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In this paper, we study double-ionization induced charge asymmetric dissociation (CAD) in heteronuclear diatomic molecules. In CO, we find a selective charge distribution in two CAD channels; i.e., $C^{2+}+O$ is abundantly produced but $C+O^{2+}$ is nearly nonexistent. This cannot be explained by the ionization energy difference between the two channels alone. Our study shows that the $C^{2+}+O$ channel is sequentially formed through an intermediate state $C^{+}+O$, and the selective charge distribution is the result of electron distribution in CO when exposed to intense laser fields.

Multielectron dissociative ionization (MEDI) in the molecule-strong field interaction is one of the most active research topics in strong field science [1-11]. In the MEDI process, a variety of dissociation channels accompanying excitation and ionization can occur during the laser pulse, due to the multiple degrees of freedom and the complex multielectron effects of molecules [1-7, 12-14]. In terms of different types of fragmentation, charge symmetric dissociation (CSD), such as $N_2^{2+} \rightarrow N^+ + N^+$, and charge asymmetric dissociation (CAD), such as $N_2^{2+} \rightarrow N^{2+} + N$, have been observed in previous MEDI studies [2, 5, 14, 15]. CAD is of particular interest since its occurrence requires more restricted conditions compared to the commonly-seen CSD, as the electronic states leading to CAD transitions usually lie much higher than the states leading to the corresponding CSD transitions and the lifetime of these states also plays a critical role [2, 3, 5, 7, 8, 10, 11, 14-17]. Furthermore, the CAD processes in molecules of different electronic structures are found to have different dynamics. For example, comparing the CAD channels in N_2 and O_2, previous studies have shown that nonsequential double ionization dominates the CAD channel $N_2^{2+} \rightarrow N^{2+} + N$ in N_2 while sequential transition dominates the CAD channel $O_2^{2+} \rightarrow O^{2+} + O$ in O_2, and the distinctly different dynamics are related to the detailed electronic structures of the two molecules since N_2 has a closed-shell electronic structure while O_2 has a half-filled outermost orbital [5].

In this work, we extend the study to double-ionization induced CAD to heteronuclear molecules. CAD in heteronuclear diatomic molecules behaves significantly different from homonuclear molecules. First, there are two CAD channels associated with two different cores, e.g., $C^{2+} + O$ and $C + O^{2+}$ following double ionization of CO. Secondly, the two CAD channels can behave dramatically different. In this work, we report that the CAD channel $C^{2+} + O$ is abundantly produced but the counterpart channel $C + O^{2+}$ is nearly nonexistent, which cannot be explained by the ionization energy difference between the two channels alone. Our study shows that the $C^{2+} + O$ channel is sequentially formed through an intermediate state $C^+ + O$, and the selective charge distribution is the result of electron distribution in CO when exposed to intense laser fields.

Experimentally, ions from ionization and dissociation of molecules are collected by a recently upgraded TOF mass spectrometer, which provides an improved temporal/energy resolution in distinguishing neighboring channels with small kinetic energy release (KER) and/or

flight time differences and allows us to accurately determine the KER from different dissociation channels [18, 19]. The laser used is a Ti:sapphire system that delivers 68-fs pulses of 1.0 mJ/pulse at a 1 kHz repetition rate with the central wavelength at 800 nm. The vacuum chamber base pressure is lower than 5.0×10^{-10} Torr.

Figure 1(a) shows TOF mass spectrum of the C^+, O^+, C^{2+}, and O^{2+} ions from ionization and dissociation of CO with linearly polarized 68-fs pulses at an intensity of 4×10^{14} W/cm^2. Different dissociation channels are identified through an ion-ion correlation technique as described previously [5]. For example, our correlation data shows that the highest peak of C^{2+} [see Fig. 1(a)] has a clear correlation to the outer pair of O^+ peaks, thus these C^{2+} and O^+ signals must come from the same parent molecular ion, i.e., $CO^{3+} \rightarrow C^{2+} + O^+$. There is no correlation between the two inner small peaks of C^{2+}, and neither of these peaks is correlated to any oxygen ion signal. Therefore, the two inner peaks are considered to come from the channel $C^{2+} + O$, which is a CAD channel from doubly ionized CO. Note that throughout this paper we will label $C^{2+} + O$ channel as C(2,0). Similarly, $C^+ + O$ channel is labeled as C(1,0), and $C + O^+$ is labeled as O(1,0), while C(2,2) and O(2,2) both indicate the $C^{2+} + O^{2+}$ channel. Figure 1(a) labels C(1,0), O(1,0), C(1,1), C(1,1)$_{slow}$, C(2,0), C(2,1), O(2,1) and C(2,2) from dissociation of CO. C(1,1)$_{slow}$ is a newly-identified $C^+ + O^+$ channel with a smaller KER compared to the commonly-seen $C^+ + O^+$ channel [19].

