International Journal of Mass Spectrometry 336 (2013) 37–42

Contents lists available at SciVerse ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

The dissociative ionization of CO_2 in the 800 nm intense laser field using time-of-flight (TOF) mass spectrometry

Mohamed Elshakre*

Chemistry Department, College of Science, Cairo University, Egypt

ARTICLE INFO

Article history:
Received 1 October 2012
Received in revised form
10 December 2012
Accepted 10 December 2012
Available online 25 December 2012

Keywords:
Dissociative ionization
Intense laser field
Femtosecond laser pulses
Carbon dioxide
Anisotropic angular distribution

ABSTRACT

The dissociation of carbon dioxide in an intense (10^{13}–10^{14} W/cm^2) femtosecond laser field has been investigated. The stepwise nature of the dissociation has been verified experimentally by analyzing the time-of-flight mass spectroscopic patterns at different laser intensities. The experimental identification shows that if the laser intensity is gradually increased, CO_2^+ is first formed, followed by a dissociation of one of the C—O bonds. Further increase of the laser intensity leads to the dissociation of the second C—O bond. Only O^+ fragment ion shows anisotropic angular distribution.

1. Introduction

The basic concepts of physics show that the intensity of the Coulomb field, which binds the electrons and nuclei together in molecules, is about 10^8 V/cm. The same basic physics concepts show that the electric field of an ultrashort intense laser pulse can be of comparable magnitude to this value. Modern ultrashort laser pulses can provide field intensities that exceed such intramolecular field strengths. For the wavelength 800 nm, the electric field amplitude in a laser beam is given by $E = 27.4(I)^{1/2}$, where I is the peak intensity expressed in Watts per square centimeter and E is in Volts per centimeter. It is now established that, if a 100 fs laser pulse is focused to a diameter of 60 μm, average intensities reaching the petawatts range ($\sim 35 \times 10^{15}$ W/cm^2) can be produced. When the field intensity reaches the value 10^{13}–10^{14} W/cm^2, the molecules ionize in a process called field ionization (*FI*) and dissociate in a process called field dissociation (*FD*). In addition, chemical bonds can be broken in all types of molecules even within a single laser shot. The interaction between such strong laser fields and molecules attracts [1–4] and continues to attract considerable interest [5–8]. The effects of the electric field present in intense light fields on molecules results in several phenomena, amongst which, are the bond softening [2], above threshold dissociation (ATD) [7], vibrational trapping [3], molecular alignment [9–12], dissociative ionization [5–8], and Coulomb explosion [13–16]. Most of the experimental investigations are performed for the dissociation of molecules at the laser intensities higher than 10^{14} W/cm^2 [2,13–18], where the results were interpreted in terms of the widely accepted Coulomb explosion mechanism. In the Coulomb explosion model, it is assumed that the molecules suddenly lose two or more electrons, followed by a fragmentation of the resulting multiply charged ion, where the intramolecular Coulomb repulsive forces drive the positively charged fragments to separate. However, it is too difficult to remove two or more electrons from a molecule at the rather moderate laser intensity 10^{13}–10^{14} W/cm^2 and only singly charged ions are expected to be produced. Kong et al. [19–22] have proposed the field-assisted step-wise dissociation (*FAD*) model, which successfully interprets the dissociation of polyatomic molecules in the intensity regime 10^{13}–10^{14} W/cm^2. The *FAD* model has been successful in the interpretation of the dissociation of methane, CH_4 [19], acetone, CH_3COCH_3 [20] and acetaldehyde, CH_3CHO [21] in the rather moderate intensity regime, 10^{13}–10^{14} W/cm^2. The field-assisted (*FA*) step-wise dissociation mechanism assumes that a singly charged molecular ion is formed at the lowest laser intensity range. The FA model also assumes that the dissociation can also take place by gradually increasing the laser intensity and monitoring the dissociation morphology versus the laser intensity, where the step-wise dissociation can be envisaged and demonstrated. This new FA dissociation mechanism implies that the cracking of the chemical bond in an intense laser field can be considered from a view point different from the widely accepted Coulomb explosion mechanism,

* Tel.: +20 2 35676702; fax: +20 2 568 35799.
E-mail addresses: elshakre@gmail.com, elshakr@yahoo.com

1387-3806/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ijms.2012.12.005

which successfully demonstrated the dissociation of molecules in the higher intensity regime 10^{15} W/cm^2 and higher.

