

# Photo double ionization of ethylene and acetylene near threshold

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We present kinematically complete measurements of the photo double ionization of ethylene (double CC bond) and acetylene (triple CC bond) hydrocarbons just above the double ionization threshold. We discuss the results in terms of the coincident kinetic energy of the photo electrons and the nuclear kinetic energy release of the recoiling ions. We have incorporated quantum chemistry calculations to interpret which of the electronic states of the dication have been populated and trace the various subsequent fragmentation channels. We suggest pathways that involve the electronic ground and excited states of the precursor ethylene dication and explore the strong influence of the conical intersections between the different electronic states. The nondissociative ionization yield is small in ethylene and high in acetylene when compared with the dissociative ionization channels. The reason for such a striking difference is explained in part on the basis of a propensity rule which influences the population of states in the photo double ionization of a centrosymmetric closed shell molecule by favoring singlet ungerade and triplet gerade final states. This propensity rule and the calculated potential energy surfaces clarify a picture of the dynamics leading to the observed dication dissociation products.

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## I. INTRODUCTION

In the Photo Double Ionization (PDI) of a target atom or a molecule, one photon is absorbed by a single electron which then interacts with another electron, ejecting both into the continuum and producing one or more charged recoil ions. The essential interaction of the two electrons make PDI an ideal process for studying electron-electron correlation. Moreover, fragmentation dynamics can be investigated by connecting electronic states to different dissociation channels. In past years, PDI has seen extensive study on two electron systems such as  $H_2$  and  $He$  with intra shell electron-electron correlation and on many electron diatomic molecules with both intra and inter shell electron-electron interactions (see, e.g. Refs. [1–5]). The natural next step is to use polyatomic molecular targets to explore the effects of chemical bonding on electron-electron correlation. PDI of these targets also offers a variety of avoided crossings and conical intersections of Potential Energy Surfaces (PESs) that produce a rich array of nuclear dynamics during dissociation.

We chose to study closed shell hydrocarbon molecules with different types of hybridization of their carbon-carbon bond, namely ethylene ( $C_2H_4$ ) and acetylene ( $C_2H_2$ ). We expect PDI of these two species to be differ-

ent because of their dissimilar geometries and electronic configurations. The double ionization of these molecules with photon and particle impact has been explored heavily in the past both in theory and experiment (ethylene [6–8] and acetylene [9–16]). Previous studies in ethylene include methods like double-charge-transfer spectroscopy [7, 17, 18], charge-stripping-mass spectroscopy [19, 20], Auger spectroscopy [21, 22], and time-of-flight mass spectrometry [23–25]. In all these experiments the detection of the doubly charged ion  $C_2H_4^{2+}$  is elusive. This is due to the fact that the Time Of Flight (TOF) of the molecular dication and the fragment ions from other breakup channels overlap. The fragmentation pathways remain unidentified in these studies and a more sensitive probe is needed to pinpoint the existence of a stable dication in the direct PDI near threshold.

Here we utilize a method that allows the coincidence detection of both electrons and the recoil ions produced by double ionization. We choose photon energies close to the PDI threshold where deviations from the Wannier law are expected to be small. By detecting the energies of all particles simultaneously we are able to verify that most electrons are emitted via direct double ionization and that any competing two-step processes such as autoionization or Auger decay play a minor role. This enables the kinematically complete study of the direct PDI

of these molecules. We are searching for answers to some basic questions: can the metastable dications of ethylene and acetylene be observed in our measurements? What are the pathways leading to the formation of such dications and competing fragmentation channels? We aim to identify the states that result from the removal of two intra shell electrons and/or two inter shell electrons and the role of these states in the subsequent fragmentation process after PDI. For this investigation it is essential to know the PESs of the dications in order to shed light on the ionization and fragmentation mechanisms at work. We have performed calculations of the excited state dication potential energy surfaces, which allow us to identify the states involved by comparison with our measured kinetic energies of the electrons and fragment ions. We also find the dominant ionization channels based on branching ratios.

We present a brief description of the experimental and theoretical methods in the next two sections. The results and discussion follow, beginning with the nondissociative ionization of ethylene molecules.

## II. EXPERIMENTAL METHOD

We used COLd Target Recoil Ion Momentum Spectroscopy (known as COLTRIMS) [26] and performed kinematically complete measurements on the PDI of single ethylene and acetylene molecules. In the COLTRIMS method the target molecules are cooled in a supersonic gas jet and crossed with the photon beam inside a 3d-momentum-imaging spectrometer. Our experimental approach is to use photons with energies just above the double-ionization threshold and measure the recoil ions resulting from both NonDissociative Ionization (NDI) and Dissociative Ionization (DI) in coincidence with the photo electrons. Details on the experimental setup and the data collection as well as the analysis schemes can be found in Ref. [27]. We only give a brief description here.

Linearly polarized photons of energies above threshold are provided by BL 10.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. The ions and electrons generated from the ionization of a single molecule are guided by the static electric field inside the spectrometer to their respective time and position sensitive detectors (located in opposite arms of the spectrometer). A magnetic field parallel to the electric field prevents the energetic electrons from leaving the spectrometer. A collection angle of  $4\pi$  is achieved for both the recoil ions and electrons (up to kinetic energy 15 eV) by using a static electric field of 5.8 V/cm and a magnetic field of 7.1 Gauss. The measured time and position of the ions and electrons are recorded for each event and later used for offline analysis. The TOF and position data are used to construct the full three-dimensional momentum vector of all the collected particles, thereby recording the complete kinematics of the breakup process. Our electron detector has a delay line hex anode for position

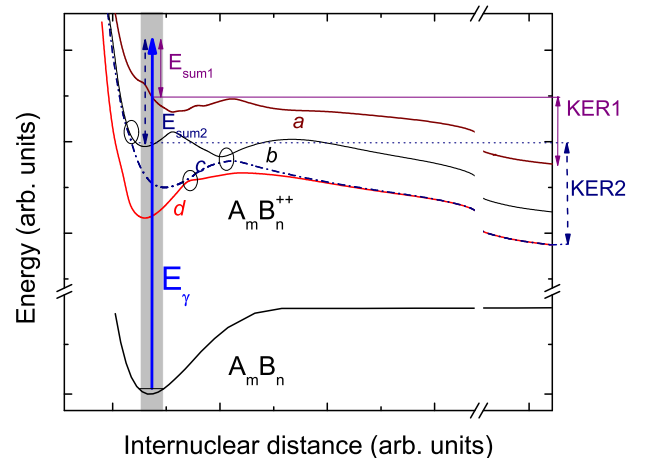


FIG. 1: (Color online) Schematic representation of the photo double ionization (PDI) of a typical  $A_m B_n$  molecule. Two pathways are considered as an example. One involving the highly excited potential energy curve (labeled *a*) that is dissociative in the given coordinate. The ionization of electrons from this state results in the sum kinetic energy of two electrons ( $E_{sum1}$ ) and the corresponding kinetic energy release (KER1) of the fragments. The horizontal line represents the vertical energy, i.e.  $E_{\gamma} - E_{sum1}$ . In a similar way, the second pathway involves a state (labeled *b* with vertical energy  $E_{\gamma} - E_{sum2}$ ) which is non dissociative in this coordinate but is coupled with another state (labeled *c*) via a conical intersection for instance. Since state *c* is dissociative the molecule fragments. KER2 is associated to the asymptotic limit of state *c* (not *b*) as the dissociating population transfers from state *b* to state *c* (which in fact is also coupled to another state *d* with the same asymptotic limit). This shows that the dissociation pathways in polyatomic molecules are more complex compared to diatomic molecules since these pathways involve non-adiabatic couplings like conical intersections and avoided crossings (marked with circles). The shaded vertical area indicates the Franck-Condon region for the given coordinate of the molecule.

read-out. The redundant position information from the hex anode is very helpful in minimizing losses from the detector dead time i.e. the ability to detect two electrons arriving at the detector within less than 8 ns and 9 mm apart.

The kinetic energies and angular distributions of the photoelectrons provide information that helps to determine the orbitals from which they were ionized. In this work, however, we focus on the energy distributions only. The photon energy, used in the PDI (i.e. removing two valence electrons in the photoionization), from BL 10.0.1 of the Advanced Light Source has an uncertainty of less than 0.1 eV. The electron kinetic energy is calibrated using single ionization of helium and the typical error is less than 0.2 eV. The recoil ion kinetic energy is calibrated using the double ionization of  $N_2$  and compared to the Kinetic Energy Release (KER) distribution in Ref. [28]. The error in our KER measurements is less than  $\pm 0.2$  eV.

Based on the principle of energy conservation, the sum of the kinetic energies of the two ejected electrons (denoted as  $E_{sum}$ ) subtracted from the photon energy ( $E_\gamma$ ) provides the vertical energy (denoted as  $E_{vert}$ ) of the state which has been populated by the ionization, i.e. the energy of the precursor dication. This is shown schematically in Fig. 1 for a typical  $A_mB_n$  molecule involving two different pathways. The KER is the difference between the energies at which the dissociation begins on the PES and the asymptotic limit of that respective state (see Fig. 1). The states with the right values of vertical energy and KER are considered to represent the most likely pathways in the dissociation process.

The probability to populate a given electronic state of the dication depends mainly on the following factors: available photon energy, the symmetries of the molecule and the emitted electrons, and the overlap between the vibrational wavefunction of the electronic state of the neutral and those of the dication (i.e. the Franck-Condon factor). For polyatomic molecules, the Franck-Condon factor is evaluated from the multidimensional overlap integrals [29]. Symmetry considerations often result in selection rules for electronic transitions. For example, the valence electron ionization of a centrosymmetric molecule favors the singlet ungerade and triplet gerade states [5, 30, 31]. In case of PDI of atomic targets the symmetry of the wave function of the two escaping electrons determine the final states of the dication that are populated (e.g. [31] for PDI of Ar). The quantum numbers of the escaping electron pair that determine the symmetry are the orbital angular momentum ( $L$ ), spin ( $S$ ), and parity ( $\Pi$ ). When these quantum numbers are all odd or all even, the two-electron wave function has no nodes at the Wannier point, which is the optimal configuration of both electrons to be emitted into the continuum (they are equidistant from the ion with equal radial velocity at  $180^\circ$  to each other); the resulting dicationic state is then favorable. The cross section of such a reaction is then proportional to  $E^n$  where  $E$  is the excess energy above threshold and  $n > 1$  (as introduced by Wannier [32]). These symmetry requirements, when applied to the PDI of centro-symmetric closed shell molecules, translate into a propensity rule that favors mainly the singlet ungerade and triplet gerade states of the dications to be populated [5, 30]. While going from a spherical symmetric atom to a centro-symmetric closed shell molecule the reduction in symmetry removes all effect from the orbital angular momentum restriction. The selection rule would further weaken for the open shell case when even  $S$  and  $\Pi$  lose their restrictive influence.

In a scenario different than discussed in the above paragraph, e.g. the core electron ionization, followed by Auger decay, favors the population of singlet states (both gerade and ungerade symmetry) as opposed to triplet states [10, 33, 34]. The contribution of triplet states from closed shell molecules in the Auger decay to the PDI is low [10, 33, 34] due to a small overlap integral. The Auger decay probability, based on the simplest spin-

restricted theory, depends on a two-electron Coulomb integral involving a core orbital, a continuum orbital and two valence orbitals. For triplet states the orbitals of the two valence electrons involved in the process must be different. Hence the transition matrix element involves the antisymmetric combination of two spatial integrals which tend to cancel for high-energy continuum orbitals [33].

For simplicity, we refer to the former as Propensity Rule (Valence) and the latter one as Propensity Rule (Auger) for the rest of this paper.