Noticeably, we see a clear pair of C(2,0) peaks whereas the counterpart O(2,0) peaks are absent in all the TOF spectra from our experiments. Obviously, it is not because of the experimental detection setup that causes the absence of O(2,0) signal, since the O^{2+} ions from other channels like O(2,1) and O(2,2) have been abundantly detected. Naturally, one would think the preferential production of C(2,0) over O(2,0) is due to different ionization potentials of these two channels [10]. According to previous photoion-photoion-coincidence measurements and electron impact measurements, the ionization threshold energy is about 58 eV for C(2,0) and 72.5 eV for O(2,0) [20, 21], indeed a 14.5 eV difference between these two channels. However, a number of ionization and dissociation channels with much higher ionization potentials are abundantly produced in our laser pulse, such as C(2,1), O(2,1), and C(2,2) with ionization threshold energy of about 84 eV, 93 eV, and 150 eV, respectively [21]. From Fig. 1(a) we can see clear signal peaks of O(2,1) and O(2,2). The energy threshold of O(2,2) is more than two

times higher than that of O(2,0); however, there is plentiful signal of O(2,2) shown in the spectra but no O(2,0). Therefore, ionization threshold difference alone is insufficient to explain why CAD of CO preferably happens in C(2,0) but not in O(2,0).

In order to inspect if the O(2,0) channel is depleted by some higher charged states, e.g. C(2,1), O(2,1) or O(2,2), we take a closer look at a TOF spectra obtained at a much lower intensity of about 0.8×10^{14} W/cm^2, as shown in Fig. 1(b). At this low intensity, fragmentation channels of high energy thresholds are significantly reduced. For example, O(2,1) and O(2,2) channels completely disappear while the C(2,1) channel is barely seen. However, the O(2,0) channel is still missing whereas the C(2,0) channel is clearly seen. Therefore, the absence of O(2,0) is not likely from depletion by higher charged states.

We also plot in Figure 1(c) the TOF spectrum obtained with circularly polarized light. Most channels are consistently seen as in the linearly polarized light such as C(1,0), O(1,0) and C(2,0), while some channels of higher ionization thresholds have a reduced signal strength. However, the O(2,0) is still missing on the spectrum. This suggests that laser polarization does not play a key role in the absence of O(2,0) either.

From above discussion we can see that, further exploration is needed to understand why the CAD channel C^{2+}+O is abundantly produced in our laser pulse but the counterpart channel C+O^{2+} is nearly nonexistent. First, we will investigate the mechanism of the C^{2+}+O formation. As shown in Fig. 1, the fact that C(2,0) is abundantly produced in both linearly and circularly polarized light indicates that this channel does not strongly involve nonsequential transitions [10, 12, 22]. Instead, the formation of the C(2,0) channel should involve a step-wise sequential transition through an intermediate state. Note, to form the C(2,0) channel, two electrons must be removed from the C side and at least one electron has to come from a bonding orbital since this is a dissociation channel. The ground-state electronic configuration of CO is $KK(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$, and 5σ is a nonbonding orbital and 1π and 4σ are bonding orbitals. If the first removed electron is from the nonbonding HOMO orbital 5σ, the intermediate state is most likely to be the metastable CO$^+$ state; if the first removed electron is from an inner bonding orbital, 1π or 4σ, the intermediate state is most likely to be the C(1,0) state.

