

# Directional deprotonation ionization of acetylene in asymmetric two-color laser fields

Qiyong Song, Xiaochun Gong, Qinying Ji, Kang Lin, Haifeng Pan, Jingxin Ding, Heping Zeng and Jian Wu

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

E-mail: [jwu@phy.ecnu.edu.cn](mailto:jwu@phy.ecnu.edu.cn)

Received 8 October 2014, revised 18 December 2014

Accepted for publication 22 December 2014

Published 10 April 2015



CrossMark

## Abstract

We experimentally investigate the deprotonation dissociative double ionization of an acetylene molecule by an asymmetric two-color laser pulse. We find that the ejection direction of the proton, and hence the directional C–H bond breaking of a polyatomic hydrocarbon molecule, can be controlled by finely tuning the phase of a two-color laser pulse.

Keywords: strong-field ionization, hydrocarbon molecule, two-color laser pulse

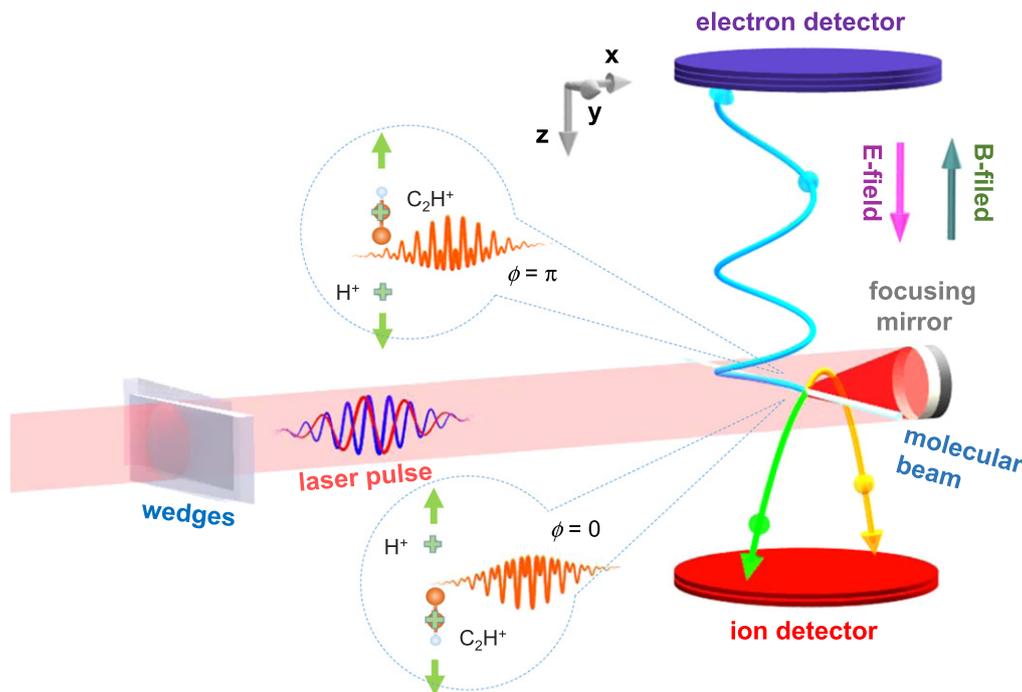
(Some figures may appear in colour only in the online journal)

Coherent control of the directional bond breaking of a molecule is interesting to steer the element chemical reactions [1]. It can be achieved by using phase-controlled asymmetric few-cycle [2, 3] or two-color [4–10] ultrashort laser pulses. The underlying physics of the directional bond breaking varies for different molecules and ionization processes. It includes the field-driven localization of the remaining electron following the single ionization of  $H_2$  when it dissociates into the  $p + H$  channel [1–5]. The ejection direction of the proton is essentially determined by the phase of laser field at the ionization moment [11]. Such electron localization is very recently demonstrated in the two-dimensional stage [12], which depends on the kinetic energy and emission direction of the ejected ionic fragment. As described by the molecular Ammosov–Delone–Krainov (MO-ADK) theory [13, 14] or the strong field approximation (SFA) [15], the directional bond breaking of a molecule with asymmetric orbital, e.g. CO, is dominated by the profile of the ionizing orbital [16] and affected by the linear Stark effect [17, 18]. As compared to the single ionization, the field direction dependent enhanced ionization at the stretched critical internuclear distance [19–24] plays an important role in directional multi-electron ionization of molecules.

