

## Dynamic modification of the fragmentation of $\text{CO}^{q+}$ excited states generated with high-order harmonics

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The dynamic process of fragmentation of  $\text{CO}^{q+}$  excited states is investigated using a pump-probe approach. EUV radiation (32–48 eV) generated by high-order harmonics was used to ionize and excite CO molecules and a time-delayed infrared (IR) pulse (800 nm) was used to influence the evolution of the dissociating multichannel wave packet. Two groups of states, separable experimentally by their kinetic-energy release (KER), are populated by the EUV and lead to  $\text{C}^+-\text{O}^+$  fragmentation: direct double ionization of the neutral molecule and fragmentation of the cation leading to  $\text{C}^+-\text{O}^*$ , followed by autoionization of  $\text{O}^*$ . The IR pulse was found to modify the KER of the latter group in a delay-dependent way which is explained with a model calculation.

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### I. INTRODUCTION

The real-time probing of wave-packet dynamics in small diatomic molecules with infrared pulses is a mature subject, having now been practiced over nearly two decades [1]. The use of extreme ultraviolet (EUV: 20–100 eV) pump pulses with infrared probe pulses is a much more recent development. The importance of the EUV pump is that it can, in a single-photon process and at a well-defined time, excite and ionize the target to a high level of excitation while maintaining, within the limits of the uncertainty principle, spectral control over the degree of excitation or ionization. Short EUV bursts pump radiation from harmonic generation have been used in several cases to populate excited or ionized states of light diatomic molecules whose subsequent fragmentation can be followed or influenced by a short infrared (IR) probe [2–5]. It is typically the case that the spectral resolution of the EUV burst is inferior to that which can be obtained with, for example, a synchrotron radiation source. It is thus profitable to combine high-resolution synchrotron work with pump-probe studies of the dynamics, exploiting the advantage of each to deepen our understanding of the fragmentation process.

The ion kinetic energy release of doubly charged carbon monoxide has been studied extensively [6–10], and vibrationally resolved measurement [6–8] and multiple pathways of  $\text{C}^+-\text{O}^+$  fragmentation [9,10] have been reported. In a recent study of the fragmentation of CO, Osipov *et al.* [11] reported high-resolution COLTRIMS measurements of  $\text{C}^+-\text{O}^+$  fragments produced by ionizing neutral CO with 43-eV photons from the Advanced Light Source (ALS). They were able to identify two main decay paths to this final channel (see Fig. 1): (a) a direct path from the population of dissociating states of the dication of CO at an energy above that necessary to surpass a predissociation crossing and/or well barrier (approximately 42 eV) and (b) an indirect path from the population of highly excited states of the cation of CO which dissociate to a  $\text{C}^+$  ion and a highly excited  $\text{O}^*$  fragment. The

excited oxygen atom then autoionizes after dissociation has taken place. With the help of model calculations they were able to identify at least two inner-valence states of the cation which could contribute to this latter process. In this paper we probe the time dependence of this fragmentation process by using an IR pulse applied during the fragmentation to alter the decay route. In principle, such a pulse could modify both the direct and indirect processes, but we conclude on the basis of our experimental results that the major effect is on the indirect pathway.

### II. RESULTS AND DISCUSSION

As preparation for the time-dependent measurements, we first look at a COLTRIMS [13,14] spectrum in the  $\text{C}^+-\text{O}^+$  fragmentation channel, taken with a monoenergetic photon beam. Figure 2 shows the kinetic-energy release (KER) in the  $\text{C}^+-\text{O}^+$  channel plotted versus the sum energy of the two electrons ejected by the EUV photon. This figure is very similar to Fig. 1 of Ref. [11], except that the photon energy is 47 eV, appropriate for our experiment, instead of the 43 eV of the synchrotron work. Energy conservation requires that, for a given dissociation limit for the  $\text{C}^+$  and  $\text{O}^+$ , the events lie on a single diagonal line. Figure 2 shows (as does Fig. 1 of Ref. [11]) that the production of the ground states of the separated ions, with an asymptotic energy of 35.8 eV, dominates. There is also a weak diagonal line below the dominant one which corresponds to events feeding the excited state  $\text{C}^+-\text{O}^{*+}$  with a probability of a few percent. The weak vertical line around the sum electron energy of 5 eV is due to random events. Thus we are entitled to assume that the ground state is the only active fragmentation channel over this range of photon energies. This greatly simplifies our task when doing the time-resolved experiment, since it shows that the KER provides the same information as would the sum energy of the two electrons. In our EUV + IR experiment, we measure only