Next, we use a technique from previous MEDI studies by analyzing the KER of the dissociation fragments, which may reveal some complex MEDI dynamics [3-5, 10]. We plot the KER of the C(1,0), C(2,0), and O(1,0) channels as a function of laser intensity in Fig. 2(a). Interestingly, we see that the KER of C(1,0) shows a strong intensity dependence; in the meantime, a similar intensity dependence is seen in the KER of the C(2,0) channel. The KER of C(1,0) increases by 0.2 eV from the low to the high intensity ends; similarly, a 0.2-eV increase is also seen in the KER of C(2,0) across our intensity range. The resemblance of the intensity dependence of KER between C(2,0) and C(1,0) suggests that C(2,0) is very likely to be sequentially formed through C(1,0). This sequential transition is schematically illustrated in Fig. 2(c). Intuitively speaking, after the C(1,0) state is created, if a second ionization happens as C(1,0) dissociate producing the C(2,0) channel, depicted by arrow 1 in Fig. 2(c), the final KER of C(2,0) will be the KER of the precursory state C(1,0) plus additional energy released from the dissociation of the C(2,0) state. Therefore, any variation in the KER of C(1,0), for example, when dissociating from a higher excited state as depicted by arrow 2, will be directly reflected in the KER of C(2,0). As a result, we see a similar increase in the KER of C(1,0) and C(2,0) as laser intensity increases.

In addition, we use a well-established technique from studying sequential and nonsequential dynamics to further verify if C(2,0) sequentially proceeds through the intermediate state C(1,0), by analyzing the intensity dependent ion ratios [5, 12]. Taking a doubly ionized molecular ion X_2^{2+} as an example, if X_2^{2+} is produced sequentially through the intermediate state X_2^+, the ion ration of X_2^{2+}/X_2^+ will reflect the ionization rate from X_2^+ to X_2^{2+} that will have a strong intensity dependence. On the other hand, if this ratio only weakly depends on intensity, it shows that the precursor to X_2^{2+} is not X_2^+ [5, 12]. We plot the intensity-dependent ion ratio curves of C(2,0)/C(1,0) in Fig. 2(b). We also plot the intensity-dependent ion ratio of C(2,0)/O(1,0) and C(2,0)/CO$^+$ in Fig. 2(b) as comparison. We can see that, compared to C(2,0)/O(1,0) and C(2,0)/CO$^+$, C(2,0)/C(1,0) shows a stronger intensity dependence within the laser intensity range of strong signal but no saturation. Obviously, the possibility to form C(2,0) from O(1,0) should be small if not zero, therefore, we see a weaker intensity dependence in C(2,0)/O(1,0) indicating that C(2,0) does not proceed through O(1,0). On the other hand, the stronger intensity dependence in C(2,0)/C(1,0) compared to that in C(2,0)/CO$^+$ indicates that C(2,0) is predominantly produced through the intermediate state C(1,0) rather than CO$^+$. This is

consistent with the hypothesis in Ref. [10]. Note, previous studies have reported a C(2,0) channel with a large KER of 3.2 eV following a vertical transition with 6-fs laser pulses [16] and a C(2,0) channel with KER > 3 eV following a recollisional excitation with 4.2-fs laser pulses [8]. Compared to those reports, our C(2,0) channel has a relatively small KER of less than 1.8 eV and does not possess signature of vertical or recollisional transitions as discussed above. The different ionization and dissociation dynamics between our observations and the previous results is most likely due to the different laser pulse durations. Intuitively speaking, a shorter pulse may not provide enough time for step-wise sequential transitions compared to a longer pulse [4, 10, 19] and therefore longer pulse durations favor a sequential C(2,0) channel, as reported in previous studies using various pulse durations from 7 to 40 fs [10].

Above analysis reveals an interesting phenomenon that in the formation of the C(2,0) channel, the first electron is removed from an inner bonding orbital leading to a dissociating C(1,0) state, which is followed by a second ionization step of removing the second electron from a HOMO or an inner orbital. To understand why such a process is favorable in forming a C(2,0) channel but not O(2,0), we next take a closer look at the detailed electronic structures of the CO molecule, as the detailed electronic structures of molecules have been found in previous studies to play a key role influencing molecule-strong field interactions [6, 11-13].