### III. CALCULATIONS

We have performed calculations of the potential energy surfaces of excited dications using the Columbus quantum chemistry program [35–39]. We calculate one-dimensional cuts that pass through the equilibrium geometry of the ground state neutral ethylene, which is taken to be  $R_{CC}=2.5303$  bohr,  $R_{CH}=2.0522$  bohr,  $\theta_{HCH}=117.6^\circ$ , the same as Ref. [6]. We have used  $R_{CC}=2.2871$  bohr and  $R_{CH}=2.0103$  bohr for acetylene. Excited state energies were calculated using Configuration Interaction with Singles and Doubles (CISD) with Dunning’s aug-cc-pvtz basis set [40]. The reference spaces included the 10 valence orbitals of acetylene and ethylene, with 11 orbitals used for the Acetylene C-H stretch calculation, including an additional  $a'$  orbital in  $c_s$  symmetry. The 1s orbitals were frozen and therefore the reference spaces were 10 electrons in 8 orbitals, 12 in 8, and 12 in 9 for the ethylene, acetylene C-C stretch, and acetylene C-H stretch calculations, yielding 41, 14, and 31 million configurations for singlets and 23, 9, and 18 million for triplets, respectively. The orbitals were obtained by state-averaged multiconfiguration self-consistent field calculations in which weighted averages of neutral and dication states’ energies were minimized. For the ethylene calculations the ground neutral and  ${}^3A_u$  ( $T_1$ ) dication state energies were averaged with a weight of 1:4. For the 10 orbital acetylene C-C stretch calculations, the ground state with weight eight and the first eight singlet and triplet dication states with weights one were averaged; for the 11 orbital C-H stretch calculation, the ground state with weight eight and the first five singlets and three triplets, with weights one. All these parameters are also summarized in Table I. Previous calculations of the excited states of ethylene can be found in Refs. [6–8, 41–44] and those of acetylene in Refs. [11, 14, 16, 45, 46].

The configuration interaction method is in general not size consistent and is expected to overestimate the dissociation energies. The dissociation under study include the fragments with no ( $H^+$ ) or one ( $H_2^+$ ) electron. For those fragments, the size consistency issue inherent in the configuration interaction does not apply. Calculated kinetic energy releases are given without any adjustment. Those for the C-C dissociation should in general be expected to be too low.

Species	Channel	Orbitals		# Configurations		MCSF weights		
		Frozen	Active	Triplet	Singlet	Ground state neutral	Triplet dication	Singlet dication
$C_2H_4^{2+}$	All	2	8	23M	41M	1	4	0
$C_2H_2^{2+}$	C-C stretch	2	8	9M	14M	8	$8 \times 1$	$8 \times 1$
$C_2H_2^{2+}$	C-H stretch	2	9	18M	31M	8	$3 \times 1$	$5 \times 1$

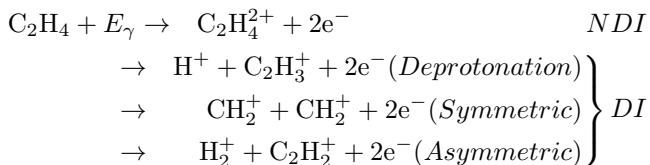
TABLE I: Parameters of quantum chemistry calculations.

#### IV. RESULTS AND DISCUSSION

We have measured the PDI of ethylene and acetylene using linearly polarized light of 40.5 eV and 42 eV photon energy, respectively.

##### A. Ethylene ( $C_2H_4$ ): $E_\gamma=40.5$ eV

The following channels are observed in our measurements on the PDI of ethylene,



where  $E_\gamma$  represents the photon energy.

Table II summarizes the results of the electronic structure calculations and includes the calculated vertical ionization potentials from the equilibrium geometry of the parent molecule, a note as to whether or not the electronic state is preferred by the Propensity Rule (Valence), and a note as to whether or not the electronic state is dissociative for each fragment channel either directly or via likely conical intersections.

We have used the typical COLTRIMS analysis of multi-particle coincidence and TOF measurements to isolate the DI channels in the data, as shown in Fig. 2(b). However, to isolate the NDI channel we exploit the available position measurement as well as the TOF, as shown in Fig. 2(a).

A useful tool for channel identification is the so called Photo-Ion Photo-Ion COincidence (PIPICO) spectrum, where the yield is plotted as a function of the TOF of the first and second recoil ions, as shown in Fig. 2(b). Two paired fragment ions resulting from a breakup channel form a stripe in the PIPICO spectrum (also e.g. [27, 47–50]). We have observed three different breakup channels: deprotonation ( $H^+ + C_2H_3^+$ ), symmetric breakup ( $CH_2^+ + CH_2^+$ ), and asymmetric breakup ( $H_2^+ + C_2H_2^+$ ). By selecting the TOF of the ions and applying momentum conservation we can single out particular breakup channels and calculate the full 3d-momentum vector of the ions and their respective electrons. For the DI we use the  $E_{sum}$  of these electrons together with the KER

State	Prop	Channels			Vertical DIP		
		I	II	III	Present	Calc [6]	Expt.
$^1A_g (S_1)$			B		30.20	29.46	
$^3A_u (T_1)$		B			31.17	30.65	31.4 [44]
$^1A_u (S_2)$	✓	B	$S_1$		31.76	31.19	30.9 [18]
$^3B_{3u}$			✓		33.71	32.78	
$^1A_g (S_3)$		✓	$S_1, ^1B_{3u}$		34.18	33.93	34.3 [18]
$^3B_{1g}$	✓		$^3B_{3u}$	✓	34.29	33.73	
$^1B_{3u}$	✓	$S_3$	✓		34.64	33.81	
$^1B_{1g}$			$^1B_{3u}$	✓	35.47	34.87	
$^3B_{3g}$	✓	B	$^3B_{3u}$		35.56	34.96	
$^3B_{1u}$			$^3B_{3u}$	✓	35.93	35.92	
$^1B_{3g}$		✓	$^1B_{3u}$		36.75	36.31	36.2 [18]
$^3B_{2g}$	✓		✓		37.59	36.87	
$^1A_g (S_4)$					??	38.37	

TABLE II: Vertical double ionization potentials (DIP) for the electronic states of the ethylene dication at the geometry  $R_{CC}=2.5303$  bohr,  $R_{CH}=2.0522$  bohr, and  $\theta_{HCH}=117.6^\circ$ . The column labeled “Prop” denotes whether or not the state is preferred by the propensity rule (double ionization preferentially populates singlet ungerade and triplet gerade states). The channel label denotes the dication breakup channels as (I)  $H^+ + C_2H_3^+$ , (II)  $CH_2^+ + CH_2^+$ , and (III)  $H_2^+ + C_2H_2^+$ , respectively. The state is check marked if it appears to be able to dissociate directly or labeled with the intersecting state if there is a likely dissociative pathway via a single conical intersection. The label B denotes that there is a barrier in the dissociative degree of freedom, however the dissociation may still happen by over the barrier.

of the fragment ions to determine the populated electronic state of the parent dication and the asymptotic final energy. Once determined, these values are used to back trace the path the molecule took through the PES, as discussed in the following subsections.

Branching ratios of the DI channels are obtained by considering two electrons measured in coincidence with two fragment ions. In case of the NDI channel we look for the yield of both photo electrons in coincidence with the metastable dication. The branching ratio for each of these channels is presented in Table III. In cases of two overlapping peaks in the  $E_{sum}$  spectrum we fit two Gaussian distributions for each of these peaks such that the sum of the two fits matches the measured distribution. Note that we cannot measure absolute cross section using COLTRIMS but produce relative yields only.

The ionization yield must also be corrected for the detector efficiency, which depends on the number of coin-

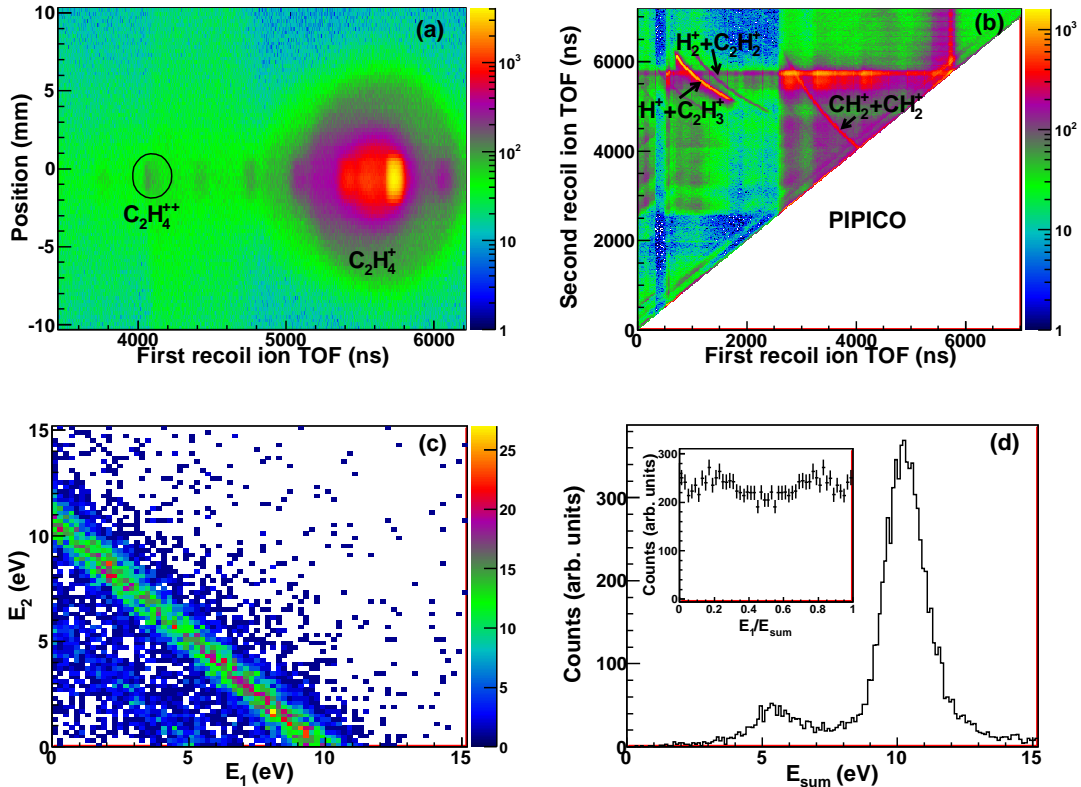


FIG. 2: (Color online) Separation of different channels in the direct photo double ionization (PDI) of ethylene at 40.5 eV photon energy. (a) Density plot of the time of flight (TOF) of the recoil ions and their position on the detector to trace the metastable dication (Nondissociative ionization, NDI). (b) Photo-Ion Photo-Ion COincidence (PIPICO) spectrum for the separation and identification of different breakup channels in time (Dissociative Ionization, DI). (c) Density plot of the kinetic energy of the two electrons measured in coincidence with the ethylene dications. (d) Electron sum kinetic energy ( $E_{sum}$ ) of the two electrons described in (c). The inset in (d) is the plot of the ratio ( $E_1/E_{sum}$ ) for the  $E_{sum}$  peak around 10.2 eV. For the error bars in this  $E_{sum}$  distribution refer to Fig. 4 where it is presented as threshold energy.

cident particles used to isolate an event. In the case of NDI two electrons and one recoil ion are recorded, but for the other DI channels two ions and two electrons must be recorded in coincidence. For the correction factor we have used the particle detection efficiency ( $\epsilon_{particle}=0.48\pm 0.1$ ) given by the product of the open-area ratio of the microchannel plate detectors (about  $60\pm 10\%$ ) as a maximum detection efficiency and the transmission (about  $80\pm 10\%$ ) of the spectrometer grid in front of the ion detector.

