J. Opt. 19 (2017) 124008 (5pp)

https://doi.org/10.1088/2040-8986/aa

Ellipticity dependent symmetric break of doubly ionized acetylene in strong laser fields

Xiaochun Gong[®], Hui Li, Peifen Lu, Qiying Song, Qinying Ji, Kang Lin, Wenbin Zhang, Junyang Ma, Hanxiao Li, Heping Zeng and Jian Wu¹

State Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062, People's Republic of China

E-mail: xcgong@lps.ecnu.edu.cn

Received 15 May 2017, revised 25 September 2017 Accepted for publication 16 October 2017 Published 3 November 2017

Abstract

We experimentally investigate symmetric dissociative double ionization of acetylene in femtosecond laser pulses of various ellipticities. Two dissociative ionization pathways with kinetic energy release of 4.8 and 6.0 eV, denoted as the low- and high- E_N pathways, are observed in the spectrum of the ejected fragment ions. The relative yield of the high- E_N gradually increases as compared to the low- E_N when the polarization of the driving laser field is adjusted from linear to circular with increasing ellipticity. The low and high- E_N fragment ions exhibit distinct angular distributions for various field ellipticities. It is attributed to the releasing of electrons from orbitals of different symmetries in producing the low- and high- E_N pathways.

Keywords: strong field laser physics, ultrafast phenomena, hydrocarbon molecule, double ionization

(Some figures may appear in colour only in the online journal)

Tracking and controlling the electronic and nuclear motions of molecules using intense ultrashort laser pulses has attracted much attention in past decades. One of the key ingredients is to coherently control the location and direction of molecular bond breaking. For instance, by tuning the carrier-envelope phase of a few-cycle or the relative phase of a two-color ultrashort laser pulses, the breaking of molecular bonds can be finely steered to desired direction [1], ranging from the simplest H₂ molecule to polyatomic hydrocarbon molecules [2–6]. The directional bond breaking control was recently achieved in two-dimensional space using phase-controlled orthogonally or circularly polarized two-color laser fields [7, 8]. For multielectron molecules, in addition to the directional bond breaking, different channels can be formed when electrons from various orbitals are released [9–12]. It allows us to steer the formation of different channels by selectively freeing electrons from various orbitals using waveform controlled ultrashort laser pulses [13].

Here, we experimentally investigate the symmetric dissociative double ionization of acetylene, i.e. $C_2H_2 + n\hbar\omega \rightarrow CH^+ + CH^+ + 2e$ denoted as (CH^+, CH^+) channel, in intense femtosecond laser pulses of various ellipticities. Two dissociation pathways of the (CH⁺, CH⁺) channel are observed with kinetic energy releases (KER) of the ejected fragment ions around 4.8 and 6.0 eV, denoted as the low- and high- E_N pathways, respectively. The low- and high- E_N ion fragments exhibit distinct angular distributions and their relative yields is altered when the field polarization is adjusted from linear to circular. The low- E_N pathway which dissociates on the ${}^{3}\Pi$ state by removing one highest occupied molecular orbital (HOMO, $1\pi_{\mu}$) and one HOMO-1 $(3\sigma_{a})$ electrons; while the high- E_N pathway is mostly formed by removing two HOMO $(1\pi_u)$ electrons and dissociates on the ${}^{1}\Sigma_{o}^{+}$ state via a trans-bent mode [14]. By changing the ellipticity of the laser field, we can selectively free electrons from



¹ This article belongs to the special issue: <u>Emerging Leaders</u>, which features invited work from the best early-career researchers working within the scope of the *Journal of Optics*. Dr Jian Wu was selected by the Editorial Board of the *Journal of Optics* as an Emerging Leader.



Figure 1. (a) Schematic diagrams of the experiment setup. (b) Potential energy curves of C_2H_2 , $C_2H_2^+$, and $C_2H_2^{2+}$ with a frozen C–H internuclear distance at $R_{CH} = 1.15$ Å. Two pathways in producing the (CH⁺, CH⁺) channel are illustrated by the black arrows. The insets schematically illustrate the profiles of the HOMO and HOMO-1 of the C_2H_2 [13, 14, 19, 21].

various orbitals and hence steer the breaking of the molecules along a favorable pathway.

