pronounced in Fig. 3(b). This observation confirms that a significant amount of $O(1,0)_{slow}$ is converted to $(C^+ + O^+)_{slow}$ by the probe pulse.

According to the analytical EI model [4,8], the R_c for CO⁺ is estimated to be 4.2 Å, which gives a Coulomb repulsion energy as $(14.4 \times p \times q)/R_c = 3.43 \text{ eV}$. Using O(1,0)_{slow} as the precursor for the enhanced ionization, the dissociation kinetic energy for $O(1,0)_{slow}$ is 0.26–0.29 eV [see Fig. 2(b)]. The summation of these two values gives a value very close to the KER of $(C^+ + O^+)_{slow}$ in our measurement [3.6 eV as seen in Fig. 2(b)]. Therefore, these calculations further confirm that the observed ionization enhancement in $(C^+ + O^+)_{slow}$ comes from EI. The expansion time for CO⁺ from equilibrium internuclear distance R_e to R_c is estimated to be 46 fs [4], and this delay time again agrees with our observation. We believe that this 46 fs delay is the main reason why $(C^+ + O^+)_{slow}$ was not clearly observable in previous high-resolution COLTRIMS studies with 40-fs pulses [17], and in our non-pump-probe experiment with 45-fs pulses [see Fig. 1(a)], since the EI efficiency will be significantly reduced at a time shorter than the required time to reach R_c .

Our observations clearly show that, for doubly ionized CO, EI occurs only in $(C^+ + O^+)_{slow}$ but not in $(C^+ + O^+)_{fast}$ as commonly believed in the past [12]. Furthermore, our observation that EI preferentially comes from $C + O^+$ rather than $C^+ + O$ is consistent with the theoretical prediction in Ref. [8] that the EI probability in an asymmetric molecule is asymmetric from two cores with different electronegativity.



FIG. 5. (Color online) TOF spectra of N^+ ion fragments (forward ions shown here) at different probe delays in the pump-probe experiment with 45-fs pulses. The spectrum at the -5 fs delay is superimposed to other spectra to guide the eye.

Further studies are needed for a more quantitative understanding in this aspect. In addition, our results show that EI is most pronounced in an intensity window, and outside of this window other ionization and dissociation mechanisms can take over, such as PDI discussed here. This is again inconsistent with the theoretical predictions in Refs. [4,5] stating that EI effect will disappear if the electric field of the laser pulse is significantly outside of the "optimal electric field."

Lastly, we apply our time-resolved study to N₂. Figure 5 shows the TOF spectra of N⁺ fragments in 45-fs pulses at different time delays 30, 40, 43, 51, 53, and 57 fs. The spectrum at -5 fs is used as a guideline. Compared to the guideline curve, we see clear enhancements in the 40-, 43-, 51-, and 53-fs delay curves around the flight time of 5.51 μ s. This channel is identified in our previous study as a slow $N^+ + N^+$ channel with a lower KER of 3.8 eV, which is different from the commonly seen fast $N^+ + N^+$ channel with a higher KER of 7.0 eV [21]. At a longer delay of 57 fs, the enhancement from this channel starts to disappear. The R_c for N₂⁺ is estimated to be 4.0 Å [4]. The Coulomb repulsion at R_c produces a KER of 3.6 eV, which is very close to our experimental value of 3.8 eV for $(N^+ + N^+)_{slow}$ [21], indicating that $(N^+ + N^+)_{slow}$ is sequentially formed through EI at R_c . The small KER difference may be attributed to the kinetic energy of the

dissociating precursor $(N^+ + N)$ before R_c . In fact, based on an improved EI model given in Ref. [20], a KER is calculated to be 3.83 eV for doubly ionized N₂, which is almost identical to our measurements. Again, our results clearly show that, for doubly ionized N₂, EI only occurs in $(N^+ + N^+)_{slow}$ but not in the commonly seen $(N^+ + N^+)_{fast}$ channel [4,12,16]. This also resolves the recent controversies that $(N^+ + N^+)_{fast}$ was consistently seen in ultrashort-pulsed experiments before R_c is reached [17–19], since $(N^+ + N^+)_{fast}$ does not require EI. In addition, the signal enhancement in $(N^+ + N^+)_{slow}$ is only observed in a certain intensity range; at a higher intensity, PDI is observed similar to what we observed above for CO and also similar to what is reported in Ref. [18].

In conclusion, we perform a direct experimental study of EI in small molecules CO and N_2 . We observe an enhanced ionization in the alternate slow dissociation channel seen here in each of these two molecules following double ionization. Surprisingly, EI does not happen in the commonly seen dissociation channels that were previously assigned undergoing EI. Instead, EI occurs only in the alternate channels seen here with a lower KER.