Between the two cores of CO, the O core has a higher electronegativity than the C core (electronegativity: C = 2.5 and O = 3.5), therefore, the bonding electrons in the 1π or 4σ orbitals between the C and O cores should shift towards the O core and the overall bonding strength of a 1π or 4σ electron is weaker when it is on the C side than on the O side [13, 23-26]. This can be seen from the electron density plots of the 1π and 4σ orbitals of CO shown in Fig. 3(a) & (b). The electron density is calculated by the Gaussian 98 package with the 6-31G* basis set [27]. As C(1,0) dissociates, if a second ionization happens and the electron is removed from a bonding orbital 4σ or 1π, it will be much easier for the electron being removed from the C side that will form C(2,0) than from the O side that will form C(1,1) since the bonding electrons are less tightly bonded on the C side than the O side. On the other hand, interestingly, the electrons in the nonbonding 5σ orbital mostly reside on the C side [Fig. 3(c)], because the electronegativity effect is screened by the strongly-bonding inner electrons and does not play an important role for this outermost electron anymore [25, 26]. Therefore, if a second ionization happens as C(1,0)

dissociates and the electron is removed from the nonbonding 5σ, it is also most likely to form C(2,0) than O(2,0) since the 5σ electrons mostly reside on the C side.

The counterpart channel of C(1,0), O(1,0), is also produced in our laser pulses as can be seen in Fig. 1. It is worth to note that O(1,0) shows a weaker signal strength than C(1,0) in the TOF spectra, and this is because the electronegativity effect also plays a key role here that leads the removal of a bonding electron to be easier from the C side than from the O side, consistent with our previous studies [24]. As O(1,0) dissociates, if a second ionization happens and the electron is removed from a bonding orbital 1π or 4σ, similar as discussed above, it is less likely to be removed from the O side to form O(2,0), since bonding electrons are more tightly bonded on the O side than the C side; instead, it will be more likely to be removed from the C side to form a O(1,1) channel. On the other hand, if the electron is removed from the nonbonding orbital 5σ, it is also more likely to be removed from the C side to form a O(1,1) than from the O side to form a O(2,0) since the 5σ electrons mostly reside on the C side. Therefore, the most probable path following a second ionization from O(1,0) would be an O(1,1) channel. In fact, this has been observed in our previous EI studies that shows the EI-induced slow O(1,1) channel is predominantly formed through O(1,0) [19].

In summary, we study double-ionization induced charge asymmetric dissociation in heteronuclear diatomic molecule CO. We find a selective charge distribution in two CAD channels; i.e., $C^{2+}+O$ is abundantly produced but $C+O^{2+}$ is nearly nonexistent. This cannot be explained by the ionization energy difference between the two channels alone. Our study shows that the $C^{2+}+O$ channel is sequentially formed through an intermediate state $C^{+}+O$, and the selective charge distribution is the result of electron distribution in CO when exposed to intense laser fields.