However, almost all the foregoing controls of the field ionization induced directional bond breaking are focused on

the diatomic or triatomic molecules. Such bond breaking control will be much more interesting for polyatomic hydrocarbon molecules [25, 26], which serves as a major building block in the chemical reactions. By using a phase-stabilized few-cycle near-infrared laser pulse, it was recently demonstrated that the directional breaking of the C–H bond of an acetylene molecule ( $C_2H_2$ ) can be controlled by the carrier-envelope-phase (CEP) of an intense 4 fs laser pulse [27]. A weak asymmetry of the directional C–H bond breaking ( $\sim 4\%$ ) was observed at the laser field intensity of  $2 \times 10^{14} \text{ W cm}^{-2}$ , which was explained as the CEP-dependent superposition of various vibrational modes. On the other hand, probed by the coincidence angular streaking with an elliptically polarized multicycle near-infrared laser pulse, we recently observed an asymmetry of  $\sim 40\%$  of the directional C–H bond breaking in the deprotonation double ionization of  $C_2H_2$  [28]. The observed directional C–H bond breaking critically depends on the internuclear distance and the laser field direction at the ionization moment, agreeing very well with the scenario of electron-localization assisted enhanced ionization [19–24, 29].

In this paper, we demonstrate the directional control of the C–H bond breaking in dissociative double ionization of  $C_2H_2$  by using a phase-controlled two-color laser pulse. As compared to the pioneering experiments [27, 28], our results



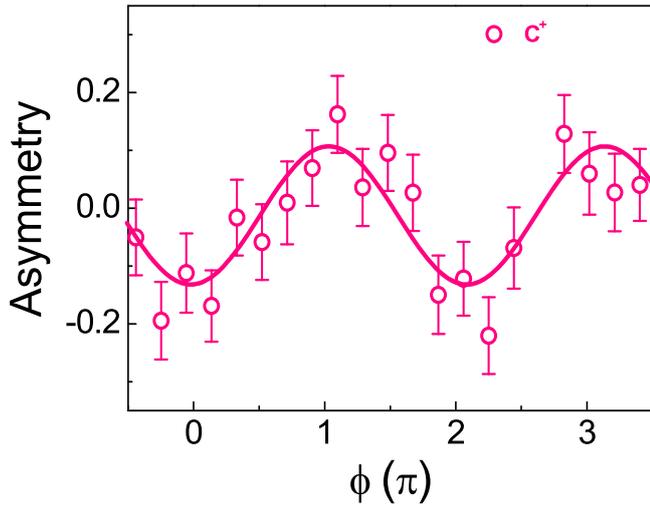
**Figure 1.** Schematic diagram of the experiment apparatus. The linearly polarized two-color laser pulse propagating along  $x$ -axis is focused by a concave mirror onto a supersonic molecular beam propagating along the  $y$ -axis. The laser ionization induced ions and electrons are accelerated by a weak static electric field and detected in coincidence by two detectors at the opposite ends of the spectrometer. A weak homogeneous magnetic field is employed to have a full  $4\pi$  solid angle of the electron detection. As schematically illustrated in the insets, the directional C–H bond breaking is investigated by tracing the ejection direction of  $H^+$  from the  $(H^+, C_2H^+)$  channel, which can be controlled by finely tuning the phase of the two-color laser pulse.

show a different phase dependence of the directional C–H bond breaking. It illustrates altered mechanisms, i.e. the roles of the asymmetric profile of the ionizing orbital and the electron recollision in the double ionization, for the directional C–H bond breaking in our two-color laser pulse of low field intensity.

