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International Journal of Mass Spectrometry 228 (2003) 81–89
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Field-induced ionization and Coulomb explosion of CO_2 by intense femtosecond laser pulses

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Received 13 April 2003; accepted 14 April 2003

Abstract

Field-induced ionization and Coulomb explosion of the triatomic molecule CO_2 were systematically investigated by using a time-of-fight (TOF) mass spectrometer under an intense femtosecond laser field of different polarization with the intensities from 1.0×10^{15} W/cm^2 to 1.2×10^{16} W/cm^2. The appearances of the highly charged atomic ions and the peak splitting indicate that these atomic ions originate from Coulomb explosion of the highly charged molecular ions. The Coulomb explosion was proved to be a concerted process and two CO bonds broke simultaneously. Compared with the linearly polarized light, suppression of ionization occurs for the elliptically and circularly polarized lights. The angular distributions of the parent molecular ions are all isotropic. The collinear O^{m+} ($m \leq 3$) and orthogonal C^{n+} ($n \leq 3$) distributions show that the molecule structure is being distorted and bent by the intense laser field. Analyzing the signal intensities obtained using linearly polarized light and circularly polarized light with equal electric field amplitude, the dynamic alignment mechanism is revealed to be responsible for the anisotropic angular distributions of O^{m+} ($m \leq 3$) and C^{n+} ($n \leq 3$) ions.

Keywords: Coulomb explosion; Mass spectrum; Field ionization; Carbon dioxide; Femtosecond

1. Introduction

Interaction of strong laser fields with atoms and molecules has been an object of interest in atomic and molecular physics for the past decades [1–3]. Multiple-photon ionization of CO_2, which is a typical linear triatomic molecule, has been widely studied [4–17]. In the earlier experiments, the identification of multifragmentation channels of the laser-induced Coulomb explosion of CO_2 was performed from triple ion correlation experiments [4]. Alignment and bending of CO_2 were also studied by using an angular measurement technique [5]. In recent experiments, field-induced spatial alignment effects in multielectron dissociative ionization (MEDI) of CO_2 were presented by employing the covariance mapping technique [6]. Geometry modification and reorientation of CO_2 [7,8] and the ionization and fragmentation of CO_2 in collisions with 5.9 MeVu^{-1} Xe^{18+} and Xe^{43+} ions utilizing a position- and time-sensitive multiparticle detector were studied [9]. The interaction of laser pulses with vibrationally excited CO_2 was also measured [10,11].

The angular distributions of fragment ions arising from the linear CO_2 molecule have been also studied using different pulse durations and wavelengths

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doi:10.1016/S1387-3806(03)00196-9

[5,12–15]. The earliest experiments using 35 ps duration at 532 nm by Mathur and co-workers [14,15] indicated that the C and O ion intensities were maximum along the detection axis. These disagree with that presented in Refs. [5,12,13]. In Refs. [5,12], anisotropic distributions of C and O fragment ions were observed in the femtosecond regime, whereas in Ref. [13], no anisotropy in the angular distribution of C^{2+} was presented using 800 nm, 200 fs laser light. The angular distributions of all the ions originated from the linear CO_2 molecule in intense femtosecond laser fields need a further investigation.

The anisotropic angular distributions of fragment ions can be attributed to two effects: dynamic alignment and geometric alignment. In the dynamic alignment mechanism, the electric field of the intense laser induces a polarization within the molecule, which in turn interacts with the field. Consequently, this set up a torque, which aligns the molecules with the field. As for the geometric alignment mechanism, the dependence of the ionization rate on laser polarization determines the angular distribution of the exploding fragments. There are two methods to disentangle the contributions of these effects. One is to measure the ratio of fragment ion yields obtained at a parallel polarization vs. an orthogonal polarization within a range of laser intensities [18]. If the ratio will increase with the increasing laser intensity, the dynamic alignment is responsible for the anisotropic angular distributions of the exploding fragments. Conversely, the geometric alignment is dominant. The other is to compare the signal intensities obtained using linearly polarized light and circularly polarized light with equal electric field amplitude [19]. If the splitting ion signals in two cases are approximately equal, geometric alignment is important. While, if the splitting ion signals for linear polarization are higher than that for circular polarization, dynamic alignment becomes more significant.