FIGURE CAPTIONS

Figure 1: TOF mass spectra of C^+, O^+, C^{2+} and O^{2+} ions from ionization and dissociation of CO with linearly polarized 68-fs pulses at an intensity of (a) 4.0×10^{14} W/cm^2 and (b) 0.8×10^{14} W/cm^2, and (c) circularly polarized light at 4.0×10^{14} W/cm^2. The left half of the spectrum in (b) is zoomed in by 10 times to show details.
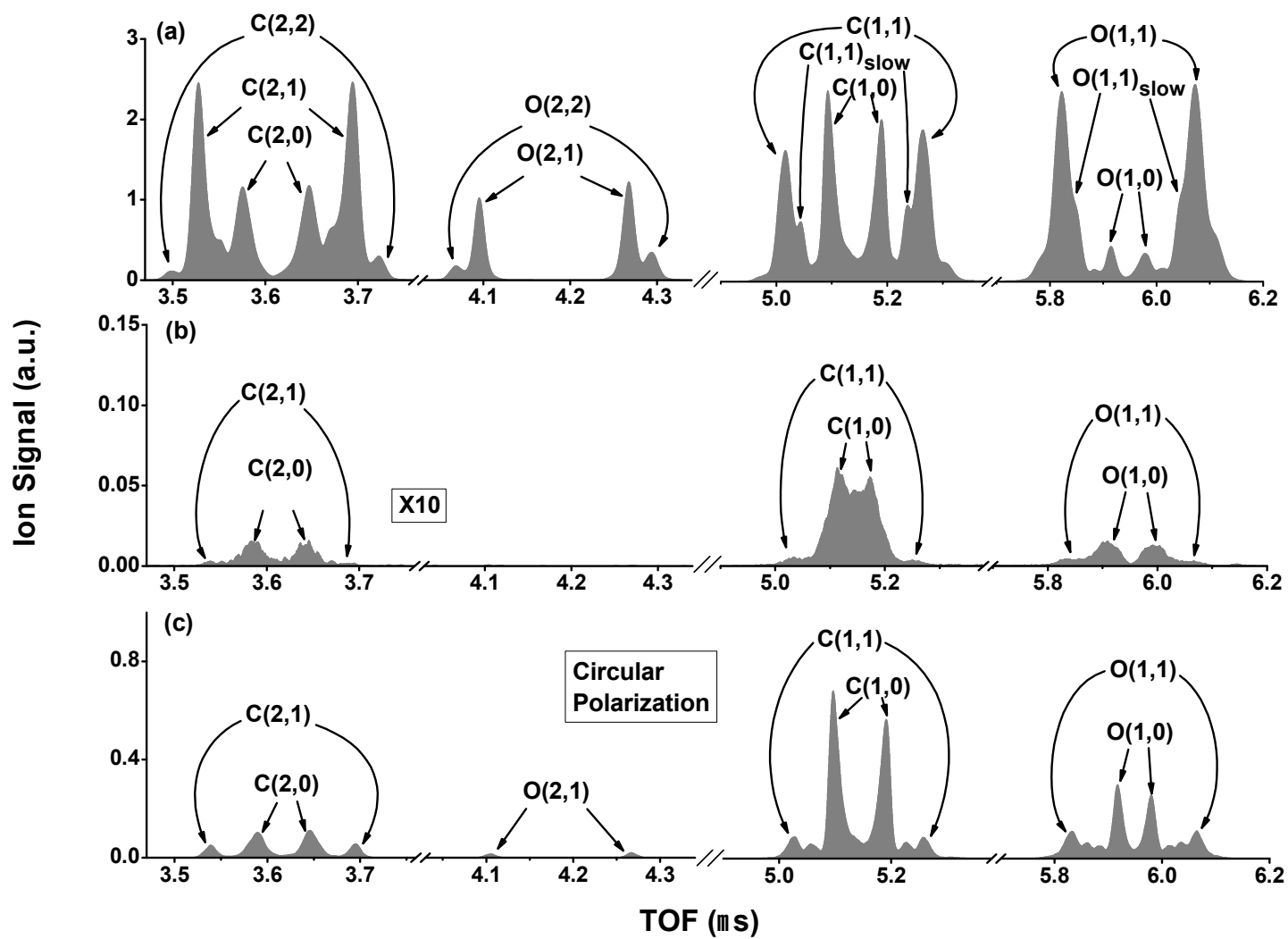
Figure 2: (Color online) (a) Intensity dependent KER with error bars of C(2,0), C(1,0) and O(1,0). (b) Intensity-dependent ion ratio curves for C(2,0)/C(1,0), C(2,0)/O(1,0), and C(2,0)/CO$^+$. The curve of C(2,0)/CO$^+$ is multiplied by 100 to make an easier comparison with other curves. (c) Illustration for the sequential transition that forms C(2,0) through C(1,0). Potential