The success of the *FA* model has been a motivation to study the dissociation of a molecule, rather smaller than those reported and it is the objective of this work to demonstrate experimentally the step-wise dissociation of the triatomic CO_2 molecule in the intensity regime 10^{13}–10^{14} W/cm^2. No intention to apply the *FA* model to the case of CO_2 presented here but to confirm that the same dissociation pattern found for CH_4, CH_3COCH_3, and CH_3CHO, is always found for CO_2 and one state that the success of the FA model to explain the dissociation of the latter molecules can be also be used to explain the dissociation of the latter. In this work the experimental results of the dissociation of CO_2 will be presented and compared with the dissociation of CO_2 under different experimental conditions. CO_2 is a triatomic molecule and is considered as one of the simplest polyatomic molecules, bridging diatomic molecules, whose dissociation in intense laser fields using the Coulomb explosion model, have been extensively investigated [23–30] and polyatomic molecules whose dissociation in intense laser fields have been investigated using the same model [17,31–44]. The dissociation of CO_2 in the high intense laser field, higher than 10^{15} W/cm^2 has been extensively investigated by Frasinski et al. [45] who first reported the multielectron dissociative ionization of CO_2 at 794 nm and intensity of 10^{16} W/cm^2. Cornaggia et al. [46] used intense laser pulse centered at 790 nm with intensity of 5×10^{15} W/cm^2 to irradiate CO_2. Their results show that the multiply charged parent ions CO_2^{2+} and the multiply charged fragment ions O^{2+}, O^{3+}, C^{2+}, C^{3+}, and C^{4+} also appeared in the mass spectra besides the singly charged parent ions CO_2^{+}, and the singly charged fragment ions CO^{+}, C^{+}, and O^{+}. Sanderson et al. [47] investigated the bending and alignment of CO_2 in the intense laser field using 60 fs, 750 nm which produces 7×10^{15} W/cm^2. Graham et al. [48] detected the angular distribution of fragment ions produced by Coulomb explosion of CS_2 and CO_2 in the intense laser field produced by pulse of 50 fs centered at 790 nm delivering an intensity of 1×10^{16} W/cm^2. Hishikawa et al. [49] investigated the ultrafast deformation geometrical structure of CO_2 in an intense laser field at 1.1×10^{15} W/cm^2 using momentum imaging of the fragment O^{p+} and C^{q+} (p,q = 1–3). It is important to mention that all of these investigations were carried out at laser intensities higher than 10^{15} W/cm^2. At such high intensity, multi-charged ions form, and hence Coulomb explosion model can be used to explain the formation of such multi-charged ions.

Alternatively, the effect of long laser pulse duration, longer than femtoseconds at similar laser intensities was also investigated for CO_2, where the results of the dissociative ionization of CO_2 at laser intensities of 10^{13}–10^{14} W/cm^2 generated from picoseconds laser pulses, show a totally different dissociation morphology, from that shown using fs laser pulses producing similar intensity. Mathur's group [50] investigated the dissociation of CO_2 using 35 ps pulses produced from the output of a laser centered at 532 nm delivering an intensity of 10^{13}–10^{14} W/cm^2. They suggested that the dissociation of molecules depends upon their bond strengths, e.g., molecules such as CS_2, CO_2, and NO_2 whose dissociation energies are less than 6 eV, fragment ions dominate the mass spectra. In contrary, molecules such as N_2 and CO, whose dissociation energies are higher than 6 eV, parent ions dominate the mass spectra.

Regarding the theoretical treatment of the interaction of intense laser fields with CO_2 molecules, the groups of Fujimura [51] and Kono [52] have investigated the electronic and nuclear dynamics of CO_2 and its cations in intense laser fields of 10^{15} W/cm^2 by using the time-dependent adiabatic state approach, where it was found that the ionization of the neutral CO_2 takes place before the field intensity becomes high enough to deform the molecule". Moreover, it was found that when the CO_2 becomes doubly ionized and CO_2^{2+} is produced accompanied by simultaneous symmetric two-bond stretching and one-bond stretching. They also demonstrated that the two-bond stretching is induced by the intense laser field in the lowest time-dependent adiabatic state $|1\rangle$ and this two-bond stretching 1 followed by the occurrence of a large-amplitude bending motion mainly in the second lowest adiabatic state $|2\rangle$ nonadiabatically created from $|1\rangle$ at large internuclear distances by the field. They concluded that that the experimentally observed stretching and bending structures of CO_2^{2+} just before the Coulomb explosion originating from the structural deformation of CO_2^{2+}.

2. Experimental

The laser system used in this study shown in Fig. 1, is a home-built mode-locked femtosecond Ti:sapphire oscillator [53] which was pumped by a diode-pumped, frequency-doubled laser (Verdi Coherent). As a seed pulse, the 800 nm 30 fs laser pulse generated by the oscillator was stretched and then led to a multipass Ti:sapphire amplifier (Quantronix, Odin) which was pumped by the second harmonic of a Nd:YLF laser. The amplified fs laser pulse was compressed to 100 fs producing energy output of ~300 μJ per pulse. The

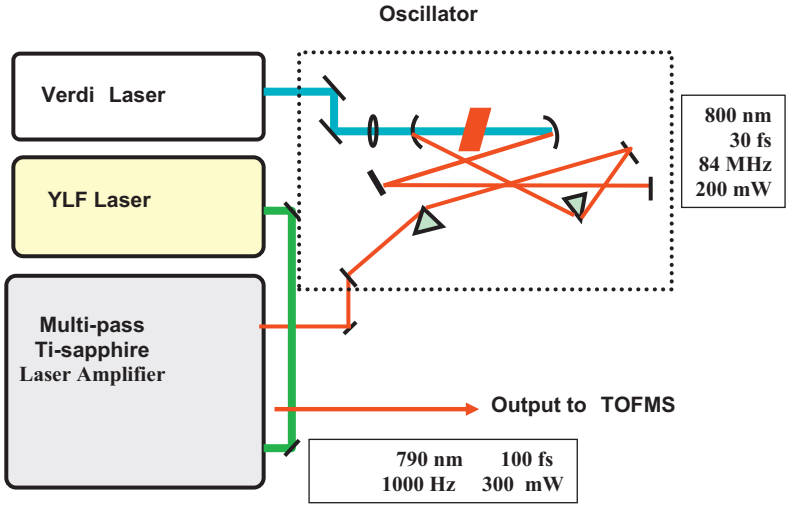

Fig. 1. Experimental lay out of the laser system coupled to the time-of-flight mass spectrometer (TOF-MS).