In this paper, the ionization and Coulomb explosion of carbon dioxide molecule are systematically investigated in an intense laser with intensity varying from 1.0×10^{15} W/cm^2 to 1.2×10^{16} W/cm^2 using the time-of-flight (TOF) mass spectrometer. The kinetic energies and angular distributions of all the ions coming from Coulomb explosion were measured and discussed. By comparing time-of-flight spectra taken under linearly and circularly polarized lights, the alignment mechanism responding for the anisotropic angular distributions is disentangled and the degree of alignment is also presented.

2. Experimental setup

The experimental setup has been described in detail in our previous reports [20,21]. A Ti:sapphire chirped pulse amplifier system (TSA-10, Spectra-Physics Inc., USA) delivered laser pulses with a central wavelength of 800 nm, pulse duration of 130 fs at a repetition rate of 10 Hz. The laser beam was focused into the vacuum chamber of a TOF mass spectrometer by a lens with a focal length of 150 mm. To measure the angular distribution, a half-wave plate was inserted into the path of the laser beam to rotate the electric field vector. A quarter-wave plate was inserted into the path of the laser beam in order to obtain the desired laser polarization at a constant intensity. A gaseous sample was introduced into the vacuum chamber via a pulsed valve (Park Inc., USA) with a 0.2 mm orifice. The produced ions were accelerated by a two-stage electric field and detected by a micro-channel plate (MCP). The signals were recorded with a 100 MHz data acquisition card and then transferred to a PC for storage and analysis.

3. Results and discussion

3.1. Typical TOF mass spectra and ion intensity distributions

Typical mass spectra of CO_2 under different laser intensities, recorded with laser polarization along the *p*-direction (i.e., collinear with the TOF axis) and *s*-direction (i.e., perpendicular to the TOF axis), are shown in Figs. 1 and 2, respectively. The collection voltages for V_1 and V_2 are 960 and 800 V, respectively. At low incident intensities, only the parent molecule mass peak CO_2^+ is observed (Figs. 1(a) and 2(a)) except

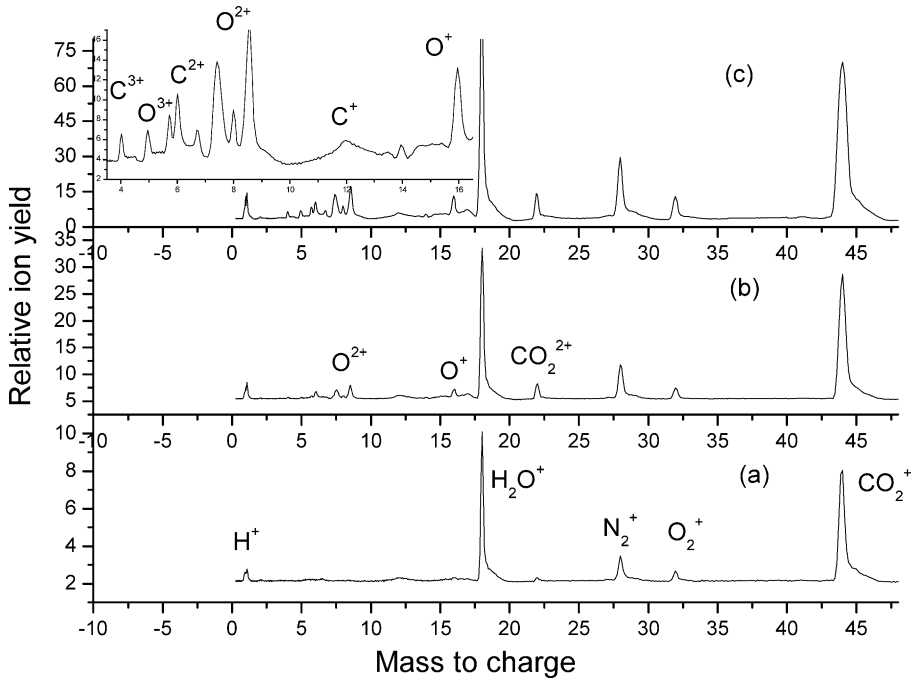

Fig. 1. Typical mass spectra of CO_2 irradiated by 800 nm, 130 fs for an intensity of (a) 1.0×10^{15} W/cm^2, (b) 2.7×10^{15} W/cm^2, (c) 6.8×10^{15} W/cm^2. The polarization axis was collinear with the TOF axis.