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- K. Codling, L. J. Frasinski, and P. A. Hatherly, J. Phys. B 22, L321 (1989); 26, 783 (1993).
- [2] T. Zuo, S. Chelkowski, and A. D. Bandrauk, Phys. Rev. A 48, 3837 (1993); T. Zuo and A. D. Bandrauk, *ibid.* 52, R2511 (1995).
- [3] T. Seideman, M. Y. Ivanov, and P. B. Corkum, Phys. Rev. Lett. 75, 2819 (1995).
- [4] S. Chelkowski and A. D. Bandrauk, J. Phys. B 28, L723 (1995).
- [5] A. D. Bandrauk and F. Légaré, in *Progress in Ultrafast Intense Laser Science VIII*, edited by K. Yamanouchi, M. Nisoli, and W. T. Hill (Springer, Berlin, Heidelberg, 2012).
- [6] J. Wu, M. Meckel, L. Ph. H. Schmidt, M. Kunitski, S. Voss, H. Sann, H. Kim, T. Jahnke, A. Czasch, and R. Dörner, Nat. Commun. 3, 1113 (2012).
- [7] G. L. Kamta and A. D. Bandrauk, Phys. Rev. A 75, 041401 (2007).

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- [8] G. L. Kamta and A. D. Bandrauk, Phys. Rev. Lett. 94, 203003 (2005).
- [9] C. Siedschlag and J. M. Rost, Phys. Rev. Lett. 89, 173401 (2002).
- [10] E. Constant, H. Stapelfeldt, and P. B. Corkum, Phys. Rev. Lett. 76, 4140 (1996).
- [11] G. N. Gibson, M. Li, C. Guo, and J. Neira, Phys. Rev. Lett. 79, 2022 (1997).
- [12] M. Schmidt, D. Normand, and C. Cornaggia, Phys. Rev. A 50, 5037 (1994).
- [13] D. Normand and M. Schmidt, Phys. Rev. A 53, R1958 (1996);
 D. Pavičić, A. Kiess, T. W. Hänsch, and H. Figger, Phys. Rev. Lett. 94, 163002 (2005); H. Chen, V. Tagliamonti, and G. N. Gibson, Phys. Rev. A 86, 051403 (2012).
- [14] I. Bocharova, R. Karimi, E. F. Penka, J.-P. Brichta, P. Lassonde, X. Fu, J.-C. Kieffer, A. D. Bandrauk, I. Litvinyuk, J. Sanderson, and F. Légaré, Phys. Rev. Lett. **107**, 063201 (2011).
- [15] C. Cornaggia, J. Lavancier, D. Normand, J. Morellec, P. Agostini, J. P. Chambaret, and A. Antonetti, Phys. Rev. A 44, 4499 (1991).
- [16] J. McKenna, M. Suresh, B. Srigengan, I. D. Williams, W. A. Bryan, E. M. L. English, S. L. Stebbings, W. R. Newell, I. C. E. Turcu, J. M. Smith, E. J. Divall, C. J. Hooker, A. J. Langley, and J. L. Collier, Phys. Rev. A 73, 043401 (2006).

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- [17] B. Gaire, J. McKenna, N. G. Johnson, A. M. Sayler, E. Parke, K. D. Carnes, and I. Ben-Itzhak, Phys. Rev. A **79**, 063414 (2009).
- [18] I. A. Bocharova, A. S. Alnaser, U. Thumm, T. Niederhausen, D. Ray, C. L. Cocke, and I. V. Litvinyuk, Phys. Rev. A 83, 013417 (2011).
- [19] S. Voss, A. S. Alnaser, X. M. Tong, C. Maharjan, P. Ranitovic, B. Ulrich, B. Shan, Z. Chang, C. D. Lin, and C. L. Cocke, J. Phys. B 37, 4239 (2004).
- [20] H. Schröder, C. Witerwaal, and K. L. Kompa, Laser Phys. 10, 749 (2000).
- [21] W. Lai, L. Pei, and C. Guo, Phys. Rev. A 84, 043413 (2011).
- [22] C. Guo, M. Li, J. P. Nibarger, and G. N. Gibson, Phys. Rev. A 61, 033413 (2000).
- [23] P. Lablanquie, J. Delwiche, M. J. Hubin-Franskin, I. Nenner, P. Morin, K. Ito, J. H. D. Eland, J. M. Robbe, G. Gandara, J. Fournier, and P. G. Fournier, Phys. Rev. A 40, 5673 (1989); D. Mathur and J. H. D. Eland, Int. J. Mass Spectrom. Ion Processes 114, 123 (1992).
- [24] C. Guo, Phys. Rev. A 73, 041401 (2006); J. Wu,
 H. Zeng, and C. Guo, J. Phys. B 40, 1095 (2007).