We performed the experimental measurements in a standard 'cold-target recoil-ion momentum spectroscopy' setup [15–17]. As schematically illustrated in figure 1(a), femtosecond laser pulses (25 fs, 790 nm, 10 kHz) of various ellipticities are focused onto a supersonic gas jet with a mixture of C₂H₂ (5%) and He (95%) by a concave reflection mirror (f = 7.5 cm) inside the apparatus. The peak intensity of the linearly polarized laser pulse in the reaction region is estimated to be $I_0 \sim 2 \times 10^{14}$ W cm⁻² [18]. The photoionization created fragment ions were accelerated and guided by a weak homogeneous static electric field to be detected by a time- and position-sensitive microchannel plate detector at the end of the spectrometer, where the 3D momenta of the ejected ions are reconstructed from the measured time-of-flights and positions of the impacts during the offline analysis.

The electronic configuration of the ground state $X^{1}\Sigma_{g}^{+}$ of the neutral acetylene is $1\sigma_{g}^{2}1\sigma_{u}^{2}2\sigma_{g}^{2}2\sigma_{u}^{2}3\sigma_{g}^{2}1\pi_{u}^{4}$. As the molecule irradiated by an intense ultrashort laser pulse, the double ionization mainly frees two HOMO $(1\pi_{u})$ electrons and may populate three lowest metastable dication states, i.e. the triplet state of ${}^{3}\Sigma_{g}^{-}$ and the singlet states of ${}^{1}\Delta_{g}$ and ${}^{1}\Sigma_{g}^{+}$. However, removing one electron from the HOMO-1 $(3\sigma_{g})$ or HOMO-2 $(2\sigma_{u})$ will populate the high excited singlet or triplet repulsive states [14, 19–25]. For example, the double ionization involving the removal of one electron from the HOMO-1 (or HOMO-2) by strong field ionization may *in*itiate the deprotonation channel $C_{2}H_{2} + n\hbar\omega \rightarrow H^{+} + C_{2}H^{+}$ and isomerization breakup channel $C_{2}H_{2} + n\hbar\omega \rightarrow C^{+} + CH_{2}^{+}$ [10, 13, 22, 23], which are denoted as $(H^{+}, C_{2}H^{+})$ and (C^{+}, CH_{2}^{+}) , respectively. Here, we focus on the (CH^{+}, CH^{+}) channel accompanied by the symmetric breakup of C-C bond.

The photoion-photoion coincidence spectrum of the ion fragments allows us to clearly identify different channels. As shown in figure 2(a), the symmetric breakup channel can be well distinguished from the other channels. The left panel of figure 2(b) presents the KER of the fragment ions, E_N , of the (CH⁺, CH⁺) channel in linearly polarized laser fields. It can be identified into the low- and high- E_N regions with E_N peaked around $E_N = 4.8$ and 6.0 eV as labeled by the yellow and green patterns, respectively. As shown in the right panel of figure 2(b), the angular distribution of the (CH^+, CH^+) channel $\phi_{(CH^+, CH^+)}$ changes as the increasing of E_N . The low and high- E_N regions exhibit two different angular distributions as plotted in figure 2(c), indicating two different routes for the C-C bond symmetric breakup. The angular distribution of the high- E_N pathway shows maxima around $\pm 30^\circ$ with respect to the polarization direction of the ionizing field, indicating the participation of the π_u electron (HOMO) of the C_2H_2 [23, 25–29] with a nodal plane of the electron density cutting along the molecular axis as illustrated in figure 1(b). The angular distribution of the low- E_N pathway maximizes along the field direction, indicating the important role of the $3\sigma_a$ electron (HOMO-1).

Figure 1(b) presents the relevant potential energy curves of C₂H₂ cutting along the C–C bond (R_{CC}) with a frozen C–H bond at the equilibrium internuclear distance of $R_{CH} \sim 1.15$ Å [13, 14, 19, 21]. The low- E_N pathway could be accessed as the following: by removing one HOMO ($1\pi_u$) and one HOMO-1 ($3\sigma_g$) electrons, the lowest triplet states ${}^{3}\Pi_u$ and singlet state ${}^{1}\Pi_u$ may be populated via an intermediate cationic state of $A^2\Sigma_g^+$. Stretching along the C–C bond, the barrier of ${}^{3}\Pi_u$ state is 1.5 eV lower than the ${}^{1}\Pi_u$ state.