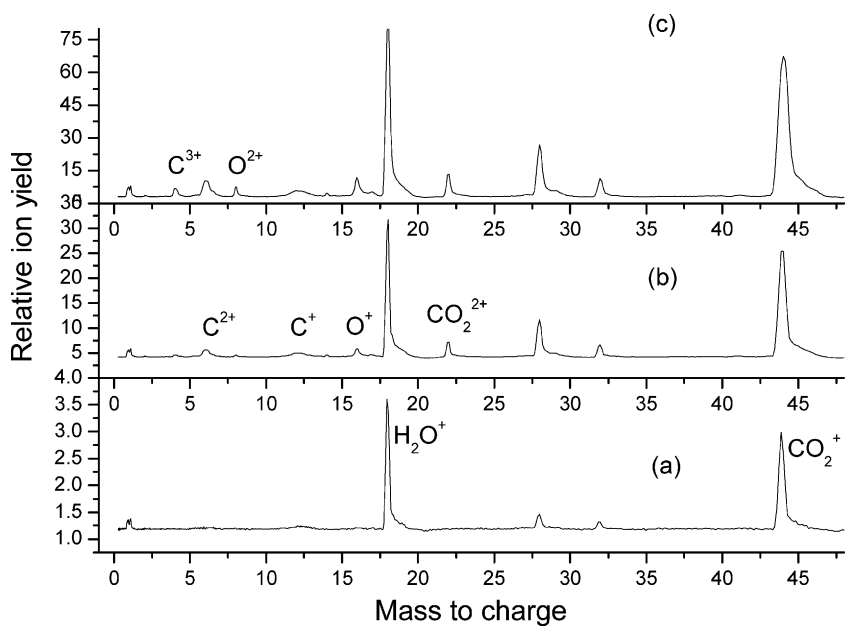

Fig. 2. Typical mass spectra of CO_2 irradiated by 800 nm, 130 fs for an intensity of (a) 1.0×10^{15} W/cm^2, (b) 2.7×10^{15} W/cm^2, (c) 6.8×10^{15} W/cm^2. The polarization axis was perpendicular to the TOF axis.

for the H_2O^+, N_2^+, and O_2^+ ions, which are from the residual water and air in the vacuum chamber. At higher laser intensities, new mass peaks corresponding to the C^+, O^+, C^{2+} and O^{2+} ions are apparent (Figs. 1(b) and 2(b)). When the laser intensity is further increased to 6.8×10^{15} W/cm^2, C^{3+} and O^{3+} ions (Figs. 1(c) and 2(c)) can be observed, which is consistent with the fact that the ionization potentials (in eV) of C^{3+} and O^{3+} ions from the CO_2 molecules are 47.887 and 54.934 eV, respectively [22]. The atom is harder to be ionized with higher ionization potential.

It is noted that singly and highly charged O ion peaks split into double or triple peaks. While the C ion peaks exhibit single peak structure because the carbon atom occupies the central position of the CO_2 molecule. The appearance of the highly charged atomic ions and the peak splitting indicated that these atomic ions are originated from Coulomb explosion of the highly charged molecular ions [12]. Moreover, there is evident difference on mass spectra of CO_2 between the *p*- and *s*-polarization irradiations. The O^{m+} ($m \leq 3$) ions and weak C^{n+} ($n \leq 3$) ions are present for the *p*-polarization. Conversely, the C^{n+} ($n \leq 3$) ions are present and O^{2+} and O^{3+} ion splitting peaks are entirely missing in the *s*-polarization mass spectra. These manifest the occurrence of alignment and bending of CO_2 molecule, as discussed below.

We also measured the variation of CO_2^+, CO_2^{2+}, O^{m+} ($m \leq 3$), C^{n+} ($n \leq 3$) and CO^+ ion yields as a function of the ellipticity (as shown in Fig. 3). It is noted that the ion yields gradually decreased when the laser polarization varied from linearly to elliptically and to circularly. These observations are consistent with the previous reports of Banerjee et al. on N^+ [23] and Liang et al. on Ar^+ yields as a function of the ellipticity [24]. Our data confirm that suppression of ionization occurs for the elliptical and circular polarized lights.