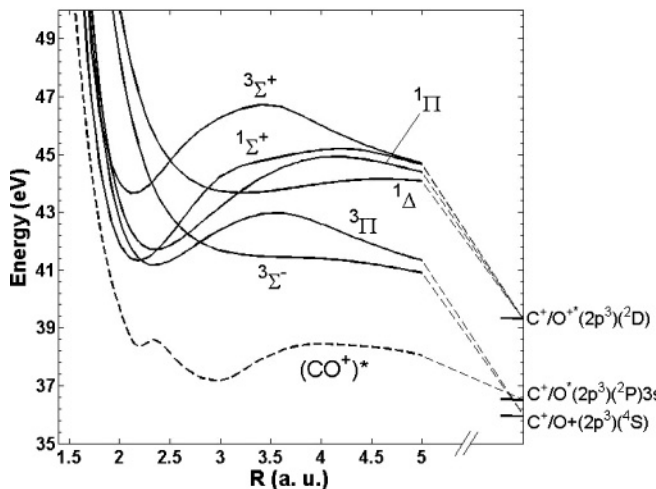


FIG. 1. Partial energy level diagram for the dication of CO (adapted from Refs. [11] and [12]). The solid lines are dication potential energy curves. The dashed line is one of the curves calculated in Ref. [11] for the cation decay, populating an autoionizing state of the oxygen neutral. Zero energy is taken to be the bottom of the neutral ground-state potential curve, which has a minimum near 2.14 a.u. (Franck-Condon region).

the momenta of the  $C^+$  and  $O^+$  ions (and not the electrons) in order to determine the energetics of the fragmentation.

Figure 2 shows two major groups along the energy conservation line. The higher KER one, beginning roughly at a KER of 6 eV, is due to the direct population of dication states in the Franck-Condon region. The population of vibrational states of the  $^3\Pi$  ground state of the dication with energies near and above the predissociation crossing of the  $^3\Pi$  curve with the  $^3\Sigma^-$  curve leads to direct fragmentation into the  $C^+-O^+$  channel. Because of the necessity that this energy surpasses

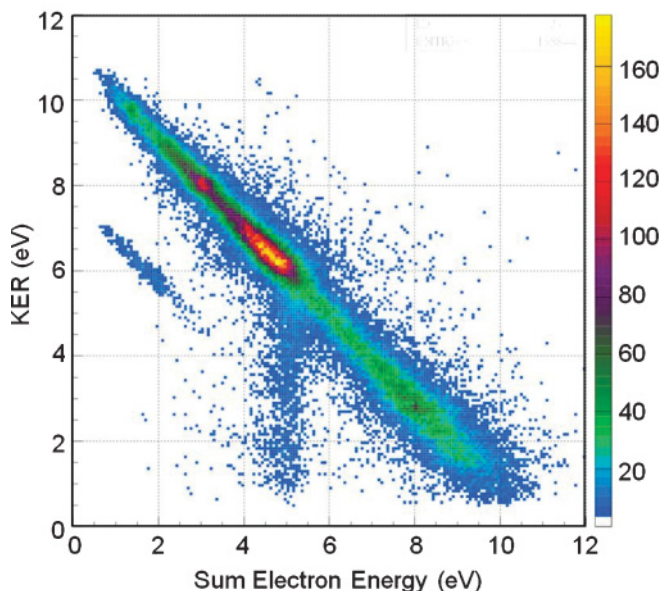


FIG. 2. (Color online) Density plot of KER in the  $C^+-O^+$  channel versus the sum energy of the two electrons. The data were taken at the COLTRIMS station at the ALS at photon energy of 47 eV. (See Osipov *et al.* [11].)

approximately 41.6 eV, the predissociation crossing, the KER from this process will lie mainly above 5.8 eV. Furthermore, population of higher states of the dication can also lead to fragmentation to the same final channel with KER above, but not below, 5.8 eV. The second group with KER peaking near 3 eV is due to the production of excited states of the cation, as discussed in Ref. [11]. These states dissociate to the ground state of  $C^+$  plus a core-excited state of  $O^*$  [3,15–17]. For example, a state of the configuration  $[\dots(2p)^3(^2P)3s]$  is one such state [10]. The  $O^*$  then autoionizes after the fragmentation has taken place. In fact, many autoionizing states of O which can participate in this process are known [15–17]. The lifetime of this autoionization process is not known precisely, but it is expected to be in the picosecond range or longer [15], longer than the dissociation time.