We performed the experiment in an ultrahigh vacuum reaction microscope setup of COLd target recoil ion momentum spectroscopy (COLTRIMS) [30, 31], as schematically illustrated in figure 1. The linearly polarized two-color laser pulse is collinearly produced by frequency-doubling a near-infrared femtosecond pulse from a multipass amplifier Ti:sapphire laser system (25 fs, 790 nm, 10 kHz) in a  $150\ \mu\text{m}$  thick  $\beta$ -barium borate crystal as detailed in [32]. The polarization of the fundamental-wave (FW) is rotated to be parallel to that of the second-harmonic (SH) (along the  $z$ -axis) by using a dual-wavelength waveplate. The time lag between them was compensated with a birefringent  $\alpha$ -barium borate crystal. The relative phase  $\phi$  between the FW and SH waves of the two-color pulse is continuously varied by scanning the inset of a pair of fused-silica wedges. The produced two-color laser pulse is focused onto the supersonic molecular beam by a concave reflection mirror ( $f=75\ \text{mm}$ ) inside the apparatus. The supersonic molecular beam is produced by co-expanding a mixture of 10% acetylene and 90% helium gas through a  $30\ \mu\text{m}$  nozzle under a driving pressure of 1.5 bar. The laser intensities of the FW and SH fields in the interaction region are measured to be  $I_{\text{FW}}=2.2\times 10^{13}$  and  $I_{\text{SH}}=7.5\times 10^{12}\ \text{W cm}^{-2}$ , respectively. The fragmented ions

and electrons ejected from the multiply ionized molecule are accelerated by a weak homogeneous electric field ( $6.87\ \text{V cm}^{-1}$ ) and detected by two time- and position-sensitive detectors at the opposite ends of the spectrometer. A weak magnetic field (8.29 Gauss) produced by a pair of Helmholtz coils is used to obtain  $4\pi$  solid angle detection of the electron. The three-dimensional momentum vectors of the electrons and ions are retrieved from the measured times-of-flight and positions of impact on the detectors during the off-line analysis.

Calibration of the absolute phase  $\phi$  of the two-color pulse is one of the most important steps to determine the phase-dependent directional C–H bond breaking of the hydrocarbon molecule. We calibrate the phase  $\phi$  of the two-color pulse by using the laser-field direction dependent dissociative double ionization of the CO molecule in the COLTRIMS apparatus. Dominated by the profile of the highest occupied molecular orbital (HOMO) and the next lower-lying one (HOMO-1) whose electron densities shift to the C site, the CO molecule is favored to be ionized when the laser field points from C to O [16]. For the dissociative double ionization channel ( $C^+, O^+$ ), i.e.,  $\text{CO} + n\ \hbar\omega \rightarrow C^+ + O^+ + 2e$ , the ionic fragment of  $C^+$  is preferred to fly to  $-z$  or  $+z$  for  $\phi=0$  or  $\pi$  in the asymmetric two-color laser pulse [32–34]. To quantify it, we define the asymmetry parameter of  $\beta=(Y_{+z}-Y_{-z})/(Y_{+z}+Y_{-z})$ , where  $Y_{+z}$  and  $Y_{-z}$  stand for the probabilities of  $C^+$  emitted to  $+z$  and  $-z$ , respectively. The laser phase dependent asymmetric emission of  $C^+$  is plotted in figure 2, which alters the emission direction