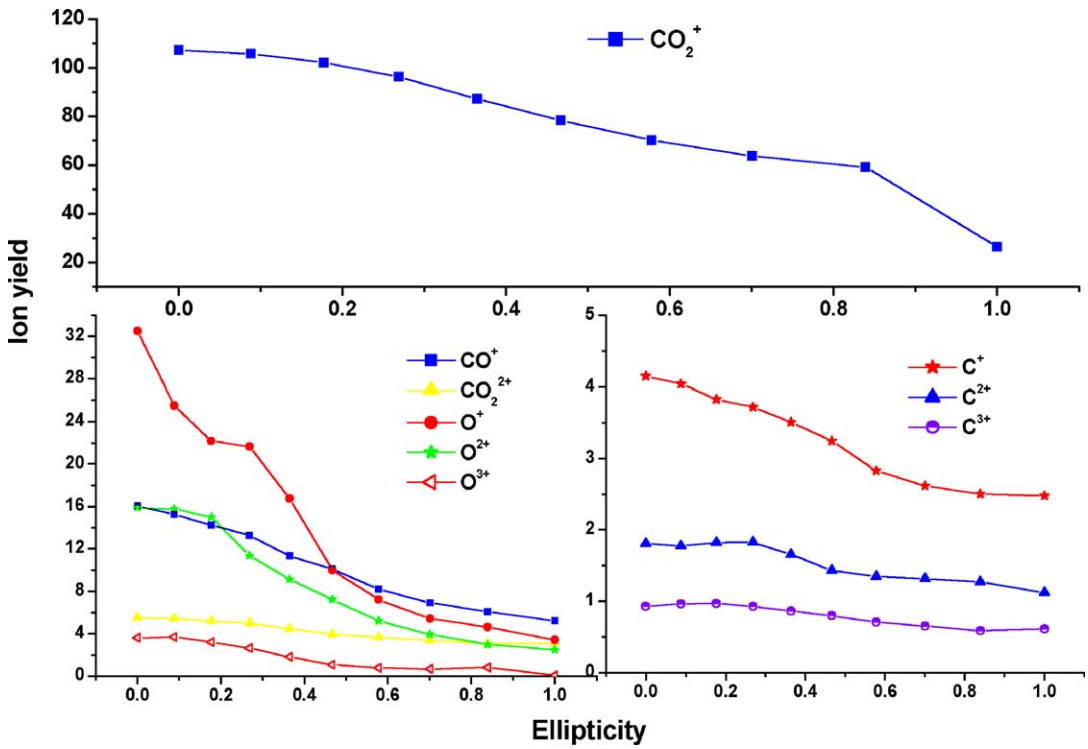

Fig. 3. Dependence of fragment ions yield on ellipticity at the laser intensity of 7.3×10^{15} W/cm^2.