### 1. NDI: $C_2H_4^{2+}$

The NDI channel results in a metastable molecular dication ( $C_2H_4^{2+}$ ) and two photoelectrons. These dications can be separated and identified from other ions by their TOF, position on the detector, and in a more advanced analysis the energy of the two electrons. The TOF of the ions in the static field of the spectrometer is proportional to their mass to charge ratio, which distin-

guishes the  $C_2H_4^{2+}$  channel from the single and double ionization channels as shown in Fig. 2(a). To distinguish the  $C_2H_4^{2+}$  channel from the  $CH_2^+$  channel (that shares the same mass to charge ratio), the position and the TOF spread must be examined. In contrast to the  $CH_2^+$  channel the metastable dications have a small kinetic energy and therefore are sharply peaked in both TOF and detector position.

A metastable dication requires a local potential well and a barrier to prevent immediate fragmentation. Note that the lifetime of the detected dications must be greater than their TOF ( $4.1\mu s$ ). In Ref. [8] the barrier to deprotonation on the ground singlet state of the dication ( $S_1$  at the equilibrium geometry of the neutral) was calculated as 68.8 kcal/mol and for a symmetric breakup as 88.4 kcal/mol. Given the vertical transition energy of 30.2 eV calculated for the  $S_1$  state, these barriers lie at 33.2 and 34 eV. We therefore would expect that the  $S_1$  state supports long-lived vibrational states.

While plotting the kinetic energy of electron 2 as a function of the kinetic energy of electron 1 in Fig. 2(c)

Channels	$E_{sum}$	$E_{vert}$	KER	States	Branching Ratio(%)
$C_2H_4^{2+}$	10.2	30.3	—	$S_1$	$5.0\pm 0.8$
	5.5	35	—	${}^3B_{1g}, {}^3B_{1u}$	$0.4\pm 0.1$
$H^+ + C_2H_3^+$	6.5	34	4.3	$S_3$	$29.5\pm 4.3$
	8.7	31.8	4.3	$S_2$	$25.8\pm 3.7$
	9.5	31	3.8	$T_1$	$8.1\pm 1.2$
$CH_2^+ + CH_2^+$	5	35.5	5.5	${}^1B_{3u}, {}^3B_{3g}$	$22.6\pm 3.4$
	7	30.5	4.1	$S_2 \Rightarrow S_1$	$1.5\pm 0.2$
$H_2^+ + C_2H_2^+$	5	35.5	4.4	${}^{1,3}B_{1g}, {}^3B_{1u}$ ${}^{1,3}B_{2u}$	$7.1\pm 1.1$

TABLE III: Electron sum kinetic energy ( $E_{sum}$ ), vertical energy ( $E_{vert}$ ), kinetic energy release (KER), the states involved, and the branching ratio of different channels measured in the photo double ionization of  $C_2H_4$  using 40.5 eV photons. All energies are in eV. We estimate the absolute photo ionization cross sections for different breakup channels at 40.5 eV photon energy by referring to the absolute  $H_2^+$  photo ionization cross section of 0.07 Mb from Ref. [24] (assuming that the  $H_2^+$  production there solely stems from the  $H_2^+ + C_2H_2^+$  channel). The photo ionization cross sections for  $C_2H_4^{2+}$ ,  $H^+ + C_2H_3^+$ , and  $CH_2^+ + CH_2^+$  channels are thus 0.05, 0.62, and 0.24 Mb, respectively.

(note: the numbering of the particles is arbitrary) we find two diagonal lines obeying the energy conservation law. The energy-sharing distribution, plotted as the ratio of one electron kinetic energy to the sum kinetic energy of both electrons, for the main peak of the  $E_{sum}$  at 10.2 eV is shown in the inset of Fig. 2(d). The flatness is stemming from direct photo double ionization processes only. No traces of secondary processes like Auger decay or auto-ionization, which would show up as distinct islands in Fig. 2(c) and result in an asymmetric energy sharing, are visible. Similar plots for the DI channels (not shown here) help us to verify that at least 80% of the double ionization events detected for both targets  $C_2H_4$  and  $C_2H_2$  so close to threshold originate from direct double ionization. The small percentage due to two-step processes will be discussed in a future article. However, for the NDI two separate features can be clearly distinguished in Fig. 2(c) and (d). The main peak of the distribution in Fig. 2(d), at around 10.2 eV, indicates that the threshold of the double ionization is at about 30.3 eV, which is in agreement with the previously reported values [6, 7, 17]. The vertical energy for this feature ( $E_{sum}=10.2$  eV) of the NDI is 30.3 eV. One can assume that these dications are produced in the lowest manifold of states, i.e. the electronic ground singlet state  ${}^1A_g(=S_1)$ , lowest triplet state  ${}^3A_u(=T_1)$ , or the electronic first excited singlet state  ${}^1A_u(=S_2)$  of the ethylene dication. However, a survey of the double ionization potentials (DIP) presented in Table II shows that only  $S_1$  has the right DIP (30.2 eV) in the Franck-Condon region. The  $T_1$  and  $S_2$  states have slightly higher DIPs, 31.17 and 31.76 eV, respectively. Therefore the most likely candidate for the main feature is the  $S_1$  state with a 30.2 eV DIP.

The  $S_1$  state exhibits barriers [8] in the deprotonation (33.2 eV) and symmetric breakup (34 eV) channels, and can therefore support the production of a metastable dication. However, the  $S_1$  state is not favored by the Propensity Rule (Valence) introduced above. From our measured branching ratio presented in Table III this channel still contributes to about 5.0% to the direct PDI of ethylene near threshold. In this regard the Propensity Rule (Valence) appears to be weak. Later on we test this assertion by using the K-shell ionization of ethylene followed by Auger decay. In Auger decay the Propensity Rule (Valence) does not apply and the  $S_1$  state is favored by the Propensity Rule (Auger) and hence is expected to be populated more (see Sec. IV A 6).

We also observe a minor peak at around 5.5 eV in Fig. 2(d). This feature has a very small branching ratio (about 0.4% of the total double ionization yield) and results from dications which are formed in highly excited electronic states with a vertical energy of about 35 eV. Based on the vertical energy, the likely states are  ${}^3B_{3u}$ ,  ${}^1A_g(S_3)$ ,  ${}^3B_{1g}$ ,  ${}^1B_{3u}$ ,  ${}^1B_{1g}$ ,  ${}^3B_{3g}$ , and  ${}^3B_{1u}$ . The  ${}^3B_{3u}$  state has a DIP (33.71 eV) which is lower than the vertical energy. This state undergoes a large excursion in the C-C stretch and hence is an unlikely candidate, however it is bound in the C-H coordinate. The  $S_3$  state has a DIP (34.18 eV) that is lower than the vertical energy. This state is dissociative along the C-H coordinate and hence not a likely candidate for this feature. The states  ${}^1B_{3u}$  (DIP=34.64 eV) and  ${}^1B_{1g}$  (DIP=35.47 eV) are also unlikely as they couple to the  $S_3$  and  $S_2$  states via a large C-C stretch. We can also exclude  ${}^3B_{3g}$  as it couples to  ${}^3B_{3u}$  and  ${}^3B_{1g}$  via a C-H stretch. The remaining states  ${}^3B_{1g}$  and  ${}^3B_{1u}$  are the most likely states.  ${}^3B_{1g}$  (DIP=34.29 eV) is bound in the C-H coordinate, has smaller excursion in the C-C stretch, and may couple to  $T_1$ , but it is favored by the Propensity Rule (Valence). The other plausible state for this feature is  ${}^3B_{1u}$ , with a DIP (35.93 eV) slightly higher than the vertical energy, but is not favored by the Propensity Rule (Valence).

## 2. Deprotonation: $H^+ + C_2H_3^+$

We present the yield as a function of  $E_{sum}$  and KER for three different DI channels in Fig. 3. These spectra provide information on the correlation of the electrons and nuclear fragments in the breakup. The projections of these spectra along the horizontal and vertical axes give the KER and the  $E_{sum}$  distributions (not shown), respectively. The measured KER is an additional tool available in the DI channels to help identify the populated states. In order to identify the most likely electronic states involved, the states in the vicinity of the vertical energy (i.e.  $E_\gamma - E_{sum}$ ) are singled out first. Then we check for barriers in the given coordinate and matching KER (for dissociative states) in addition to the validity of the Propensity Rule (Valence). We have listed the likely states for different channels in Table III.

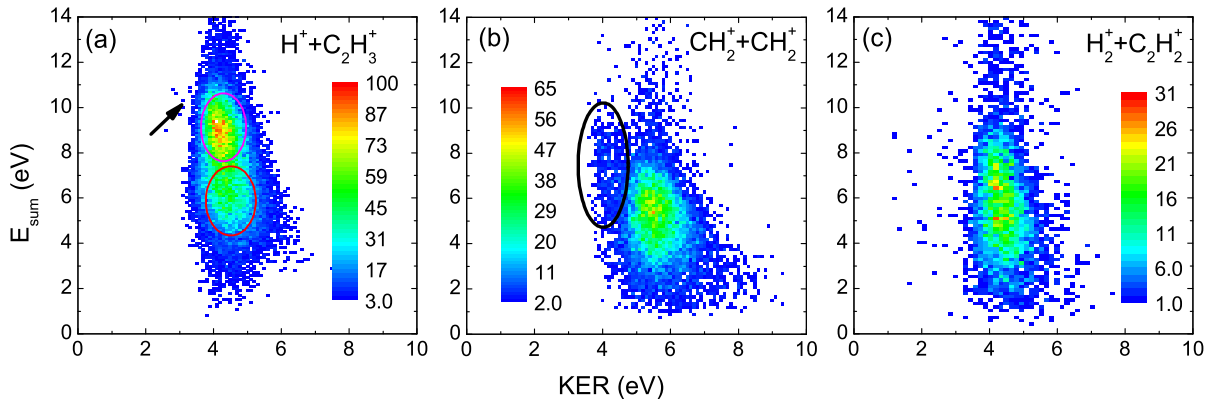


FIG. 3: (Color online) Energy correlation map between the ionic Kinetic Energy Release (KER) along the horizontal axis and the  $E_{sum}$  along the vertical axis for the (a)  $H^+ + C_2H_3^+$ , (b)  $CH_2^+ + CH_2^+$ , and (c)  $H_2^+ + C_2H_2^+$  channels of ethylene using 40.5 eV photons. The color scale is linear and the dynamic range is about the same for all plots.

The KER for the deprotonation channel ( $H^+ + C_2H_3^+$ ) is a narrow distribution, which peaks at around 4.3 eV while the  $E_{sum}$  distribution is wider and exhibits two peaks (at about 6.5 eV and 8.7 eV marked with two ellipses in Fig. 3(a)). We have identified these two peaks by looking at the experimental vertical energy given in Fig. 4 (open blue circles). The presence of the two peaks in the  $E_{sum}$  distribution indicates that at least two different manifolds of electronic states are populated in the ionization step. This leads to two different fragmentation pathways.

Let us first consider the deprotonation channel with an  $E_{sum}$  peak at 6.5 eV that gives a vertical energy of 34 eV. According to the DIP energy the possible states are  $^1A_g$  (i.e.  $S_3$  state, DIP=34.18 eV),  $^3B_{1g}$  (DIP=34.29 eV) and  $^1B_{3u}$  (DIP=34.64 eV). These states are shown in Fig. 5 as a function of the C-H distance. The energy difference between the vertical energy and the DIP can point to a vibrational excitation of the dications in a particular state. Vibrational excitations can lead to a broad  $E_{sum}$  distribution for a given KER. In Fig. 3(a) one can see that the KER distribution is relatively narrow compared to the  $E_{sum}$  distribution, indicating the influence of vibrational excitation in our measurements. Note that in the DI channels the fragments (with the exception of free protons) can be vibrationally excited.