Figure 2. (a) Photoion–photoion coincidence spectrum of the dissociative double ionization channels of C_2H_2 , including (H⁺, C_2H^+), (C⁺, CH₂⁺) and (CH⁺, CH⁺), where the C–C bond breaking channels are enlarged as the inset. The 'tof1' and 'tof2' are the TOFs of the first and second hits measured by the ion detector. (b) Kinetic-energy (E_N) distribution of (CH⁺, CH⁺) versus the angular distribution $\phi_{(CH^+, CH^+)}$ in *y*–*z* plane. The left panel shows the KER spectrum of the (CH⁺, CH⁺) channel. (c) Angular distributions of the fragments ions of the (CH⁺, CH⁺) channel for the low- E_N (4.2 eV < E_N < 5.5 eV, labeled by red circles) and high- E_N (5.8 eV < E_N < 9.0 eV, labeled by solid blue boxes) pathways, respectively.

Meanwhile, the asymmetric C-H elongation can induce an avoided crossing between the triplet state ${}^{3}\Pi_{\rho}$ and ${}^{3}\Pi_{u}$, which makes the distorted ${}^{3}\Pi$ state to be dissociative along the C–C bond. The Π states can also interact with the dissociative excited state of ${}^{3}\Sigma_{u}^{+}$, ${}^{1}\Sigma_{u}^{-}$, or ${}^{3}\Delta_{u}$ via conical intersections to promote the C–C bond breaking. The high- E_N pathway may originate from the metastable dication states of ${}^{3}\Sigma_{g}^{-}, {}^{1}\Delta_{g}$, and ${}^{1}\Sigma_{\rho}^{+}$ by removing two $1\pi_{u}$ electrons [14, 19]. In general, the bond breaking probability of the low-lying metastable states is much lower than the excited dissociative states. However, a molecular bent transition process [30] can lead to a conical intersection between the states of ${}^{1}\Sigma_{g}^{+}$ and ${}^{1}\Delta_{g}$ [14], which is governed by the vibronic couplings. It promotes dissociation of the doubly ionized acetylene to produce the (CH⁺, CH⁺) in the high- E_N region. As compared to the single-photon excitation by the synchrotron radiation, the ionization and dissociation of molecules are complicated in strong laser fields where the molecular orientation, electron recollision, and distorted potential curves will alter the dynamics.

Interestingly, the KER spectrum and angular distributions of the low- and high- E_N pathways change when the polarization of the ionizing field is changed from linear to circular. The right panels of figures 3(a)-(c) show the angular distribution of $\phi_{(CH^+,CH^+)}$ versus E_N for various field ellipticities of $\varepsilon = 0.23$, 0.65, and 0.94, respectively. The double peak structure of the KER spectrum is very sensitive to the polarization of the ionizing field. The low- and high- E_N pathways become well separated in the KER spectrum of the (CH⁺, CH⁺) channel as the increasing of the field ellipticity. However, the peak position is independent on the change of the ellipticity of the ionizing laser field. As shown in figure 3, the angular distribution of the fragment ions of the high- E_N pathway changes dramatically as compared to the low- E_N pathway when the ellipticity of the driving laser field increases. The angular distribution of the low- E_N pathway is much narrow and concentrates around the major axis of the elliptically polarized ionizing field. It indicates the important role of the $3\sigma_{g}$ electron which is favored to be freed along the maximum of the laser field, i.e. the molecule orientating along the major axis of the elliptical field is preferred to be ionized. However, the angular distribution of high- E_N pathway becomes much broad when the ellipticity of the driving laser field increases. As shown in figure 3(c), for the high- E_N pathway, a homogenous angular distribution is observed in a nearly circularly polarized laser pulse ($\varepsilon = 0.94$). For the high- E_N pathway by breaking the C–C bond via the distorted metastable dication states of ${}^{1}\Sigma_{g}^{+}$, the generated CH⁺/CH⁺ fragment pair may undergo a spatial rotation during the dissociation process [14], which slightly broadens the angular distributions of the fragment ions. Owing to the releasing of two $1\pi_{\mu}$ electrons, the angular distribution of the high- E_N pathway is much broader than the low- E_N pathway, as already demonstrated in linearly polarized field as shown in figure 1(c).