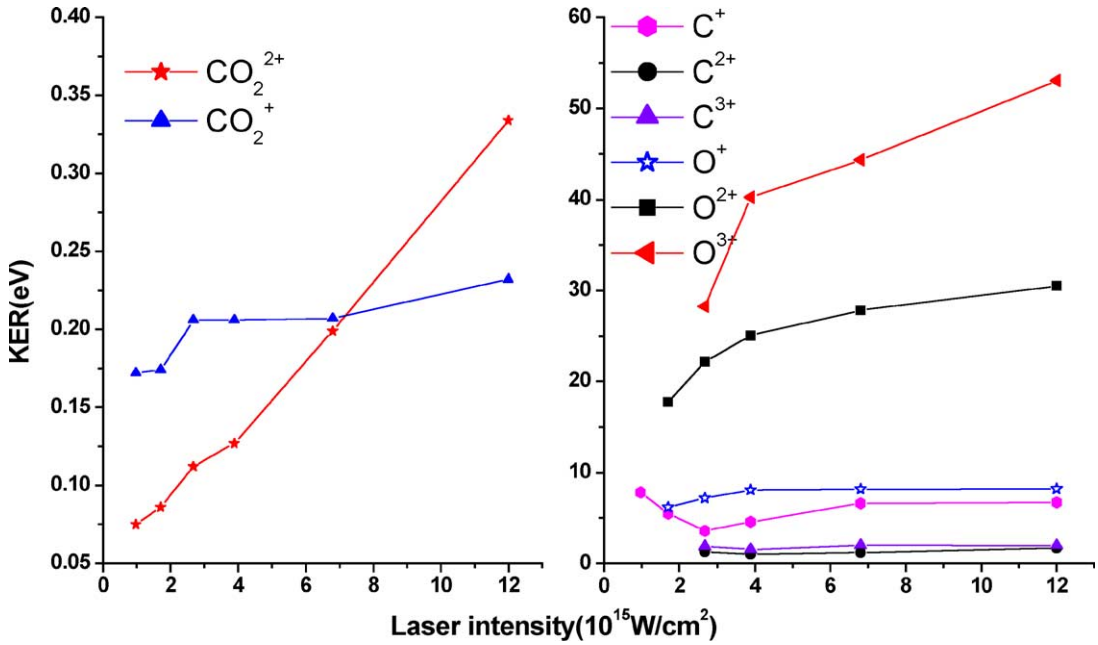

Fig. 4. Measured kinetic energies for CO_2^+, CO_2^{2+}, O^{m+} ($m \leq 3$) and C^{n+} ($n \leq 3$) as a function of laser intensity.

3.2. Kinetic energy for CO_2^+, CO_2^{2+}, O^{m+} ($m \leq 3$) and C^{n+} ($n \leq 3$)

Fig. 4 shows the average kinetic energies for CO_2^+, CO_2^{2+}, O^{m+} ($m \leq 3$) and C^{n+} ($n \leq 3$) as a function of laser intensities. It indicated that the average kinetic energies increase slightly with increasing of laser intensity, which is consistent with the theoretic prediction [25–27] and earlier works on benzene [28]. While, our result is conflicted with previous publications of Lavancier et al. [29] and Cornaggia et al. [30] showed that independent of the kinetic energies of fragment ions on the laser intensity. They suggested that this lack of the dependence of ion energies on laser intensity could be an indication of an intensity-tuned resonance process.

From Fig. 4, we also note that C ions have smaller kinetic energies than that of O ions at the same charge states. If the Coulomb explosion is stepwise, the Coulomb energy should be mainly distributed into carbon ions according to momentum conservation law, which is conflicted with our observations. Therefore, we may suggest that the Coulomb explosion is a concerted process and two CO bonds break simultaneously. On the other hand, the parent molecular ion CO_2^+, CO_2^{2+} have very small kinetic energies, which is consistent with their isotropic angular distributions.

3.3. Fragment angular distributions

Fig. 5 shows angular distributions of the parent molecular ion CO_2^+ and CO_2^{2+}. The two molecular ions exhibit strong isotropic angular distributions, which indicates that the intact parent ions have a random orientation. The angular distributions of specific fragment ions differ significantly with that of the multiply charged parent ions. The angular distributions for the CO^+, O^{m+} ($m \leq 3$), and C^{n+} ($n \leq 3$) ions are shown in Figs. 6, 7 and 8, respectively. The distributions of CO^+, C^+ and O^+ have two components ("soft" dissociation and "hard" dissociation). The weakly underlying isotropic component of O^{2+} ion may be derived from multiply charged H_2O. The angle where the maximum ion count occurs is the

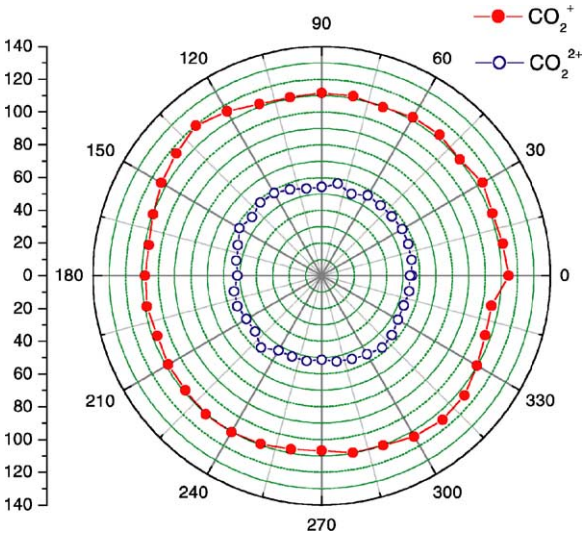

Fig. 5. Angular distributions of the CO_2^+ and CO_2^{2+} parent ions. The CO_2^{2+} ion intensity has multiplied by 10, for ease of viewing.

same for three O ion fragments and the direction is collinear with the TOF axis (0° and 180°). Conversely, the occurrence of maximum ion count is the same for three C ion fragments at the perpendicular direction (90° and 270°). There is also an underlying isotropic component for C^{2+}, C^{3+} distributions, which is similar to C^+ ion.