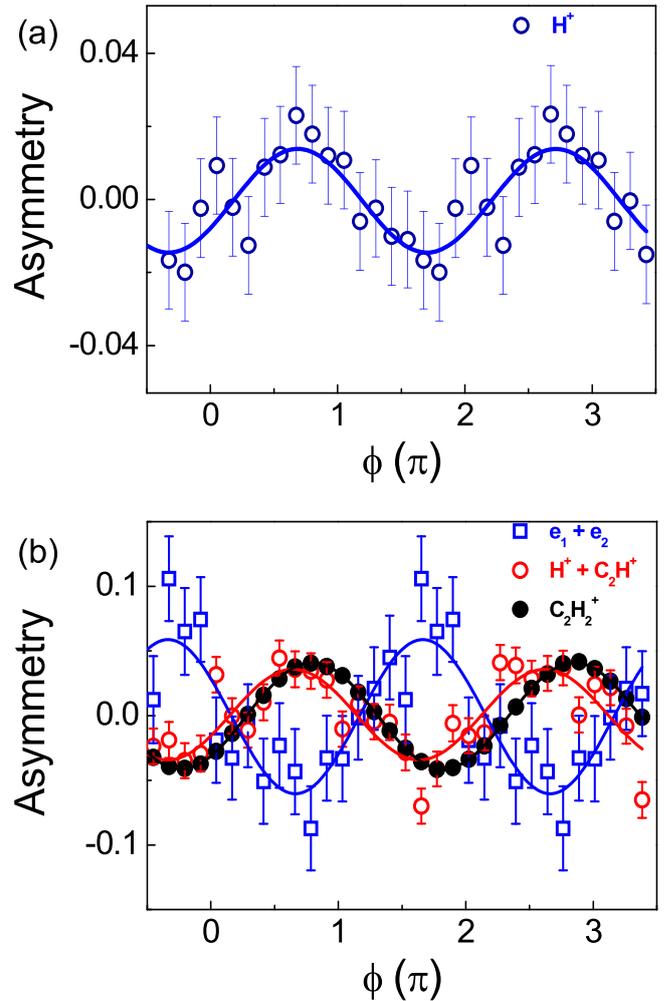


**Figure 2.** Measured phase-dependent asymmetry of the directional ejection of  $C^+$  from the  $(C^+, O^+)$  channel for the calibration of the phase of the two-color laser pulse. The solid curve is the numerical fit of the measured data.

with a period of  $\pi$  of our two-color laser pulse and is consistent with the pioneering observations [32–34].

We now study the directional C–H bond breaking by tracing the phase-dependent ejection of the  $H^+$  fragment from the deprotonation dissociative double ionization of acetylene, i.e.,  $C_2H_2 + n \hbar\omega \rightarrow H^+ + C_2H^+ + 2e$ , denoted as the  $(H^+, C_2H^+)$  channel. Figure 3(a) shows the measured directional emission of  $H^+$  versus the phase  $\phi$  of the two-color laser pulse. The solid curve is a numerical fit of the measured data. The asymmetry oscillates as a function of the laser phase with amplitude of  $\sim 1.5 \pm 0.2\%$ . The  $H^+$  alters the emission direction with a period of  $\pi$ . Interestingly, the  $H^+$  is favored to eject to  $+z$  or  $-z$  when the laser phase  $\phi = 0.68\pi$  or  $-0.32\pi$ . It strikingly differs from pioneering observations by using near-infrared multicycle [28] or phase-controlled few-cycle laser pulses [27], where the  $H^+$  is favored to fly to  $+z$  or  $-z$  when the laser phase  $\phi = 0$  or  $\pi$ . This different phase dependence suggests an alternative mechanism for the here-observed directional C–H bond breaking, rather than the electron-localization assisted enhanced ionization [28] or the CEP-dependent superposition of vibrational degrees of freedom [27].

We notice that the field intensity of our two-color laser pulse,  $I_{FW} = 2.2 \times 10^{13}$  and  $I_{SH} = 7.5 \times 10^{12} \text{ W cm}^{-2}$ , is much lower than the intensity of  $2 \times 10^{14} \text{ W cm}^{-2}$  used in preceding experiments [27, 28]. As we probed using the coincidence angular streaking with a multicycle near-infrared laser pulse, the electron-localization assisted enhanced ionization strongly depends on the field intensity [28]. At low intensity, the laser field is not sufficient to suppress the barriers to boost the tunneling probability of the localized electron into the continuum from the up-field potential well. In contrast to the scenario of electron-localization assisted enhanced ionization, the here-observed phase-dependent asymmetric emission of  $H^+$  illustrates that the electrons are favored to be freed when the laser field vector pointing from the H site to the C site. For



**Figure 3.** (a) Measured phase-dependent asymmetry of the directional ejection of  $H^+$  from the  $(H^+, C_2H^+)$  channel. (b) Measured asymmetries of the electron (blue squares) and ion sum-momenta (red circles) of the  $(H^+, C_2H^+)$  channel, and the momentum of  $C_2H_2^+$  (black filled circles) along the polarization direction of the two-color laser pulse. The solid curves are the numerical fits of the measured data.