A vertical DIP of 34.18 eV is given by our configuration interaction calculations for the  $^1A_g(S_3)$  state shown in Fig. 5. This state is not clearly bound in the C-H stretch direction and is therefore the only candidate for the 6.5 eV deprotonation peak. The experimental vertical energy may be compared with a recent calculation of 33.94 eV [6] and previous values ranging from 33 to 36 eV. In the cut in Fig. 5 the H-C-C angles are all held constant at 121.2°. The linear  $(CH_2)$ -C-H geometry corresponds to a local minimum on the  $C_2H_3^+$  cation ground state singlet potential energy surface, which is approximately 1.5 eV lower than depicted. The asymptotes of the diabatic  $S_2$  and  $T_1$  states in Fig. 5 are, in contrast,

approximately 1 eV higher in the linear  $(CH_2)$ -C-H geometry compared to the geometry where the H-C-C angles are all held constant at 121.2°.

The one-dimensional cut in the potential energy surface of the  $^1A_g(S_3)$  state, shown in Fig. 5, is flat when ap-

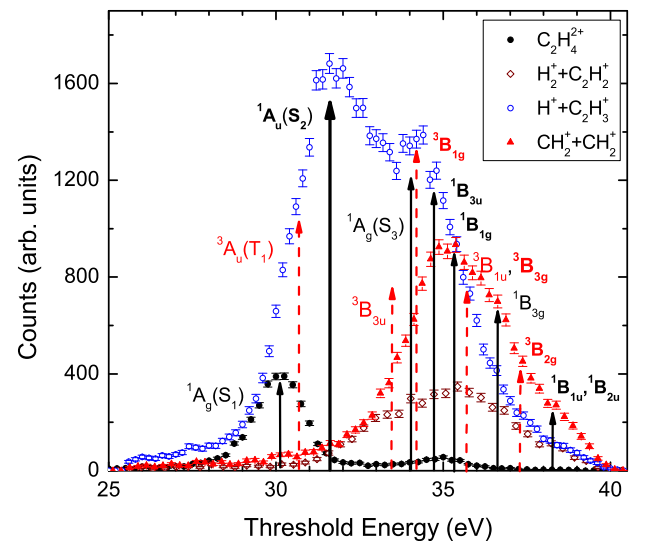


FIG. 4: (Color online) Ionization yield as a function of threshold energy, defined as  $E_{sum}$  subtracted from  $E_\gamma$  (40.5 eV, linearly polarized), for all PDI channels of ethylene. This energy is equivalent to the vertical energy on the potential energy surface (PES) which is crucial to identify the ionization pathways. The error bars represent the statistical errors only. The distribution is corrected for the higher detection efficiency of the NDI channel (black solid circles) compared to the ion-pair channels. The relevant states are indicated with vertical arrows (solid black lines for singlet and red dashed lines for triplets) based on their DIPs. States in bold are favored by the Propensity Rule (Valence).

proaching the avoided crossing with the  $^1A_g(S_1)$  state at approximately 4 bohr. Furthermore, as shown in Fig. 6, the  $S_3$  state is metastable with respect to the C-C stretch (although the conical intersection with the  $S_1$  state will allow some C-C dissociation via the  $S_1$  state). The minimum energy path to the avoided crossing must be lower in energy than the path depicted in Fig. 5 and therefore the avoided crossing will be accessible by a downhill path from the initial geometry. Furthermore it is likely that an accidental conical intersection [51] between these two states exists and is accessible, though we have found no discussion of this point in the literature.

The diabatic  $S_3$  state correlates with the ground state of the  $C_2H_3^+$  cation. The state then proceeds to a conical intersection with the  $^1A_u(S_2)$  state at approximately 5 bohr in Fig. 5. The diabatic  $S_3$  state continues to become the lowest asymptote. The diagram implies two options for the dissociative mechanism: dissociation on the diabatic  $S_2$  asymptote with a peak KER of 4.6 eV, and dissociation on the diabatic  $S_3$  state with maximum and peak KER values of 7.3 and 5.8 eV, respectively. The narrow distribution of the measured KER supports the former mechanism, but the multidimensional nature of the landscape on which the dynamics occurs precludes a conclusion on this point. It should be noted that an adiabatic transition to the diabatic  $S_2$  asymptote (an avoidance of the conical intersection) occurs for nonplanar dication geometries only, i.e. a molecular conformation change is indispensable since the neutral molecule's ground state is planar.

In a similar way, we have identified two more states ( $S_2$  and  $T_1$ ; see Table III) contributing to another feature in the deprotonation (i.e.  $E_{sum}$  peak around 8.7 eV). This feature corresponds to a vertical energy of 31.8 eV. The  $S_2$  state, favored by the Propensity Rule (Valence), has a DIP of 31.76 eV. The lowest triplet  $T_1$  state has a DIP of 31.17 eV but is not favored by the Propensity Rule (Valence) and contributes to the shoulder-like feature only (discussed below). The  $S_2$  and  $T_1$  states have similar behaviors in the C-H and C-C stretch as can be seen in Figs. 5 and 6. The superior agreement of the calculated DIP of the  $S_2$  state with the observed DIP (31.8 eV), along with its satisfaction of the Propensity Rule (Valence), supports the assignment of the  $E_{sum}$  peak at the 8.7 eV feature to this state.

Once  $S_2$  is populated there are a number of possible pathways to dissociation. Without enumerating the many options, note that if the dissociation proceeds to the diabatic  $S_3$  asymptote via a conical intersection between the  $S_2$  and diabatic  $S_3$  states, the maximum KER is approximately 4.9 eV. This is very close to the value we have measured. We conclude that this pathway is responsible for the deprotonation channel with a vertical energy of 31.8 eV.

A careful inspection of the threshold energy spectrum of the deprotonation channel, displayed in Fig. 4 (blue open circles), reveals a shoulder-like structure just above 30 eV. This is a result of the dication population in the  $T_1$

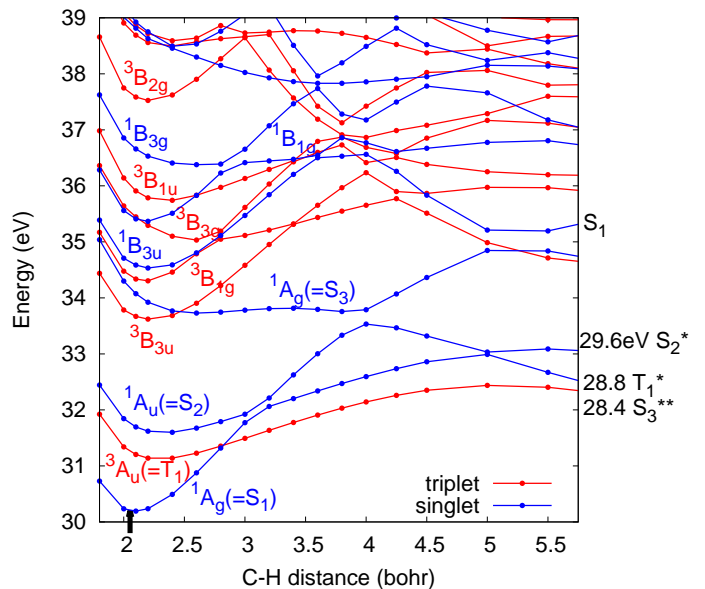


FIG. 5: (Color online) Cut of the PESs (singlet and triplet states) of the ethylene dication for C-H distance calculated using the multi-configuration self-consistent field (MCSCF) method. The Franck-Condon region is indicated with an arrow at the bottom on the horizontal axis. The energies of the asymptotes of the diabatic  $S_2$ ,  $S_3$ , and  $T_1$  states within this cut are given on the right side. \*\*The asymptote of the diabatic  $S_3$  state is approximately 1.5 eV lower in the linear  $CH_2$ -C-H geometry compared to the planar geometry. \*The asymptotes of the  $S_2$  and  $T_1$  are 1 eV higher at such (planar) geometries than in the linear  $CH_2$ -C-H geometry. States are labeled with the  $d_{2h}$  irreducible representations appropriate at the equilibrium geometry of the neutral.

state dissociating along the C-H bond. For this process to occur, the initial ionization step must populate the  $T_1$  state with sufficient energy (e.g. by vibrational excitation) to surmount the potential barrier to dissociation. The top of the barrier is near 32.4 eV (see Fig. 5) and the dissociation leads to a KER value of 3.6 eV. The feature is visible in Fig. 3(a) as counts below 4 eV KER and is marked with an arrow based on the  $E_{sum}$  and KER values.

### 3. Symmetric breakup: $CH_2^+ + CH_2^+$

The symmetric breakup channel data, shown in Fig. 3(b), is comprised of two features: a dominant peak with  $E_{sum}$  and KER centered at about 5 eV and 5.5 eV, respectively, and a minor shoulder-like feature with a broad  $E_{sum}$  distribution around 7 eV with a narrow KER peak at 4.1 eV.

We begin the discussion with the major feature. The vertical energy of 35.5 eV suggests the following states as possible candidates:  $^{1,3}B_{3u}$ ,  $^1A_g(S_3)$ ,  $^{1,3}B_{1g}$ ,  $^{1,3}B_{3g}$ , and  $^3B_{1u}$ , all are shown in Fig. 6 as a function of the C-C distance.



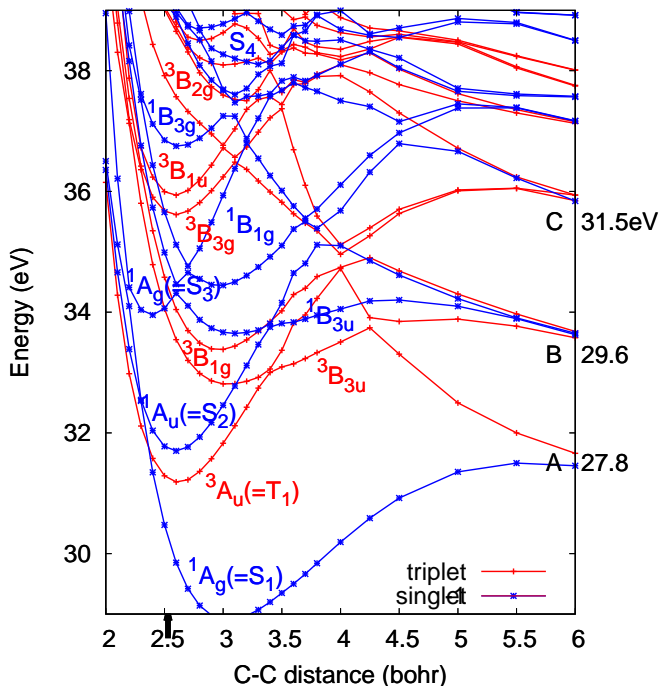


FIG. 6: (Color online) Cut of the PESs (singlet and triplet states) of the ethylene dication as a function of the C-C distance calculated using the multi-configuration self-consistent field (MCSCF) method. The arrow at the bottom indicates the Franck-Condon region. The asymptotes A, B, and C correlate with the A' and A'' components of the ground  ${}^2\Pi$  state of both  $\text{CH}_2^+$  fragments. With  $\text{CH}_2^+$  being linear these asymptotes are degenerate at approximately 27.8 eV.