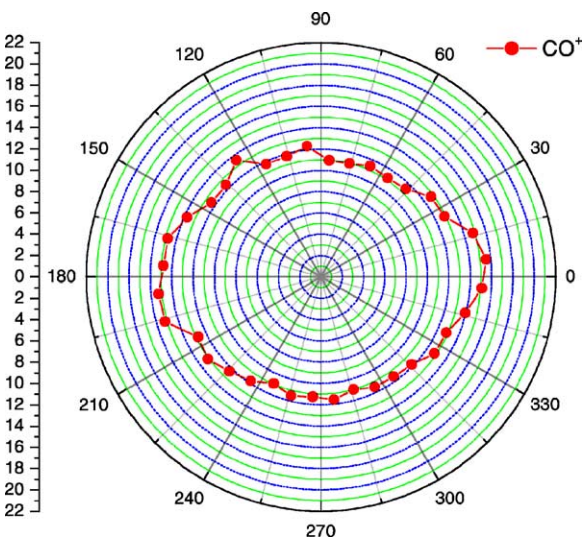

Fig. 6. Angular distributions for the CO^+ ion from CO_2.

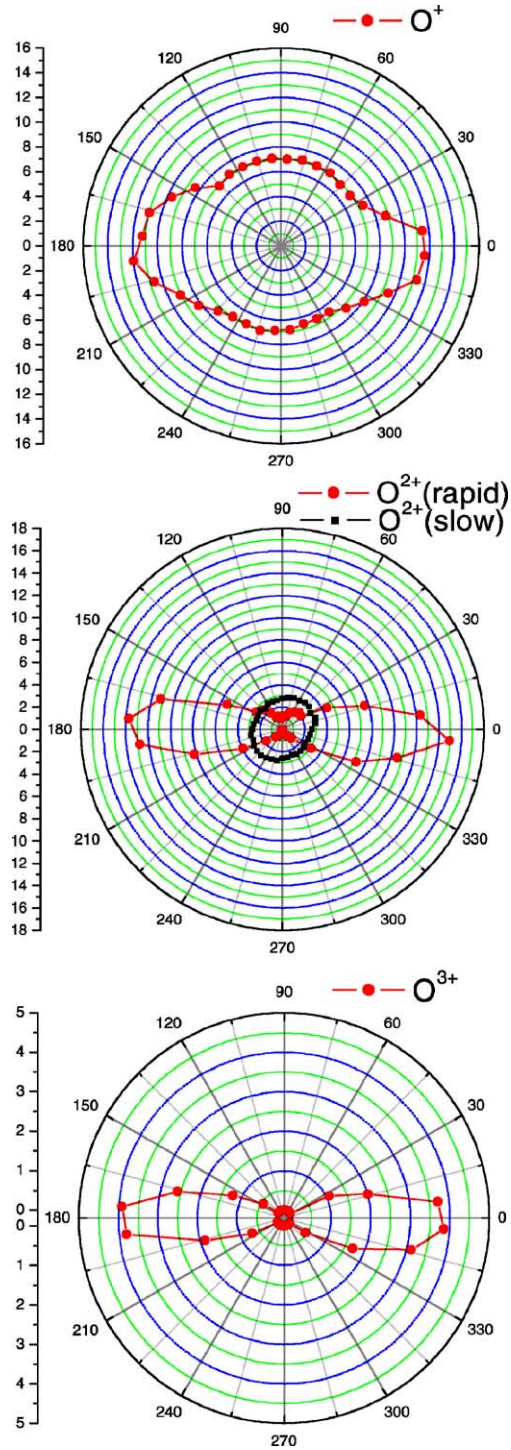

Fig. 7. Angular distributions for the O^{m+} ($m \leq 3$) ion from CO_2.