The accessibility of the high- E_N pathway increases as the polarization of the laser field changes from linear to circular. To quantify it, as presented in figure 4, the yield ratio of the high- to low- E_N pathway increases gradually when the ellipticity of the laser field increases from 0 to 1. The yield ratio of the high- to low- E_N pathway in linear polarization is about 0.8, i.e. the probability of the C-C bond breaking via the metastable dication state of ${}^{1}\Sigma_{g}^{+}$ almost equals to the pathway upon ${}^{3}\Pi$ state. As we change the ellipticity of the ionizing laser field to be close to circular polarization $(\varepsilon = 0.94)$, the relative yield ratio increases to 3.0, i.e. the high- E_N pathway is favored to be accessed than the low- E_N pathway. To understand this ellipticity dependence of the accessibility of different pathways, we track back to the population mechanism of different dication states. The low- E_N pathway originates from the dissociative ${}^3\Pi$ state which is about 3.0 eV above the ${}^{1}\Sigma_{g}^{+}$ state. The electron recollision excitation plays an important role in populating the excited state from the ground state, which is suppressed in



Figure 3. KER distributions of the (CH⁺, CH⁺) channel as a function of the angular distribution $\phi_{(CH^+, CH^+)}$ at various ellipticities of the laser field. The left pannels plot the corresponding KER spectra.

circular polarization [13, 22, 31, 32] and thus may reduce the yield of low- E_N pathway. On the contrary, the high- E_N dissociation pathway originates from the distorted metastable states ${}^{1}\Sigma_{g}^{+}$ induced by conical intersection and a bent transition mode during the C–C bond breaking. The bent geometry of the conical intersection distorted ${}^{1}\Sigma_{g}^{+}$ state is not closed by the elliptically polarized laser field owning to the polyatomic



Figure 4. Relative yield ratio of high- E_N over low- E_N pathway as a function of the ellipticity of the ionizing laser pulse.

molecular orientation dependence [33, 34]. The rotational– vibrational coupling of the metastable state ${}^{1}\Sigma_{g}^{+}$ may also induce a slight rotation of the molecule prior to dissociation. Meanwhile the elliptically polarized laser field may enhance the rotation of the molecule during its dissociation, which will increase the yield of the high- E_{N} pathway when the laser field is changed from linear to circular.

In summary, we experimentally investigated the symmetric dissociative double ionization of acetylene in ultrafast strong laser pulses of various ellipticities. Our results demonstrate that the low- and high- E_N pathways of the symmetric C–C bond breakup channel is governed by the releasing of electrons from different orbitals with the σ -type and π -type symmetries. Furthermore, the relative yield between low- and high- E_N pathways can be controlled by changing the ellipticity of the ionizing laser field. Our experiments give a new impetus to control the complex fragmentation dynamics of polyatomic molecules in strong laser field.

Acknowledgments

This work is supported by the National Natural Science Fund (Grants No. 11425416, No. 61690224, and No. 11621404), and the 111 project of China (Grant No. B12024).

ORCID iDs

Xiaochun Gong () https://orcid.org/0000-0002-4826-6049

References

 Kling M F et al 2006 Control of electron localization in molecular dissociation Science 312 246

- [2] Ray D *et al* 2009 Ion-energy dependence of asymmetric dissociation of D₂ by a two-color laser field *Phys. Rev. Lett.* 103 223201
- [3] Wu J et al 2013 Understanding the role of phase in chemical bond breaking with coincidence angular streaking *Nat. Commun.* 4 2177
- [4] Kling M F, von den Hoff P, Znakovskay I and de Vivie-Riedle R 2013 (Sub-)femtosecond control of molecular reactions via tailoring the electric field of light *Phys. Chem. Chem. Phys.* 15 9448
- [5] Alnaser A S *et al* 2014 Subfemtosecond steering of hydrocarbon deprotonation through superposition of vibrational modes *Nat. Commun.* 5 3800
- [6] Song Q, Gong X, Ji Q, Lin K, Pan H, Ding J, Zeng H and Wu J 2015 Directional deprotonation ionization of acetylene in asymmetric two-color laser fields J. Phys. B: At. Mol. Opt. Phys. 48 094007
- [7] Gong X, He P, Song Q, Ji Q, Pan H, Ding J, He F, Zeng H and Wu J 2014 Two-dimensional directional proton emission in dissociative ionization of H₂ *Phys. Rev. Lett.* **113** 203001
- [8] Lin K et al 2016 Directional bond breaking by polarizationgated two-color ultrashort laser pulses J. Phys. B: At. Mol. Opt. Phys. 49 025603
- [9] Akagi H, Otobe T, Staudte A, Shiner A, Turner F, Dörner R, Villeneuve D M and Corkum P B 2009 Laser tunnel ionization from multiple orbitals in HCl Science 325 1364
- [10] Gong X, Song Q, Ji Q, Pan H, Ding J, Wu J and Zeng H 2014 Strong-field dissociative double ionization of acetylene *Phys. Rev. Lett.* **112** 243001
- [11] Wolter B et al 2016 Ultrafast electron diffraction imaging of bond breaking in di-ionized acetylene Science 354 308
- [12] Ji Q et al 2015 Orbital-resolved strong-field single ionization of acetylene Phys. Rev. A 92 043401
- [13] Xie X et al 2012 Attosecond-recollision-controlled selective fragmentation of polyatomic molecules *Phys. Rev. Lett.* 109 243001
- [14] Duflot D, Robbe J-M and Flament J-P 1995 Ab initio study of the acetylene and vinylidene dications fragmentation J. Chem. Phys. 102 355
- [15] Ullrich J, Moshammer R, Dorn A, Dörner R, Schmidt L Ph H and Schmidt-Böcking H 2003 Recoil-ion and electron momentum spectroscopy: reaction-microscopes *Rep. Prog. Phys.* 66 1463
- [16] Dörner R, Mergel V, Jagutzki O, Spielberger L, Ullrich J, Moshammer R and Schmidt-Böcking H 2000 Cold target recoil ion momentum spectroscopy: a 'momentum microscope' to view atomic collision dynamics *Phys. Rep.* 330 95
- [17] Jagutzki O et al 2002 Multiple hit readout of a microchannel plate detector with a three-layer delay-line anode IEEE Trans. Nucl. Sci. 49 2477