The  ${}^3B_{3u}$  (DIP=33.71 eV) and  $S_3$  (DIP=34.18 eV) are too low in their vertical energy, not favored by the Propensity Rule (Valence), and hence are not likely candidates. As mentioned in the previous section,  $S_3$  dissociates by deprotonation. Given that the reduced mass in the C-H degree of freedom is small, the deprotonation will strongly compete with the symmetric breakup on the  $S_3$  state. The  ${}^3B_{1g}$  (DIP=34.29 eV) state is favored by the Propensity Rule (Valence) but its vertical DIP appears to be too low in comparison to the experimental value. It is also an unlikely candidate due to its inability to couple to  ${}^3B_{3u}$ . The other states, namely  ${}^1B_{1g}$  (DIP=35.47 eV),  ${}^3B_{1u}$  (DIP=35.93 eV), and  ${}^1B_{3g}$  (DIP=36.75 eV), are not favored by the Propensity Rule (Valence).

The  ${}^1B_{3u}$  (DIP=34.64 eV) and  ${}^3B_{3g}$  (DIP=35.56 eV) states are favored by the Propensity Rule (Valence) and considered the most likely candidates. The  ${}^1B_{3u}$  state is dissociative along the C-C coordinate and the expected KER is 5 eV. The  ${}^3B_{3g}$  state is bound along the C-C coordinate near the Franck-Condon region but it intersects directly with the dissociative  ${}^3B_{3u}$  state. The expected KER of this path is 5.96 eV. Both KER values agree with our measured KER peak value of 5.5 eV.

The shoulder-like feature in the KER distribution at

around 4.1 eV (marked with an ellipse in the density plot Fig. 3(b)) amounts to about 1.5% of the total double ionization yield. The pathway leading to this minor channel involves the  $S_1$  and  $S_2$  electronic states. A dissociation of the ethylene dication on  $S_1$  leads to the breaking of the central C-C bond, which then produces two  $\text{CH}_2^+$  ions [6]. We suggest that the fragmentation pathway to this minor channel starts with the population of the  $S_2$  state, which is allowed by the Propensity Rule (Valence). This population transfers to the  $S_1$  state of the dication via the conical intersection. Any extra energy can go into electronic or vibrational excitations of the product ions (both are molecular ions in this symmetric breakup channel). The expected KER for the fragmentation of the dication in the electronic ground state is 4.0 eV and is close to our measured KER of 4.1 eV.

#### 4. Asymmetric breakup: $\text{H}_2^+ + \text{C}_2\text{H}_2^+$

The  $\text{H}_2^+ + \text{C}_2\text{H}_2^+$  channel energy map in Fig. 3(c) has a KER distribution peak around 4.4 eV and a broad  $E_{sum}$  distribution peaking around 5 eV (corresponding to a vertical energy of 35.5 eV) that is similar to the  $E_{sum}$  distribution of the symmetric channel.

The hydrogen molecular ion ( $\text{H}_2^+$ ) can be formed in the fragmentation of ethylene dication in two ways: (i) one of the hydrogen atoms travels across the C=C double bond forming an ethylidene like ( $\text{CH}_3\text{CH}^{2+}$ ) intermediate state [18, 43] which is followed by a fragmentation that leaves an acetylene type ion ( $\text{HCCH}^+$ ) behind and (ii) two hydrogen atoms that are initially bound to the same carbon atom form a bond between them and increase the distance to the parent ion which results in a vinylidene like ( $\text{CCH}_2^+$ ) structure in the dissociation. Most likely both cases contribute to the yield of the asymmetric channel in our measurements. In order to identify the relevant states we consider only the latter direct asymmetric mechanism in our calculations and discussion.

With the given broad  $E_{sum}$  of 3 eV (full width at half maximum) no repulsive state in the C-H<sub>2</sub> coordinate can be populated directly. The pertinent states in the Franck-Condon region depicted in Fig. 7(b) exhibit barriers towards dissociation. We conclude that the H-C-H angle has to decrease first in order to circumnavigate these barriers on the PES. We therefore present the cut of the PESs as a function of the H-C-H angle in Fig. 7(a). The broad  $E_{sum}$  distribution indicates that several electronic states of the dication contribute to this dissociation channel. We consider electronic states that have a bonding H-H interaction, with potential energy surfaces that comprise minima at small H-C-H bond angles. As proposed above, the distance between the terminal carbon atom and the center of mass of the two hydrogen atoms must now increase while the H-C-H bond angle decreases in order to circumnavigate the barriers in the C-H<sub>2</sub> coordinate and expel an  $\text{H}_2^+$  fragment in the subsequent dissociation.

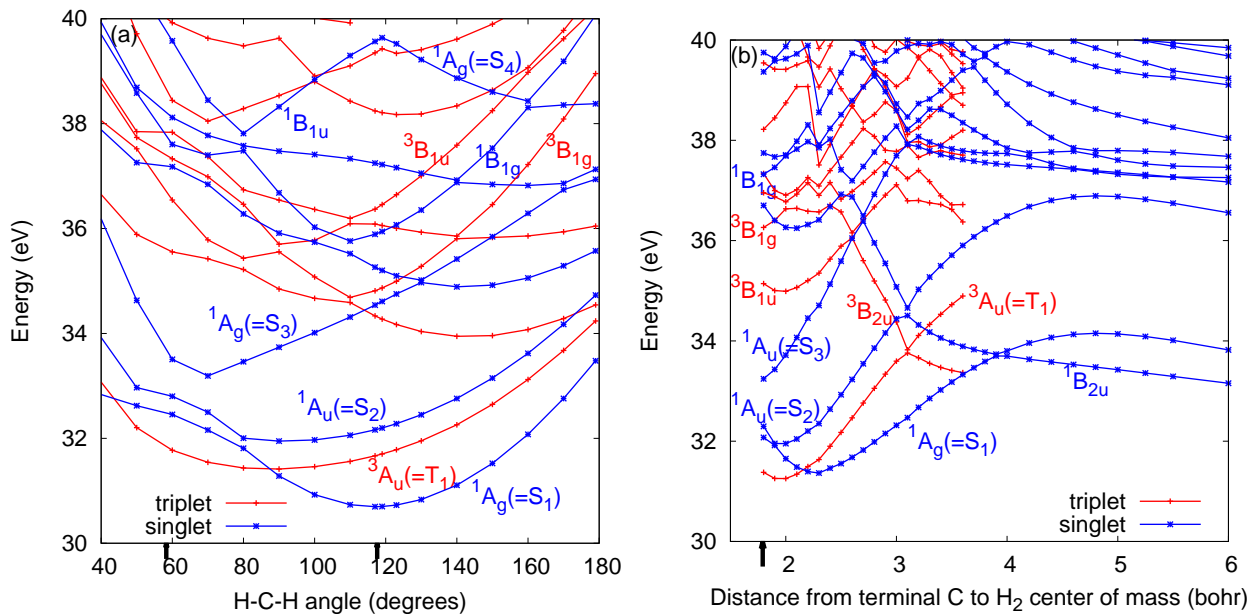


FIG. 7: (Color online) Cut of the PESs of the ethylene dication relevant to the asymmetric breakup ( $H_2^+ + C_2H_2^+$ ) channel. (a) Potentials as a function of the H-C-H bending angle. The initial angle ( $117.6^\circ$ ) and the angle ( $58.3^\circ$ ) at which the H<sub>2</sub> distance is 2.0 bohr are marked with arrows. (b) Potentials as a function of the distance between the last C (in  $C_2H_2$  in HHCC configuration) and the center of mass of H<sub>2</sub>. The arrow corresponds to the arrow in (a) at  $58.3^\circ$ . States are labeled with the  $d_{2h}$  irreducible representations appropriate at the equilibrium geometry of the neutral.

In Fig. 7(a) one can identify a number of singlet and triplet states with decreasing energy as the H-C-H angle decreases from its equilibrium value marked by the arrow at  $117.6^\circ$ . These are the  $^1,^3A_u$  ( $S_2$  and  $T_1$ ),  $^1A_g(S_3)$ ,  $^1,^3B_{1g}$ , and  $^1,^3B_{1u}$ . The  $^1,^3B_{1g}$  and  $^1,^3B_{1u}$  states are likely populated based on their vertical energy at the equilibrium geometry. However, at the initial scissoring angle of  $117.6^\circ$  these states exhibit barriers towards dissociation in the C-H<sub>2</sub> coordinate (not shown in Fig. 7(b)) and hence do not dissociate immediately. On the other hand, while undergoing a full scissoring mode reaching an H-C-H angle of  $58.9^\circ$ , the H-H bond distance would decrease to that of  $H_2^+$  at its equilibrium geometry (i.e. 2.0 bohr). This H-C-H angle is marked with an arrow in Fig. 7(a), and corresponds to the same geometry as that indicated by the arrow in the Fig. 7(b). While this H-H bond length may be considered favorable for expelling a stable  $H_2^+$  ion, we can see that at a C-H<sub>2</sub> distance of 1.8 bohr the dication states have potential barriers. Obviously, by the time the protons reached the equilibrium geometry of the  $H_2^+$  ion the wagging mode of the C-H<sub>2</sub> distance has progressed to a contracted ethylene dication. A hydrogen elimination must have taken place before this happens. We deduce that while the H-C-H angle was decreasing from the initial value of  $117.6^\circ$  during the approach of the potential minima, the C-H<sub>2</sub> distance was stretched beyond 2.6 bohr from its value (around 1.0 bohr) at equilibrium. The C-H<sub>2</sub> distance of 2.6 bohr is critical in order to couple to some low-lying repulsive states ( $^1,^3B_{2u}$ ) via conical intersections.

In the Fig. 7(b), one can see that these repulsive curves ( $^1,^3B_{2u}$ ) are singlet and triplet states that correlate with the ground state of the vinylidene cation, which has  $A_1$  symmetry in the  $c_{2v}$  point group and electronic configuration ( $1-4a_1^2 5a_1^1 1b_2^2 1b_1^2$ ); we have an additional singly occupied  $a_1$  orbital, the  $H_2^+$   $\sigma_g$ . We find that this configuration correlates with the transition  $1b_{3g}^{-2} 3a_g^{-1} 3b_{1u}^+ 1$  from the ground state neutral configuration, which gives the dication configuration ( $1-2a_g^2 3a_g^1 1-2b_{1u}^2 1b_{2u}^2 1b_{3u}^2 3b_{1u}^1$ ) overall  $^1,^3B_{2u}$  symmetry. Both repulsive dication states ( $^1,^3B_{2u}$ ) have the same geometry and thus have the similar C-H<sub>2</sub> distance (around 3 bohr) at the conical intersection, however they differ in their energies by about 0.75 eV due to the different electron spin orientation. The  $^1,^3B_{2u}$  triplet and singlet states have about the same asymptotic limit in this geometry (not shown in Fig. 7(b)) which agrees with the much narrower KER spread than the  $E_{sum}$  distribution for this asymmetric channel.

In conclusion it seems plausible that the observed asymmetric dissociation is produced by a transition from the  $^1,^3B_{1g}$  and  $^1,^3B_{1u}$  states (populated by the ionization step) through conical intersection to the  $^1,^3B_{2u}$  states that dissociate to the observed products.

##### 5. Summary: Ethylene photo double ionization

The sum of the photo double ionization cross sections for the channels measured in this work is about 10%

of the total photo absorption cross section of 10 Mb at 40 eV photon energy [24, 52, 53]. We do not have a direct comparison for the double ionization cross sections of ethylene estimated in this work to previous works, but a similar percentage of double ionization relative to the single ionization was observed for alkanes with two carbon atoms in Ref. [54].