$C_2H_2$ , the electron densities of HOMO-1 and HOMO-2 in the C–H bond shift to the H site [35]. According to the MO-ADK [13, 14] or SFA [15], the electrons in HOMO-1 or HOMO-2 in the C–H bond are favored to be removed by laser field pointing from H to C. It is consistent with the observed phase-dependent asymmetry of the  $H^+$  ejection upon the breaking of the C–H bond as shown in figure 3(a), indicating an important role of the orbital profile in the deprotonation double ionization of  $C_2H_2$  by our two-color laser pulse at low field intensity. The weak asymmetry of  $\sim 1.5 \pm 0.2\%$  might be also because of the relatively low field intensity of the employed two-color laser pulse. The domination of the orbital profile at low field intensity has also been observed in the C–C bond breaking, leading to a butterfly angular distribution of the  $CH^+$  ejected from the  $C_2H_2 + n \hbar\omega \rightarrow CH^+ + CH^+ + 2e$  channel [28].

In addition to the profile of the ionizing orbital, the electron recollision in the nonsequential double ionization

depends on the laser phase and thus influences the resulted directional bond breaking [36, 37]. By varying the CEP of an intense few-cycle laser pulse, as a result of the momentum recoil of the released electrons, it is shown that the emission direction of the doubly charged ion is opposite to the singly charged ion for the ( $e$ ,  $2e$ ) electron impact nonsequential double ionization [36, 37]. However, at low field intensity, due to the limited energy of the recolliding electron gained from the laser field, the double ionization is ruled by the process of recollision-induced excitation with subsequent ionization (RESI). As compared to the ( $e$ ,  $2e$ ) mechanism, the RESI leads to different laser phase dependences of the emission directions of the doubly and singly charged ions which shift from each other with a phase interval between 0 and  $\pi$  [37]. To get insight into the mechanism of the double ionization in our experiment, we plot the measured phase-dependent directional emissions of the  $C_2H_2^+$  (black filled circles) and the ion sum-momentum of the ( $H^+$ ,  $C_2H^+$ ) channel (red circles) along the laser polarization in figure 3(b), which shift by  $0.13\pi$  from each other. It suggests that the RESI plays a role for the double ionization here at low field intensity as compared to the ( $e$ ,  $2e$ ) impact ionization. In our experiments, the maximum energy of the recolliding electron gained from the laser field is estimated to be  $3.17 \times U_p \approx 4.4$  eV ( $U_p$  is the ponderomotive energy), which is much smaller than the ionization potential of the  $C_2H_2^+$  ( $\sim 20.7$  eV). The observed double ionization hence is mostly accessed by the RESI, which depends on the phase and intensity of the employed two-color laser pulse. This laser phase dependent electron recollision process impacts the double ionization for the breaking of the C–H bond. As shown in figure 3(a), rather than at the phase of 0 or  $\pi$  solely governed by the asymmetric profile of the ionizing orbital, the asymmetry maximum of the directional C–H bond breaking is observed at the laser phase of  $0.68\pi$ . Comprehensive numerical simulation is desired to further quantify the roles of the orbital profile and the electron recollision in the deprotonation dissociative double ionization.

Differing from the directional ejection of the fragment ion from the dissociation channel upon the bond breaking, we note that the phase-dependent asymmetry of the ion sum-momentum shown in figure 3(b) is due to the streaking of the freed electrons by the laser field after the ionization instants [11, 23, 24, 28]. For the ( $H^+$ ,  $C_2H^+$ ) channel, the momentum of the fragmentized ions ( $\sim 20$  a.u. gained from the Coulomb explosion process) is much larger than the sum of them ( $< 1$  a.u. as a recoil of the released electrons). Due to the momentum conservation of the molecular system, the recoiled sum-momentum of the fragment ions is equal and opposite to the sum-momentum of the ejected electrons. The blue squares in figure 3(b) shows the measured asymmetry of the directional emission of the freed two electrons (blue squares) correlated to the ( $H^+$ ,  $C_2H^+$ ) channel as a function of the phase of the two-color laser pulse, which is exactly  $\pi$  phase shifted as compared to the correlated ion sum-momentum (red circles). The smaller error bar of the sum-momentum of the ions as compared to the electrons is due to the increased statistical significance of the data by merely detecting two

fragment ions as compared to the four-particle (two ions and two electrons) coincidence measurement.