The time-dependent experiment, the main subject of this paper, addresses the following question: Can one modify the fragmentation process by the application of a short IR pulse during the fragmentation process? One might expect that such an IR pulse could modify the behavior of the wave packet of the dication at the predissociation crossing for the direct process. One might similarly expect that the IR pulse could modify the indirect wave packet in the cation by possibly removing an electron from this highly excited molecule.

A schematic of the experimental setup for the time-dependent measurement is shown in Fig. 3. A 10-fs, 1-mJ pulse was generated by passing a 35-fs pulse of 800-nm radiation through a spectrum-broadening capillary-containing Ne gas, followed by chirped mirrors. The EUV pulses were generated by focusing the 10-fs pulse into a gas cell containing 20 Torr of Ar gas. The resulting harmonic spectrum spans from the 21st to the 31st harmonics (32–48 eV), as measured both with an EUV spectrometer and from the photoelectron spectrum of He. The spectrum is centered at the 25th harmonic (38.9 eV) with a full width at half maximum of about 7 eV. The harmonics were recombined with a fraction of the infrared beam using a recombination mirror and both beams were focused onto a diffusive jet located in the center of a COLTRIMS spectrometer [13,14]. Ions resulting from the fragmentation of the  $CO^{q+}$  molecule were projected by a uniform electric field onto the

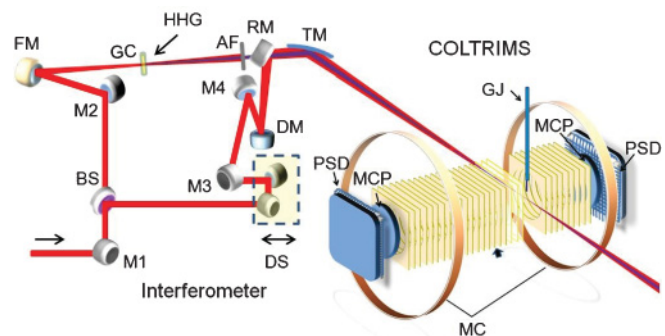


FIG. 3. (Color online) Schematic of the experimental apparatus used in the time-resolved study. M1-M4: plane mirror; BS: beam splitter; RM: recombination mirror; MCP: microchannel plate; FM: focusing mirror; GC: gas cell; DS: delay stage; PSD: position-sensitive detector; DM: diverging mirror; AF: Al filter; TM: toroidal mirror; MC: magnetic coils; GJ: effusive gas jet; HHG: high-order harmonic generator.

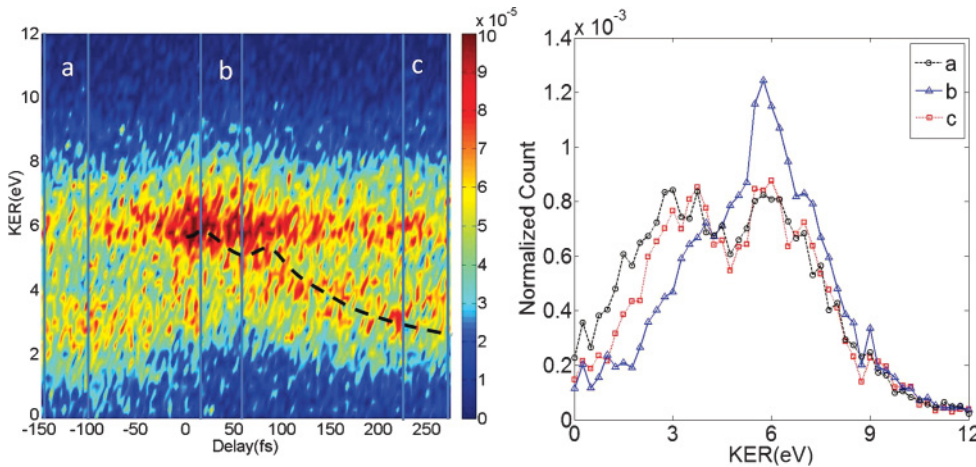


FIG. 4. (Color online) (Left) Density plot of KER versus delay of the IR pulse with respect to the EUV pulse. (Right) Projection of this spectrum onto the KER axis for delays indicated by a, b, and c in the left-hand panel.