We have found that, in the PDI of ethylene, the higher manifolds of the electronic excited states are responsible for all the DI channels as well as the minor feature in the NDI channel. The first excited electronic singlet ( $S_2$ ) state is directly responsible for the  $H^+ + C_2H_3^+$  channel. In addition the  $S_2$  state creates the minor feature in the  $CH_2^+ + CH_2^+$  breakup via the conical intersection to the electronic ground state ( $S_1$ ).

There are a number of reasons to expect a higher branching ratio of metastable dications presented in Table III. First, there are multiple states with barriers in both C-H and C-C coordinates. Second, as discussed above, the  $T_1$  and  $S_2$  states of the ethylene dication, shown in Fig. 6, seem to have potential wells that may support a number of long-lived vibrational levels. Third, both Palaudoux and Furuhashi [15, 55] have reported vibrational levels in similar dication states of acetylene, though the potential wells in the acetylene dication are about 1 eV deeper than in the ethylene dication.

A high barrier to torsion of the molecular geometry on the  $S_1$  state may explain the observed low NDI yield. Here we define the torsion angle as the angle between the planes containing the  $CH_2$  group. The neutral molecule has a planar geometry with a torsion angle of  $0^\circ$  while the metastable electronic ground state of the dication has a twisted non-planar geometry with a torsion angle of  $90^\circ$ . The change in geometry leads to small ‘‘Franck-Condon factors’’ as mentioned in Ref. [18].

The low NDI yield may also be caused by the Propensity Rule (Valence), postulated 25 years ago [5, 30, 31]. The rule states that whenever two electrons are removed from a centrosymmetric closed shell molecule in a direct double ionization by a single photon, predominantly the triplet gerade and singlet ungerade states of the dication are populated. In neutral ethylene the electronic ground state,  $^1A_g$ , has the configuration  $1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u}^2$  [6] (in  $D_{2h}$  symmetry group). The removal of two electrons from the outermost orbital  $1b_{3u}^2$  results in the electronic ground state  $S_1$  of the dication. This is a singlet state with  $A_g$  symmetry and hence is not favored by the Propensity Rule (Valence). However the  $E_{sum}$  value indicates that the majority of the NDI channel yield results from the  $S_1$  state.

In spite of the small ‘‘Franck-Condon factors’’ and the Propensity Rule (Valence) to produce a metastable dication in the PDI of  $C_2H_4$  we have experimental evidence of the NDI channel (5.4%). The specific geometries of the electronic ground state of the neutral ethylene (planar) and the dication (non-planar) lead to definitive ‘‘Franck-Condon factors’’ regardless of the ionization

Channels	$E_{Auger}$	$E_{vert}$	KER	States	Branching Ratio(%)
$C_2H_4^{2+}$	260	30.8	—	$S_1$	$5.3 \pm 1.0$
$H^+ + C_2H_3^+$	257.5	33.3	4.5	$S_3, S_2$	$46.3 \pm 7.2$
	265	25.8	4.5	Satellite ( $S_0$ )	$3.6 \pm 0.6$
$CH_2^+ + CH_2^+$	254	36.8	5.9	$^1B_{3g}, ^1B_{3u}, S_4$	$41.1 \pm 6.3$
	258	32.8	4	$S_2 \Rightarrow S_1$	$2.4 \pm 0.4$
$H_2^+ + C_2H_2^+$	253	37.8	4.6	$^1B_{1g,u}, S_4, ^1B_{2u}$	$1.2 \pm 0.2$

TABLE IV: Auger electron kinetic energy ( $E_{Auger}$ ), vertical energy ( $E_{vert}$ ), kinetic energy release (KER), the states involved, and the branching ratio of different channels produced in the ionization of  $C_2H_4$  by 310 eV photons. All energies are in eV. The photo absorption cross section for ethylene at a photon energy of 310 eV is about 2 Mb [56]. Since the photon energy is above the carbon K-shell ionization threshold, we assume that the single ionization is followed by 100% effective Auger decay leading to the double ionization with the same absolute probability. The branching ratios given above for  $C_2H_4^{2+}$ ,  $H^+ + C_2H_3^+$ ,  $CH_2^+ + CH_2^+$ , and  $H_2^+ + C_2H_2^+$  then translate to absolute cross sections of 0.11, 1.0, 0.87, and 0.02 Mb, respectively.

mechanism. But the propensity rules are based on the ionization mechanism. We thus can test the applicability of the Propensity Rule (Valence) by comparing the NDI channel yield in the Auger decay after core shell ionization (i.e. photoionization of a K-shell electron) to that of the PDI (i.e. removing two valence electrons in the ionization) of  $C_2H_4$ .

## 6. Comparison to Auger Decay: $C_2H_4$

Dications of ethylene molecules can also be produced by single photon ionization through Auger decay after K-shell ionization of the carbon atoms. This is an alternative mechanism useful in testing the effects of propensity rules in regards to the NDI channel.

We have measured this process by collecting the Auger electrons in coincidence with the recoiling ions after ionization by 310 eV photons (circularly polarized). In this measurement, the collection angle of the Auger electrons is limited to a cone of  $12^\circ$  with respect to the spectrometer axis. We implemented a retarding static electric field of about 20 V/cm to resolve the energy of the fast Auger electrons. The ion spectrometer arm retained a full collection angle of  $4\pi$  for fragments from the ion-pair channels.

The main results from the Auger decay after K-shell ionization are summarized in Table IV. Surprisingly, we have detected a 5.3% metastable dication ( $C_2H_4^{2+}$ ) branching ratio in both the K-shell ionization and PDI measurements while the branching ratios of the DI channels are very different. In terms of absolute cross sections the NDI of the K-shell ionization (0.1 Mb) is also very similar to that of the valence ionization (0.05 Mb) within the uncertainty of our cross section estimation ( $\pm 50\%$ ).

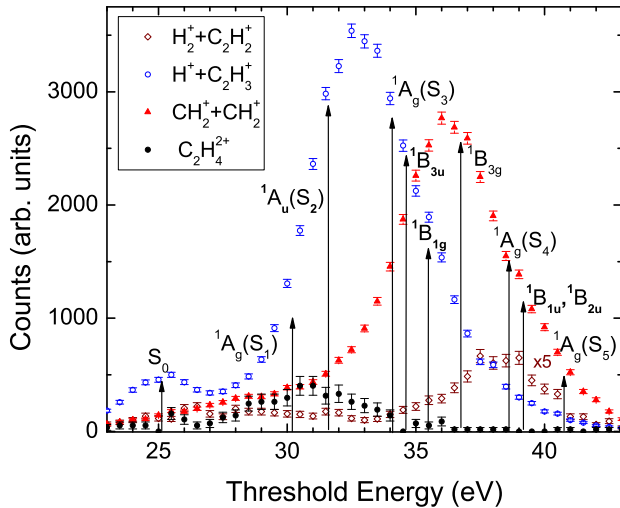


FIG. 8: (Color online) The same as Fig. 4 but for the K-shell ionization of ethylene by 310 eV photons (circularly polarized light).

These cross sections are deduced from the data in the literature and our experimental branching ratios that are given in the captions of Tables III and IV. The yields of both the deprotonation and the asymmetric breakup channels have decreased and that of the symmetric channel has almost doubled in the K-shell ionization. The vertical energies for some DI channels in the Auger decay, shown in Fig. 8, are also different from the PDI measurement at 40.5 eV. These differences may be caused by the Propensity Rule (Auger) which favors the population of singlet states (both gerade and ungerade symmetry) as opposed to triplet states in the Auger decay [33, 34]. For this reason we have only listed the singlet states in Table IV and in Fig. 8 as probable candidates. We have also observed an increased contribution from higher excited states in the DI channels produced by the Auger decay.

The Auger electron energy for the NDI ( $C_2H_4^{2+}$ ) channel is 260 eV. With the carbon  $1s$  ionization potential of 290.8 eV [57], the vertical energy is thus 30.8 eV. This vertical energy suggests that the dications are produced in the electronic ground state  $S_1$  with a possible vibrational excitation. In contrast to PDI, the propensity rule (Auger) allows the  $S_1$  state to be populated in the Auger decay. The surprising fact that there is almost no change on the NDI branching ratio between the two measurements, involving Auger decay and PDI, indicates that the propensity rules have little impact in the NDI channel. We conclude that the torsional barrier plays a larger role than the Propensity Rule (Valance) in controlling the population of metastable dications of ethylene in the  $S_1$  state.

For completeness we also briefly report on the DI channels produced by Auger decay and compare them to the PDI of  $C_2H_4$ .

The deprotonation channel has an Auger electron energy of about 257.5 eV and a vertical energy of 33.3 eV. Compared to the multiple features observed in the PDI (see Fig. 4), we found one dominant channel in the Auger decay only but the vertical energy is different (Fig. 8). The 33.3 eV vertical energy indicates that the  $S_3$  state is populated and dissociates along  $S_2$  through an avoided crossing. The expected KER of 4.6 eV is in agreement with the measured KER of 4.5 eV.

A minor feature at an electron energy of about 265 eV (i.e.  $E_{vert}=25.8$  eV) is observed in the Auger decay (see Fig. 8). We suggest that this minor channel involves a satellite state resulting from the lowest unoccupied molecular orbital, i.e. it stems from the promotion of a  $\pi$  electron to an unoccupied  $\pi^*$  orbital [58, 59]. This feature is not observed in our PDI measurements.

The symmetric breakup retains similar features observed in the PDI data. The major feature (around  $E_{Auger}=254$  eV) stems from electronic states with vertical energies around 36.8 eV. By surveying the PESs in Fig. 6 the likely states are  $^1B_{3u}$  (DIP=34.64 eV),  $^1B_{3g}$  (DIP=36.75 eV), and  $^1A_g(S_4)$  (DIP=38.37 eV [6]). Though the DIP of the  $^1B_{3u}$  state is low compared to the  $^1B_{3g}$  state, the Auger electron energy distribution is broad enough to cover the energy range. The  $S_3$  state may represent an alternative pathway, however the estimated KER of 5 eV for this pathway is lower than the measured KER of 5.9 eV.

The pathway to the minor feature (around  $E_{Auger}=258$  eV) is similar to the one discussed in the PDI and involves the electronic states  $S_1$  and  $S_2$ . A vibrationally excited population on the  $S_2$  state feeds the  $S_1$  state through a conical intersection and thereby dissociates along the C-C coordinate while breaking the central C=C bond.

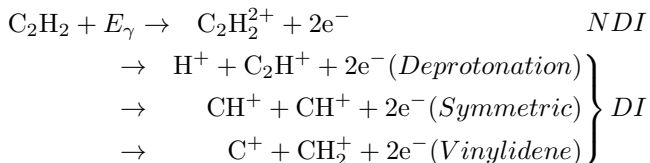
The Auger electron energy for the asymmetric channel is 253 eV. As in the PDI the singlet state  $^1B_{1g}$  can be populated and which then dissociates via coupling to the  $^1B_{2u}$  state. However, we only notice a small contribution of these states (see Fig. 8) at the corresponding Auger electron energy of 255 eV in the K-shell ionization. We instead observe Auger electrons at 253 and 251 eV. This suggests that the corresponding excited singlet states  $^1B_{3g}$  and  $^1A_g(S_4)$  are directly populated in the ionization process and dissociate via a coupling to the  $^1B_{2u}$  state. In the PDI we also found triplet states that can couple to the repulsive  $^3B_{2u}$  state via conical intersections and hence contribute to the yield of the asymmetric channel. However, since the population of triplet states is not favored by the Propensity Rule (Auger) in the K-shell ionization the branching ratio of this asymmetric channel is smaller for the Auger decay compared to the PDI of valence electrons.