In summary, by finely controlling the phase of an asymmetric two-color laser pulse, we have experimentally observed directional breaking of the C–H bond in the deprotonation dissociative double ionization of a polyatomic hydrocarbon molecule. As compared to the pioneering experiments using intense near-infrared laser pulses [27, 28], the observed different phase-dependent asymmetry of the  $H^+$  emission upon the C–H bond breaking illustrates important roles of the profile of the ionizing orbital and the electron recollision in the double ionization process in our low-intensity two-color laser pulse.

## Acknowledgments

This work is supported by the National Natural Science Fund (11425416 and 11374103), the ‘Eastern Scholar’ program, the NCET in University (NCET-12-0177), project from the SSTC (13QH1401400), the ‘ShuGuang’ project (12SG25), and the National Key Project for Basic Research (2011CB808105).

## References

- [1] Zewail A H 1988 Laser femtochemistry *Science* **242** 1645
- [2] Kling M F *et al* 2006 Control of electron localization in molecular dissociation *Science* **312** 246
- [3] Kremer M *et al* 2009 Electron localization in molecular fragmentation of  $H_2$  by carrier-envelope phase stabilized laser pulses *Phys. Rev. Lett.* **103** 213003
- [4] Sheehy B, Walker B and DiMauro L F 1995 Phase control in the two-color photodissociation of  $HD^+$  *Phys. Rev. Lett.* **74** 4799
- [5] Ray D *et al* 2009 Ion-energy dependence of asymmetric dissociation of  $D_2$  by a two-color laser field *Phys. Rev. Lett.* **103** 223201
- [6] Betsch K J, Pinkham D W and Jones R R 2010 Directional emission of multiply charged ions during dissociative ionization in asymmetric two-color laser fields *Phys. Rev. Lett.* **105** 223002
- [7] Kotsina N, Kaziannis S, Danakas S and Kosmidisa C 2013 Selective ionization/ dissociation of oriented  $N_2O$  molecules by asymmetric fs laser field *J. Chem. Phys.* **139** 104313
- [8] Kaziannis S, Kotsina N and Kosmidis C 2014 Interaction of toluene with two-color asymmetric laser fields: controlling the directional emission of molecular hydrogen fragments *J. Chem. Phys.* **141** 104319
- [9] Ohmura H, Saito N and Morishita T 2014 Molecular tunneling ionization of the carbonyl sulfide molecule by double-frequency phase-controlled laser fields *Phys. Rev. A* **89** 013405
- [10] Ohmura H and Saito N 2014 Molecular tunnelling ionization of allylhalides induced by phase-controlled two-colour laser fields *J. Phys. B: At. Mol. Opt. Phys.* **47** 204007
- [11] Wu J *et al* 2013 Understanding the role of phase in chemical bond breaking with coincidence angular streaking *Nat. Commun.* **4** 2177
- [12] Gong X *et al* 2014 Two-dimensional directional proton emission in dissociative ionization of  $H_2$  *Phys. Rev. Lett.* **113** 203001