energy surfaces are schematically drawn. Arrows 1 & 2 depict the ionization and transition pathways from C(1,0) to C(2,0) (see text for details).
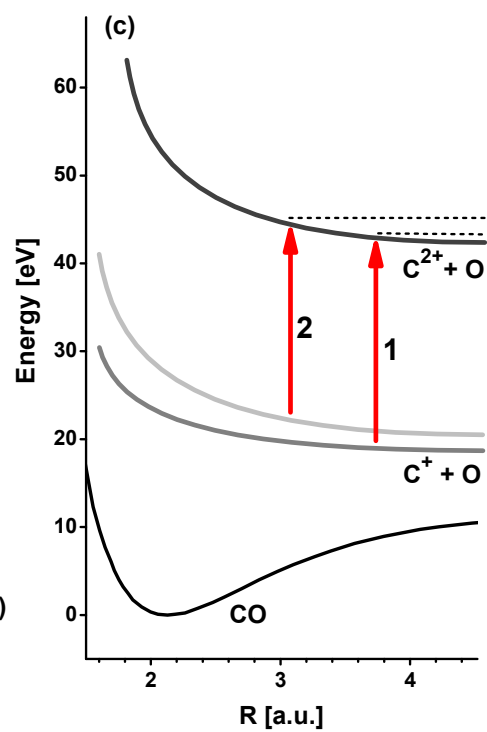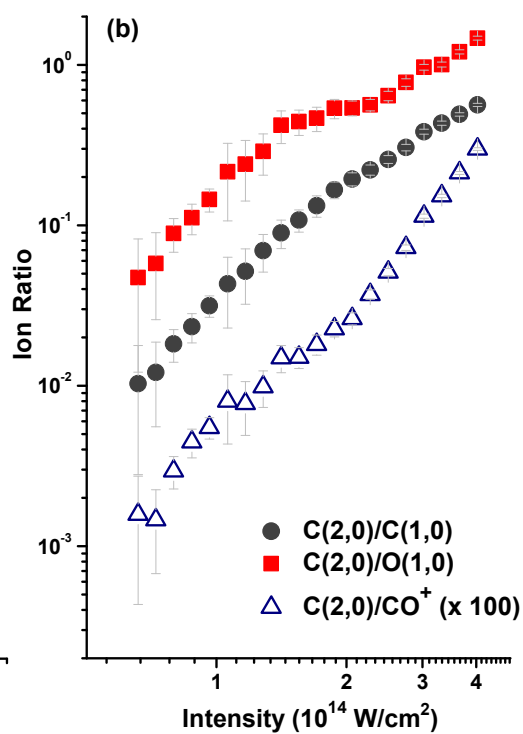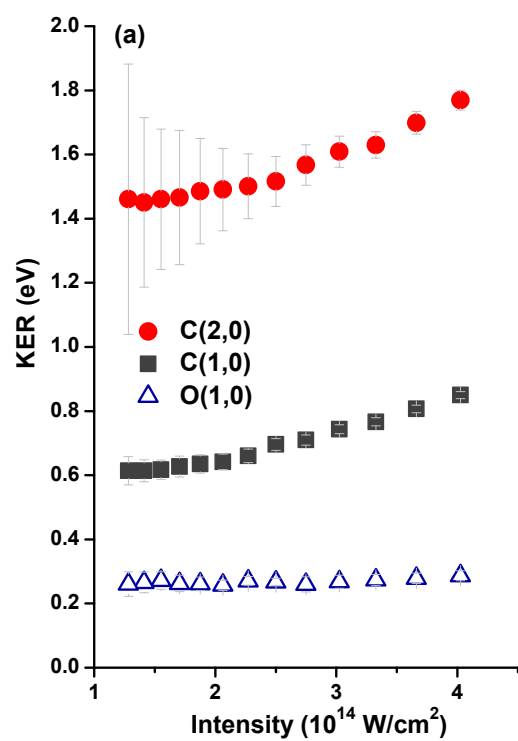
Figure 3: (Color online) Surface plots of the electron density of CO in the ground electronic configuration for (a) 4σ, (b) 1π, and (c) 5σ orbitals. The C core is located at 0 a.u. and the O core is located at 2.128 a.u. in all three panels, as marked in panel (a). The electron density is calculated by the Gaussian 98 package with the 6-31G* basis set [27].

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Electron density (a.u.)

Molecular plane (a.u.)

(a) C O 4σ (HOMO-2)

(b) 1π (HOMO-1)

(c) 5σ (HOMO)