surface of a time- and position-sensitive detector, and the initial momenta of the fragments were determined from the times and positions of arrival of the particles using classical equations of motion [13]. From the measured momenta of the  $C^+$  and  $O^+$  ions it was first verified that the ions came from the same molecule, and then the KER was determined. Although the electron momenta were also measured in determining the harmonic content of the beam, they were not used in the present data analysis for CO fragmentation. The 1-kHz repetition rate of the laser was too low to allow us to do a four-particle coincidence experiment, as was done in generating Fig. 2. The delay of the IR pulse relative to the arrival of the EUV pulse was varied using a Mach-Zender interferometer. The intensity of the IR pulse was about  $5 \times 10^{12} \text{ W/cm}^2$ .

The left-hand panel of Fig. 4 shows a density plot of KER versus EUV-IR delay. The determination of the time zero in this figure was made by removing the aluminum foil and observing the delay for which the interference pattern between IR pulses traveling on the pump and probe paths was optimized. A small correction was then made for the fact that the EUV burst arrives slightly earlier than the center of the driving IR pulse, since the EUV burst is generated on the rising edge of the IR pulse. This small shift (approximately 5 fs) was determined by measuring the sideband pattern generated by the EUV and IR pulses in the photoelectron spectrum of argon and comparing the time delay for which this peaked with the time delay observed in the IR interference pattern. We estimate a possible error of 5 fs on our determination of the time zero.

The right-hand panel of Fig. 4 shows the KER spectra taken for different windows on the delay of the IR pulse. If the IR pulse comes before the EUV pulset, the KER spectrum is the same as it is when no IR pulse is used at all. The KER spectrum for this case (a) shows two main peaks. Direct double ionization is responsible for the peak above 5.8 eV, while delayed double ionization gives the lower peak centered near 3 eV. (We note that the KER alone is sufficient to determine the energy deposited in the molecule in this case, although a range of photon energies and corresponding electron sum energies are involved for each KER. A monoenergetic photon

is not necessary for the identification of the decay channel.) When the IR pulse is coincident with the EUV pulse (case b) the delayed double ionization peak is seen to move to much higher KER, now overlapping with the direct double ionization peak. This increase in KER from this channel then gradually decreases as the IR pulse comes later after the EUV pulse, finally returning nearly to the same spectrum as when the IR pulse comes first (case a).

Our interpretation of Fig. 4 is that the major effect of the IR pulse is on the autoionization channel, not the direct double ionization channel. The KER through the cation states is modified because the IR pulse can ionize them to form dications. An electron with a binding energy  $I_p$  is driven over-barrier at the peak field by an IR pulse with an intensity given by  $I = (I_p/12.4)^{1/4}$ , where  $I$  is in units of  $10^{14} \text{ W/cm}^2$  and  $I_p$  is in electron volts. At a laser intensity of  $10^{12} \text{ W/cm}^2$ , electrons with binding energies below 3.9 eV are over-barrier at the peak of the electric field. Excited molecular states are quite fragile in modest IR fields. The gain in KER results from the conversion of the cation to the dication during the fragmentation, which adds a large Coulomb contribution to the dissociation energy if the conversion occurs early in the fragmentation.

To support this interpretation quantitatively, we have modeled this process using one of the two potential curves for the autoionizing cation given in Ref. [11]. A schematic of the process is shown in Fig. 5(a). The cation is assumed to be populated by the EUV with a vibrational wave function corresponding to the vibrational ground state of neutral CO. This wave function is allowed to propagate on the cation curve. After some delay ( $\tau$ ) the IR pulse is assumed to move the molecular ion onto a potential curve of the dication and the vibrational wave function is allowed to propagate on this potential curve. The KER accumulated over the entire process to large internuclear distance ( $R$ ) is then evaluated. A plot of the resulting average KER versus  $\tau$  is shown in Fig. 5(b). In calculating this result we have assumed that the wave packet is promoted to the  $^3\Pi$  state of the dication for internuclear distances inside the predissociation crossing at 2.8 a.u., and to the  $^3\Sigma^-$  state for larger internuclear distances. For about the first 90 fs, the wave packet is traveling on the complicated