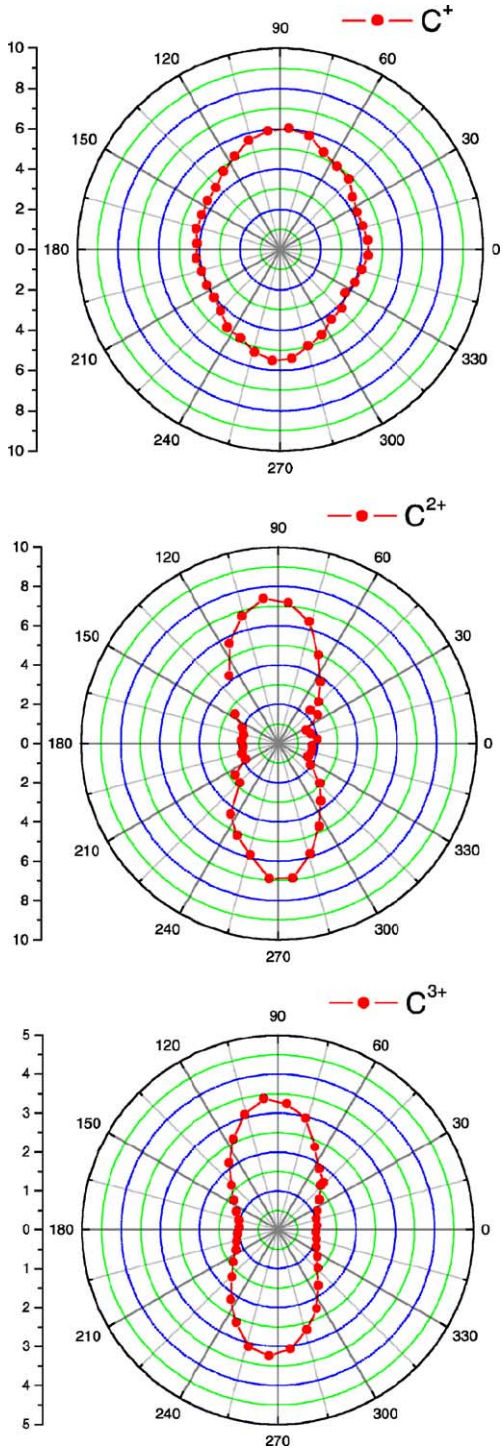

Fig. 8. Angular distributions for the C^{n+} ($n \leq 3$) ion from CO_2.

The origin of the completely opposite behavior for C and O fragments ions is a result of the molecular geometry in the ion state, where the carbon atom occupies the central position of the CO_2 molecule. The CO_2 molecule is slightly bent when irradiated by intense femtosecond laser pulses. The two O–C bonds have a small angle to the electric field of the laser. When the laser field is collinear with the TOF axis, the O^{m+} ($m \leq 3$) ions are ejected along the polarization direction (actually along the bonds) and resulting in the most efficient detection. The greatly reduced C^{n+} ($n \leq 3$) signal is a result of the fragments being ejected perpendicular to the laser polarization after Coulomb explosion.

The anisotropic angular distributions of O^{m+} ($m \leq 3$) and C^{n+} ($n \leq 3$) ions can be attributed to two effects: dynamic alignment and geometric alignment. The method of Ref. [19] is used in this paper. Fig. 9 shows the splitting ion signals of O^+, O^{2+}, O^{3+} of CO_2 for linear polarization and circular polarization with equal electric field amplitude. The signal intensity of O^+ and O^{2+} ions arising from Coulomb explosion for parallel polarization is about 1.2 and 2 times higher than that for circular polarization, respectively. The signal intensity of O^{3+} for circular polarization is near zero, which is consistent with a higher degree of dynamic alignment for higher charge states. This indicates that the dynamic alignment mechanism is responsible for the anisotropic angular distributions of O^{m+} ($m \leq 3$) and C^{n+} ($n \leq 3$) ions.

We have obtained that the FWHM (full width at half maximum) values of the measured angular distributions for the O^+, O^{2+}, O^{3+} are $49.2 \pm 5.3°$, $41.9 \pm 0.1°$, $35.7 \pm 2.2°$, respectively, using Gaussian fit. We observe that the measured angular distributions of O^{m+} ($m \leq 3$) ions from CO_2 become narrower as the charge of the ion increased. These are in agreement with discussion in Refs. [5,12]. As the electric field of the intense laser field could induce a higher dipole moment in the more highly charged molecular ions, the fact that the FWHM become narrower for the higher charge state indicated that dynamic alignment was the main reason for the observed anisotropic angular distribution, which is consistent with the