Channels	$E_{sum}$	$E_{vert}$	KER	States	Branching Ratio(%)
$C_2H_2^{2+}$	8.8	33.2	—	$^3\Sigma_g^-$	$60.4\pm 1.9$
$H^+ + C_2H^+$	4.25	37.75	4.75	$^1\Pi_u, ^3\Pi_u$	$26.2\pm 0.9$
	7.25	34.75	3.75	$^3\Sigma_g^-$	$7.0\pm 0.2$
$CH^+ + CH^+$	3	39	5	$^3\Sigma_g^-, ^3\Pi_g, ^1\Sigma_u^-$	$5.0\pm 0.2$
$C^+ + CH_2^+$	6.75	35.25	4.5	$^1\Sigma_g^+$	$1.3\pm 0.1$

TABLE V: The same as Table III but for the PDI of acetylene at 42 eV photon energy. We have estimated the absolute photo ionization cross sections of these channels by normalizing to the total photo absorption cross section of 8 Mb at 42 eV photon energy [60, 61] and 0.01 Mb of the  $C^+ + CH_2^+$  channel [11]. The absolute photo ionization cross sections for the  $C_2H_2^{2+}$ ,  $H^+ + C_2H^+$ , and  $CH^+ + CH^+$  channels are 0.46, 0.25 and 0.04 Mb, respectively. Based on these numbers the ratio of double to single ionization at a photon energy of 42 eV turns out to be 10%.

### B. Acetylene ( $C_2H_2$ ): $E_\gamma=42$ eV

The following channels are observed in our measurements of the photo double ionization of acetylene using single linearly polarized 42 eV photons:



These channels are identified and analyzed in a similar way as in the PDI of ethylene. The NDI of acetylene results in a metastable dication ( $C_2H_2^{2+}$ ) and two free electrons. The energy correlation maps for the DI channels of acetylene are shown in Fig. 9. The measured  $E_{sum}$ , KER, and the vertical energies, the most likely electronic states, and the branching ratio of the different channels for the PDI of acetylene are presented in Table V. Table VI summarizes the results of the electronic structure calculations on acetylene.

Before we analyze each channel we give a general overview of the dissociation dynamics. The acetylene dication is comprised of several excited  $\Pi$  states which are conically intersected by the trio of fast dissociating  $^1\Sigma_u^-$ ,  $^3\Sigma_u^+$ , and  $^3\Delta_u$  states. The symmetric dissociation (C-C coordinate) with high  $E_{sum}$  is produced by one of these three states. The lower two  $\Pi$  states, the  $^3\Pi_u$  and the  $^1\Pi_u$  dissociate directly to the deprotonation (C-H coordinate). The deprotonation at lower  $E_{sum}$  probably stems from a nonadiabatic coupling to the higher  $\Pi$  states. The high  $E_{sum}$  peak for the deprotonation likely results from a dissociation along the surfaces of lower lying states.

State	Prop	Channels			Vertical DIP			
		I	II	III	Calculated			Expt.
					Present	Ref.[62]	Ref.[11]	
$^3\Sigma_g^-$	✓				31.98	31.35	32.0	31.7 [63] 32.7 [16]
$^1\Delta_g$					32.89	32.47	32.9	33.4 [15]
$^1\Sigma_g^+$				✓	33.57	33.24	33.5	
$^3\Pi_u$		✓	X		37.30	31.35	37.1	37.9 [16]
$^1\Pi_u$	✓	✓	X		38.08	37.64	37.8	
$^3\Pi_g$	✓		X		38.82	38.15	38.7	39.6 [16]
$^1\Sigma_u^-$	✓		✓		39.47		39.2	
$^3\Sigma_u^+$			✓		39.92		39.5	
$^3\Delta_u$			✓		40.21		39.7	

TABLE VI: Vertical double ionization potentials (DIP) for the electronic states of the acetylene dication at the geometry  $R_{CC}=2.2871$  bohr and  $R_{CH}=2.0103$  bohr. The column labeled “Prop” denotes whether or not the state is preferred by the propensity rule (double ionization preferentially populates singlet ungerade and triplet gerade states [5, 30, 31]). The channel label denotes the dication breakup channels as (I)  $H^+ + C_2H^+$ , (II)  $CH^+ + CH^+$ , and (III)  $C^+ + CH_2^+$ , respectively. The state is check marked if it can dissociate directly, and marked with an X if there is a likely dissociative pathway via a single conical intersection, to the indicated channel.

#### 1. NDI: $C_2H_2^{2+}$

The  $E_{sum}$  distribution of the electrons measured in coincidence with the metastable dications ( $C_2H_2^{2+}$ ) from the NDI channel of acetylene has a peak at about  $E_{sum}=8.8$  eV which suggests a 33.2 eV vertical energy for the double ionization. This value is in good agreement with previous measurements [15, 16, 63], as shown in Table VI. The likely states with the vertical energy of around 33 eV are the electronic ground state,  $^3\Sigma_g^-$ , and the singlet  $^1\Delta_g$  and  $^1\Sigma_g^+$  states with the possibility of simultaneous vibrational excitation during the ionization. All of these states have quasi-bound potential wells (see Fig. 10). The  $^3\Sigma_g^-$  state is favored over the other two singlet states based on the Propensity Rule (Valence) which states that singlet ungerade and triplet gerade states of the dication are favored [5, 30, 31] in the photo double ionization near threshold. The dication ground state corresponds to the electronic configuration  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2$ , with two electrons removed from two different  $\pi$  orbitals [16].

The NDI is the dominant channel (with a branching ratio of 60.4%) in the PDI of acetylene near threshold, which is in contrast to the ethylene case (5.4% NDI only). The fact that the electronic ground state of  $C_2H_2^{2+}$  is populated the most is also in accordance with the Propensity Rule (Valence). However, in the ethylene dication case both the electronic ground singlet state and the first triplet state are not favored by the Propensity Rule (Valence).

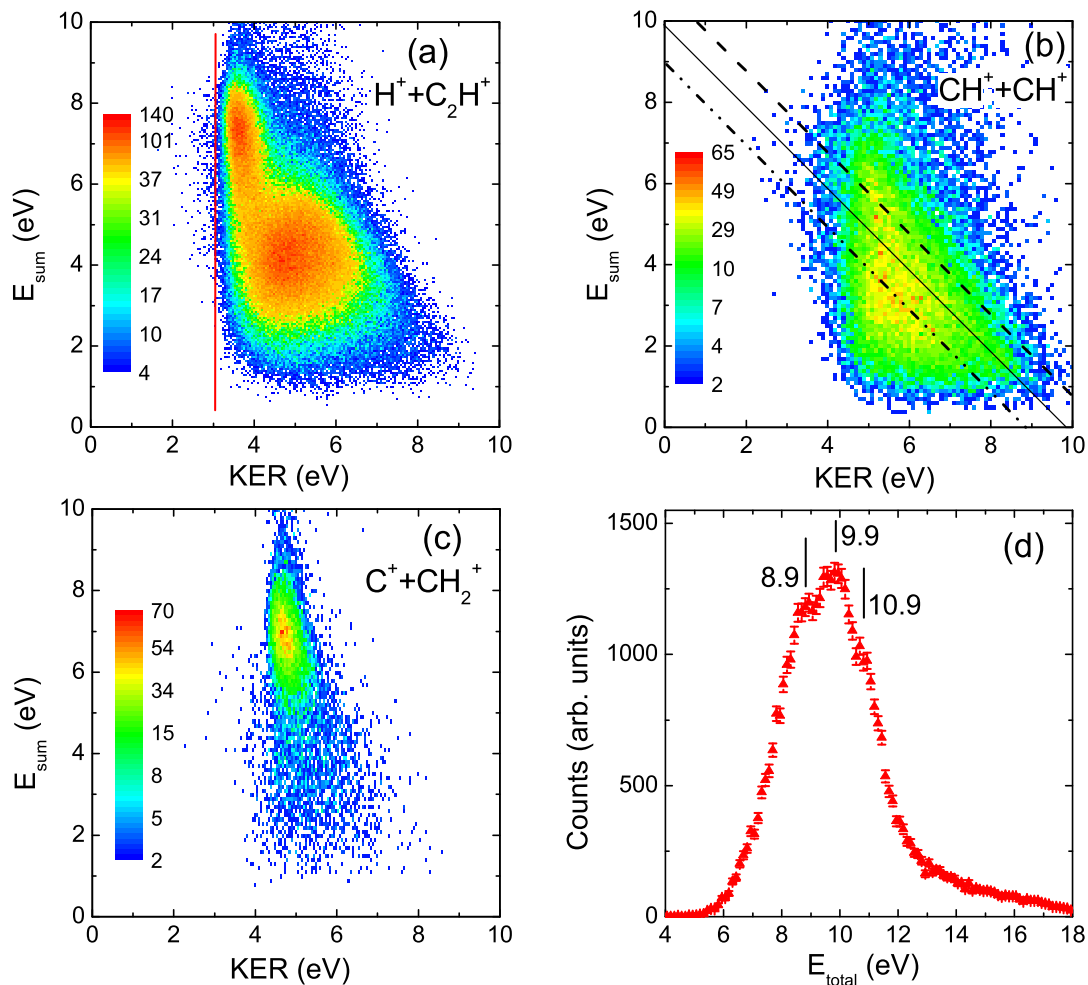


FIG. 9: (Color online) Energy correlation map of the kinetic energy release (KER) along the horizontal axis and  $E_{sum}$  along the vertical axis for the (a)  $H^+ + C_2H^+$ , (b)  $CH^+ + CH^+$ , and (c)  $C^+ + CH_2^+$  channels, respectively. The lines in (b) indicate possible three different pathways. The color scale is logarithmic with the same dynamic range for all the plots. (d) The total energy ( $KER + E_{sum}$ ) distribution of the symmetric breakup channel displayed in (b).

## 2. Deprotonation: $H^+ + C_2H^+$

The energy correlation map of the deprotonation channel, shown in Fig. 9(a), has two distinct features. The major feature has KER and  $E_{sum}$  peaks at around 4.75 and 4.25 eV, respectively, while the minor feature has a KER peak around 3.75 eV and an  $E_{sum}$  peak around 7.25 eV. The KER values from this measurement are in good agreement with the values in the literature [9, 11]. There are some extra features in our measured KER distributions compared to that of Ref. [9] due to a slightly higher photon energy which enables access to higher-lying excited states. For example, one can see two distinct peaks in the KER distribution of the deprotonation channel in Fig. 9(a). To the best of our knowledge, there is no data in the literature to compare our  $E_{sum}$  values. However, the vertical energies can be compared to our previous measurement of the carbon K-shell ionization of

acetylene followed by Auger decay [10] despite the drastically different photon energy and ionization mechanism. Many of the states identified in the present study (see Table V) are the same as identified in Ref. [10]. However, in that paper only singlet states were considered because of the Propensity Rule (Auger) [33, 34]. While this work is focused on the PDI of valence electrons we consider both singlet and triplet states that are allowed to be populated by the Propensity Rule (Valence).

The two distinct features in the deprotonation channel are the result of at least two different pathways. As shown below, one feature stems from the lower manifold of the electronic states and the other feature from the electronic excited states of the acetylene dication.