- [13] Tong X M, Zhao Z X and Lin C D 2002 Theory of molecular tunneling ionization *Phys. Rev. A* **66** 033402
- [14] 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
- [15] Muth-Böhm J, Becker A and Faisal F H M 2000 Suppressed molecular ionization for a class of diatomics in intense femtosecond laser fields *Phys. Rev. Lett.* **85** 2280
- [16] Wu J, Schmidt L P H, Kunitski M, Meckel M, Voss S, Sann H, Kim H, Jahnke T, Czasch A and Dörner R 2012 Multiorbital tunneling ionization of the CO molecule *Phys. Rev. Lett.* **108** 183001
- [17] Holmegaard L *et al* 2010 Photoelectron angular distributions from strong-field ionization of oriented molecules *Nat. Phys.* **6** 428
- [18] Dimitrovski D *et al* 2011 Ionization of oriented carbonyl sulfide molecules by intense circularly polarized laser pulses *Phys. Rev. A* **83** 023405
- [19] Codling K, Frasiniski L J and Hatherly P A 1989 On the field ionisation of diatomic molecules by intense laser fields *J. Phys. B: At. Mol. Opt. Phys.* **22** L321
- [20] Seideman T, Ivanov M Y and Corkum P B 1995 Role of electron localization in intense-field molecular ionization *Phys. Rev. Lett.* **75** 2819
- [21] Zuo T and Bandrauk A D 1995 Charge-resonance-enhanced ionization of diatomic molecular ions by intense lasers *Phys. Rev. A* **52** R2511
- [22] Chelkowski S and Bandrauk A D 1995 Two-step coulomb explosions of diatoms in intense laser fields *J. Phys. B: At. Mol. Opt. Phys.* **28** L723
- [23] Wu J, Meckel M, Schmidt L P H, Kunitski M, Voss S, Sann H, Kim H, Jahnke T, Czasch A and Dörner R 2012 Probing the tunnelling site of electrons in strong field enhanced ionization of molecules *Nat. Commun.* **3** 1113
- [24] Wu J *et al* 2013 Strong field multiple ionization as a route to electron dynamics in a van der waals cluster *Phys. Rev. Lett.* **111** 083003
- [25] Xie X *et al* 2014 Selective control over fragmentation reactions in polyatomic molecules using impulsive laser alignment *Phys. Rev. Lett.* **112** 163003
- [26] Xie X *et al* 2014 Role of proton dynamics in efficient photoionization of hydrocarbon molecules *Phys. Rev. A* **89** 023429
- [27] Alnaser A S *et al* 2014 Subfemtosecond steering of hydrocarbon deprotonation through superposition of vibrational modes *Nat. Commun.* **5** 3800
- [28] 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
- [29] Lötstedt E, Kato T and Yamanouchi K 2012 Enhanced ionization of acetylene in intense laser fields *Phys. Rev. A* **85** 041402
- [30] Dörner R, Mergel V, Jagutzki O, Spielberger L, Ullrich J, Moshhammer R and Schmidt-Böcking H 2000 Cold target recoil ion momentum spectroscopy *Phys. Rep.* **330** 95
- [31] Ulrich J, Moshhammer R, Dorn A, Dörner R, Schmidt L P H and Schmidt-Böcking H 2003 Recoil-ion and electron momentum spectroscopy: reaction-microscopes *Rep. Prog. Phys.* **66** 1463
- [32] Wu J, Vredenberg A, Schmidt L P H, Jahnke T, Czasch A and Dörner R 2013 Comparison of dissociative ionization of H<sub>2</sub>, N<sub>2</sub>, Ar<sub>2</sub>, and CO by elliptically polarized two-color pulses *Phys. Rev. A* **87** 023406
- [33] Ohmura H, Saito N and Morishita T 2011 Quantum control of molecular tunneling ionization in the spatiotemporal domain *Phys. Rev. A* **83** 063407
- [34] Li H, Ray D, De S, Znakovskaya I, Cao W, Laurent G, Wang Z, Kling M F, Le A T and Cocke C L 2011 Orientation dependence of the ionization of CO and NO in an intense femtosecond two-color laser field *Phys. Rev. A* **84** 043429
- [35] 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
- [36] Xie X *et al* 2012 Attosecond-recollision-controlled selective fragmentation of polyatomic molecules *Phys. Rev. Lett.* **109** 243001
- [37] Bergues B *et al* 2012 Attosecond tracing of correlated electron-emission in nonsequential double ionization *Nat. Commun.* **3** 813