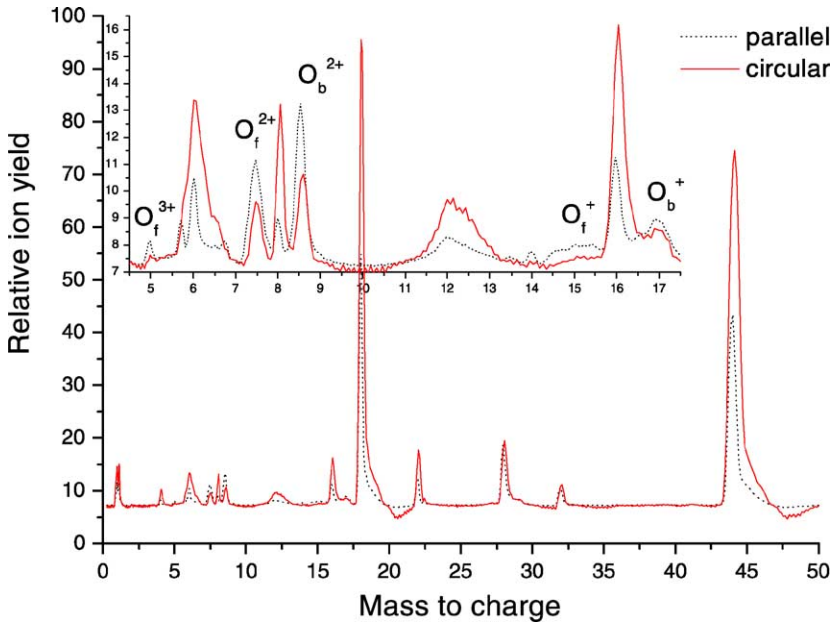

Fig. 9. The splitting ion signals of O^+, O^{2+}, O^{3+} of CO_2 for parallel linear polarization and circular polarization with equal electric field amplitude.

above discussions. We have also obtained that the FWHM values for the C^+, C^{2+}, C^{3+} are $65.1 \pm 7.3^\circ$, $65.1 \pm 0.5^\circ$, $66.2 \pm 1.7^\circ$, respectively. Within the experimental error, the values of the C^{n+} ($n \leq 3$) ions are equal, which is different from that of O^{m+} ($m \leq 3$) ions. So these cannot be interpreted purely in terms of preferential ionization and partial laser-induced alignment of the CO_2 molecule should be involved.

The behavior of the C^{2+} ions is worthy to pay more attention. In our experiments, the C^{2+} ion was aligned orthogonal to the laser electric field in agreement with that presented in Refs. [5,12], where a laser intensity of 1×10^{16} W/cm^2 at a wavelength of 790 nm and pulse duration of 50 fs has been used. But this data is in contrast to that reported by Couris et al. [13] who observed no anisotropy in the angular distribution of C^{2+}, produced by the interaction of CO_2 with 800 nm, 200 fs laser light. Furthermore, the pulse duration dependence of the angular distribution of C^+ ion arose from the dissociation of CS_2, has been investigated by Graham et al. [12]. The results are that the distributions for 150 fs and 1 ps pulses show a similar behavior to that for 50 fs pulse. The isotropic distribution is observed for the longer pulse duration of 300 ps.

The results observed for CO_2 molecule here are different from that obtained with 35-ps second harmonic (532 nm) of Nd:YAG laser pulse [14,15], where the fragment distributions lie totally along the TOF axis. This can be interpreted by the fact that the longer pulse duration of the laser allows the molecule to be aligned sufficiently along the laser field, resulting in C distribution peak with parallel polarization.

4. Conclusions

The interaction of the linearly triatomic molecule CO_2 and intense femtosecond laser fields was experimentally investigated by using a time-of-flight mass spectrometer under different laser polarizations. The observation of C ions have smaller kinetic energies than that of O ions at the same charge states indicates that the Coulomb explosion is a concerted process and two CO bonds break simultaneously. By comparing

time-of-flight spectra under linearly and circularly polarized light, the dynamic alignment mechanism is responsible for the anisotropic angular distributions of O^{m+} ($m \leq 3$) and C^{n+} ($n \leq 3$) ions as well as the degree of dynamic alignment is increasing for higher charge states. The FWHM values of the measured angular distributions for the O^+, O^{2+}, O^{3+} become narrower for the higher charge state. However, the FWHM values of the C^{n+} ($n \leq 3$) ions are equal.

Acknowledgements

This work was supported by the National Key Basic Research Special Foundation (NKBRSF) under grant No. TG1999075207 and the National Natural Science Foundation of China under grant Nos. 10104003, 90206003 and 90101027.

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