- [18] Alnaser A S, Tong X-M, Osipov T, Voss S, Maharjan C M, Shan B, Chang Z and Cocke C L 2004 Laser-peak-intensity calibration using recoil-ion momentum imaging *Phys. Rev.* A 70 023413
- [19] Thissen R, Delwiche J, Robbe J M, Duflot D, Flament J P and Eland J H D 1993 Dissociations of the ethyne dication $C_2H_2^{2+}$ J. Chem. Phys. **99** 6590
- [20] Osipov T et al 2008 Fragmentation pathways for selected electronic states of the acetylene dication J. Phys. B: At. Mol. Opt. Phys. 41 091001
- [21] Gaire B *et al* 2014 Photo-double-ionization of ethylene and acetylene near threshold *Phys. Rev.* A **89** 013403
- [22] Xie X et al 2014 Selective control over fragmentation reactions in polyatomic molecules using impulsive laser alignment *Phys. Rev. Lett.* **112** 163003
- [23] Doblhoff-Dier K, Kitzler M and Gräfe S 2016 Theoretical investigation of alignment-dependent intense-field fragmentation of acetylene *Phys. Rev.* A 94 0134
- [24] Li Z *et al* 2017 Ultrafast isomerization in acetylene dication after carbon *K*-shell ionization *Nat. Commun.* **8** 453
- [25] Lötstedt E, Kato T and Yamanouchi K 2013 Intramolecular electron dynamics in the ionization of acetylene by an intense laser pulse J. Chem. Phys. 138 104304
- [26] Lin C D, Tong X-M and Zhao Z 2006 Effects of orbital symmetries on the ionization rates of aligned molecules by short intense laser pulses J. Mod. Opt. 53 21
- [27] Tolstikhin O I, Morishita T and Madsen L B 2011 Theory of tunneling ionization of molecules: weak-field asymptotics including dipole effects *Phys. Rev.* A 84 053423
- [28] Tong X-M, Zhao Z and Lin C D 2002 Theory of molecular tunneling ionization *Phys. Rev.* A 66 033402
- [29] Alnaser A S, Maharjan C M, Tong X-M, Ulrich B, Ranitovic P, Shan B, Chang Z, Lin C D, Cocke C L and Litvinyuk I V 2005 Effects of orbital symmetries in dissociative ionization of molecules by few-cycle laser pulses *Phys. Rev.* A **71** 031403
- [30] Wells E et al 2013 Adaptive strong-field control of chemical dynamics guided by three-dimensional momentum imaging *Nat. Commun.* 4 2895
- [31] Corkum P B 1993 Plasma perspective on strong field multiphoton ionization *Phys. Rev. Lett.* 71 1994
- [32] Dietrich P, Burnett N H, Ivanov M and Corkum P B 1994 High-harmonic generation and correlated two-electron multiphoton ionization with elliptically polarized light *Phys. Rev.* A 50 R3585
- [33] Demekhin P V and Cederbaum L S 2013 Light-induced conical intersections in polyatomic molecules: general theory, strategies of exploitation, and application *J. Chem. Phys.* **139** 154314
- [34] Petrovic V S *et al* 2013 Enhancement of strong-field multiple ionization in the vicinity of the conical intersection in 1,3cyclohexadiene ring opening *J. Chem. Phys.* **139** 184309