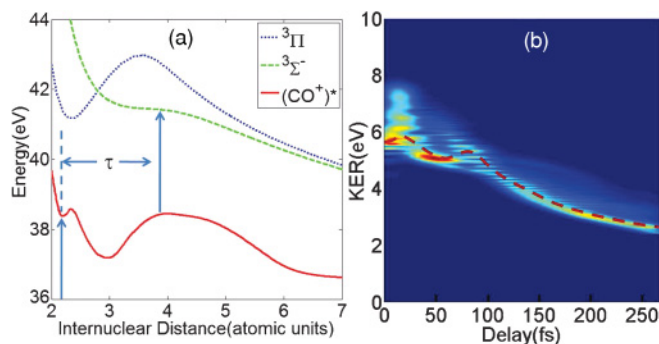


FIG. 5. (Color online) (a) Schematic of potential curves used in the model calculation. (b) Density plot of KER versus time delay  $\tau$ . The dashed red line is drawn through the major population and used in Fig. 4 to compare this result with the experiment. See text for details.

part of the potential curves inside an internuclear distance  $R$  of 6 a.u. Over this range of  $R$ , the difference between the cation and dication potentials is not yet decreasing monotonically as it does later. The calculated KER for times less than 90 fs is thus complex, but not yet systematically decreasing. For larger delays, the wave packet travels on the rapidly descending Coulomb part of the dication potential curve and the KER decreases monotonically with  $\tau$ . This behavior is very similar to that observed in the experimental data of Fig. 4. The qualitative shape of the calculated curve is not very sensitive to the exact dication potential curve on which the final dissociation is assumed to occur. For example, using either the  $^3\Pi$  or  $^3\Sigma^-$  dication potential curve alone produces a similar result, as does the use of the other autoionizing cation curve given in Ref. [11]. In order to compare the model calculation with the data, we have drawn a smooth dashed curve through the model result in Fig. 5(b), and we show the same curve superimposed on the data of Fig. 4(a). It is seen that the model curve agrees well with the observation, supporting our interpretation of the influence of the IR pulse on the fragmentation of the ionized or excited CO molecule by the EUV pulse.

If the only role of the IR pulse were to promote the autoionizing state of the cation to the dication, one would expect that the total yield in the  $C^+-O^+$  channel should not vary as a function of  $\tau$ . In fact, a small increase of yield in the region where the IR and EUV pulses overlap is observed, as is shown in Fig. 6. It is possible that this increase could be caused by an enhancement of the predissociation crossing of the  $^3\Pi$  and  $^3\Sigma^-$  curves due to the IR pulse, which might enhance the direct double ionization channel. It should take the wave packet approximately 20 fs to reach this crossing, and thus such an effect should maximize not at  $\tau = 0$  but nearer

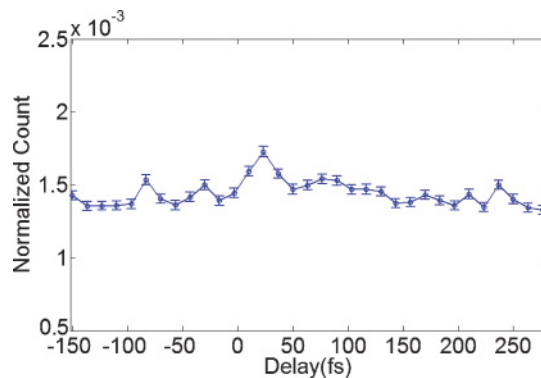


FIG. 6. (Color online) Total yield in the  $C^+-O^+$  channel versus  $\tau$ , normalized to the number of laser shots at each delay.

to  $\tau = 20$  fs. The data are consistent with such an effect. Thus while the main effect of the IR pulse is certainly on the indirect double ionization channel, there is some weak evidence for enhancement of the direct channel as well.

### III. CONCLUSION

In summary, we have found that the effect of applying a delayed IR pulse to a fragmenting CO molecule, following excitation and ionization by a 32–48 eV EUV pulse, is primarily to convert the autoionizing path discussed by Osipov *et al.* [11] into a direct double ionization path. This finding is very much in accord with two previous experiments on the EUV-IR pump-probe investigations of the dynamics of fragmentation in light molecules [2,3]. Whereas ground-state molecules and molecular ions are rather immune to the application of weak IR pulses, excited states with loosely bound electrons are not. Since EUV ionization usually populates a wide range of excited states, ionization by the IR pulse is readily enabled by this process. The dominant fragmentation pathways then become very sensitive to being guided by the IR pulse. It is likely that this general situation will reign in most EUV-IR pump-probe experiments, including those in which the branching ratios of final products are modified by the presence of a delayed IR field.

### ACKNOWLEDGMENTS

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