The feature with a broad KER distribution (peak around 4.75 eV) and an  $E_{sum}$  peak around 4.25 eV results from the states whose vertical energy is about 37.75 eV. The likely states are  $^1\Pi_u$  and  $^3\Pi_u$ . Both of the states are

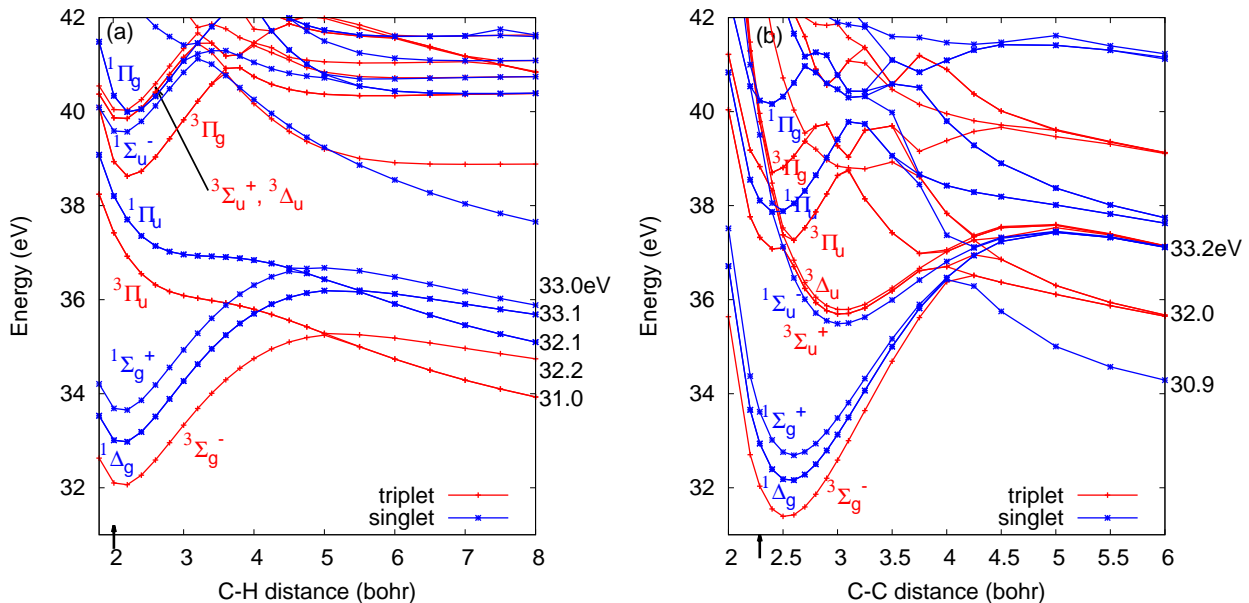


FIG. 10: (Color online) Cut of the potential energy surfaces (singlet and triplet states) of the acetylene dication for (a) C-H and (b) C-C distances calculated using the multi-configuration self-consistent field (MCSCF) method. The vertical arrows indicate the Franck-Condon region. States are labeled with the irreducible representations appropriate at the equilibrium geometry of the neutral molecule.

dissociative in the C-H coordinate as shown in the cut of the PESs as a function of the C-H distance in Fig. 10(a). The dissociation along the surface of the  $^1\Pi_u$  state results in a KER of 6.0 eV and the DI along the  $^3\Pi_u$  state leads to a KER value of 6.3 eV. The Propensity Rule (Valence) favors the  $^1\Pi_u$  state.

The next feature in the deprotonation channel has KER and  $E_{sum}$  values of 3.75 and 7.25 eV, respectively. This feature has a narrower KER distribution than the other feature (described in the previous paragraph). Based on the vertical energy of 34.75 eV the likely pathway for this feature involves the lowest manifold of electronic states, namely  $^3\Sigma_g^-$ ,  $^1\Delta_g$ , and  $^1\Sigma_g^+$ , with possible vibrational excitation. By surveying the cuts of the PESs of these states along the C-H coordinate (shown in Fig. 10(a)), the barrier height of the  $^3\Sigma_g^-$  state is about the same as the measured vertical energy. So the dications with sufficient energy to overcome the barrier dissociate. This manifests itself in the sharp cut-off on the lower energy side of the KER distribution as seen in Fig. 9(a), marked with a vertical line around a KER of 3 eV for easier visualization.

The ground state has an asymptote calculated to be 31.0 eV. Taking 34.25 eV as the barrier height [14], one expects a KER of 3.25 eV at the onset, which agrees well with the present result of KER 3.75 eV. The barrier height of the other two singlet states ( $^1\Delta_g$ , and  $^1\Sigma_g^+$ ) in the C-H coordinate is higher than that of the triplet state ( $^3\Sigma_g^-$ ). Hence  $^3\Sigma_g^-$  is the most likely state responsible for this feature.

### 3. Symmetric breakup: $\text{CH}^+ + \text{CH}^+$

In the case of the symmetric breakup (acetylene products) broad KER and  $E_{sum}$  distributions are observed in Fig. 9(b). The KER distribution extends from 4 to 8.5 eV with a peak at 5 eV. The  $E_{sum}$  distribution has an energy range from 1 to 7.5 eV with a peak at about 3 eV. This wide range of energy means that states with vertical energies from 41 eV to 34.5 eV are responsible for the symmetric breakup of acetylene.

Several excited states, namely the  $^1\Sigma_u^-$  (DIP=39.47 eV),  $^3\Sigma_u^+$  (DIP=39.92 eV), and  $^3\Delta_u$  (DIP=40.21 eV) contribute to the lower  $E_{sum}$  feature. These states are fed through conical intersections with a manifold of  $\Pi$  states, specifically  $^3\Pi_g$  (DIP=38.82 eV),  $^1\Pi_u$  (DIP=38.08 eV), and  $^3\Pi_u$  (DIP=37.3 eV). These  $\Pi$  states are populated by the photo ionization in the Franck-Condon region. The cut of the PESs of these states are shown in Fig. 10(b). The  $^1\Sigma_u^-$ ,  $^3\Sigma_u^+$ , and  $^3\Delta_u$  states also have quasi-bound potential wells (at around 3 bohr) in a downhill dissociation path. When the dissociation begins at much higher energies in the Franck-Condon region the barriers can be circumvented. There are three different asymptotic limits (with about 2.3 eV separation) to which the dissociation products may end up. This in turn results in a broad KER like the one that is measured.

For the higher  $E_{sum}$  value (say 7.0 eV) the vertical energy is 35.0 eV and the states responsible for this feature are the lowest lying states, i.e.  $^3\Sigma_g^-$ ,  $^1\Delta_g$  and  $^1\Sigma_g^+$ . The barriers to the symmetric breakup channels are around

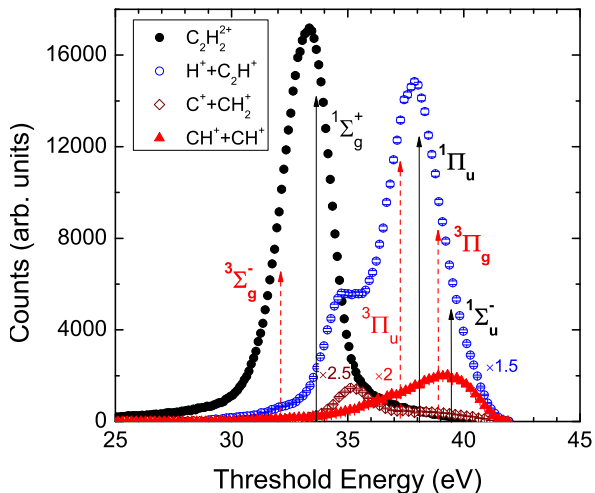


FIG. 11: (Color online) The same as Fig. 4 but for the PDI of acetylene using 42 eV photons (linearly polarized light).

34.56 [45] and 35.12 eV [14] for a bent geometry. But the plots in Fig. 10(b) are for a linear geometry, where the barrier is much higher (approximately at 36 eV). The barrier clearly controls the maximum  $E_{sum}$  that is observed for the symmetric breakup channel. A typical dissociation involving a state with the asymptotic limit of 30.9 eV (Fig. 10) would thus result in a KER of 4.1 eV, which agrees well with our measured KER for the higher  $E_{sum}$  shown in Fig. 9(b).

The combination of all these pathways is expected to lead to a convoluted energy distribution like the one we have observed. The individual features associated with each pathway overlap. However, we see structure (marked with lines) in the energy correlation map shown in Fig. 9(b). One can see the individual features in the total energy (KER+ $E_{sum}$ ) distribution of the symmetric channel displayed in Fig. 9(d). The peaks are about one eV apart from one another and so are the asymptotic limits of the lower-lying states in Fig. 10(b) that are responsible for this channel.

#### 4. Vinylidene: $C^++CH_2^+$

The energy correlation map of the vinylidene channel ( $C^++CH_2^+$ ) is shown in Fig. 9(c). One can see a distribution that peaks around KER=4.5 eV and  $E_{sum}$ =6.8 eV. The vertical energy of 35.2 eV indicates that the lowest manifold of states (namely,  $^3\Sigma_g^-$ ,  $^1\Delta_g$ , and  $^1\Sigma_g^+$ ) with vibrational excitation are responsible for the vinylidene channel. The vertical energy and KER are in agreement with the K-shell ionization measurements in Ref. [10]. This suggests that the same pathway, involving the  $^1\Sigma_g^+$  state with 35.35 eV barrier height [10], is responsible for the vinylidene channel in the direct photo double ionization of acetylene.

#### 5. Summary: Acetylene photo double ionization

The threshold energy plot, shown in Fig. 11, reveals that the NDI of acetylene involves the states with a vertical energy around 33 eV. At a slightly higher threshold energy of about 34.5 eV the vinylidene and the deprotonation channels open up. As we go further up in the threshold energy the major feature of the deprotonation and the symmetric breakup channels dominate over the NDI channel.

Among the DI channels of acetylene the deprotonation has the highest branching ratio (33.2%) as in the case of the PDI of ethylene. The vinylidene channel has the smallest branching ratio (1.3%) and the symmetric breakup channel branching ratio is about 5.0%. By looking at the PESs in Fig. 10, one can see that the PESs in the C-H coordinate have smaller barriers than in the C-C coordinate, and hence breaking the C-H bond, leading to a deprotonation, is more likely than breaking the  $C\equiv C$  bond. Since the ground state ( $^3\Sigma_g^-$ ) can be populated by the Propensity Rule (Valence) and also has a deep potential well, the NDI channel is the dominant channel (60.4%) in the PDI of acetylene.

## V. SUMMARY

In conclusion, we have presented kinematically complete measurements of the direct photo double ionization of ethylene and acetylene molecules near threshold. With our COLTRIMS setup we are able to identify both nondissociative and dissociative double ionization of these molecules. In accordance with the Propensity Rule (Valence), suggested decades ago, and the barrier to torsion around the C-C bond, our results clearly show that the electronic ground state of the ethylene dication is hardly populated. The likelihood of removing the two  $\pi$  electrons from the outermost occupied orbital, which is responsible for restricting the torsion of the ethylene molecule, by direct PDI must be very small. The same scenario applies to the PDI of acetylene molecules where the electronic ground state of the dication (a triplet state,  $^3\Sigma_g^-$ ) is a product of removing two electrons from different orbitals. The measured branching ratio of the NDI channel is relatively higher in acetylene.

Our theoretical results allow us to unravel the states for the NDI channel and the dissociation dynamics for the DI channels. We have found that the electronic excited states of the ethylene dication contribute mainly to the DI channels and very little to the NDI channel. We have also found that the first excited singlet state contributes directly to the deprotonation channel and indirectly to the symmetric channel via the ultrafast population transfer through the conical intersection to the electronic ground state ( $S_1$ ). Both processes are interesting candidates for time resolved studies employing pump-probe techniques. We theorize that the passage through the conical intersection will produce interesting effects



on the electron angular distributions. On another note, our observation of similar yields of metastable ethylene dications produced by PDI of valence electrons or Auger decay via K-shell ionization is intriguing, and warrants further theoretical investigation.

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