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Authors
Osipov, Timur
Rescigno, Thomas N.
Weber, Thorsten
et al.

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Fragmentation pathways for selected electronic states of the acetylene dication

T. Osipov,[1] T.N. Rescigno,[1] T. Weber,[1] S. Miyabe,[1] T. Jahnke,[2] A. Alnaser,[3] M.P. Hertlein,[1] O. Jagutzki,[2]
L.Ph.H. Schmidt,[2] M. Schöffler,[2] L. Foucar,[2] S. Schössler,[2] T. Havermeier,[2] M. Odenweller,[2]
S. Voss,[2] B. Feinberg,[1] A.L. Landers,[4] M.H. Prior,[1] R. Dörner,[2] C.L. Cocke,[3] and A. Belkacem[1]

[1] *Lawrence Berkeley National Laboratory, Chemical Sciences, Berkeley, California 94720, USA*
[2] *Institut für Kernphysik, J. W. Goethe-Universität Frankfurt am Main,*
Max-von-Laue-Str. 1, D-60438 Frankfurt Germany
[3] *Department of Physics, Kansas State University, Manhattan, Kansas 66506, USA*
[4] *Department of Physics, Auburn University, Alabama 36849, USA*
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Coincident measurement of the Auger electron and fragment ion momenta emitted after carbon core-level photoionization of acetylene has yielded new understanding of how the dication fragments. *Ab initio* calculations and experimental data, including body-frame Auger angular distributions, are used to identify the parent electronic states and together yield a comprehensive map of the dissociation pathways which include surface crossings and barriers to direct dissociation. The Auger angular distributions show evidence of core-hole localization.

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Nature's smallest stable hydrocarbon, the symmetric linear acetylene molecule, C_2H_2, is an important polyatomic system for the study of photo initiated processes. Important features of the intramolecular dynamics in neutral acetylene have been revealed over many years through numerous spectroscopic studies. More recently, the availability of synchrotron radiation and intense laser sources has lead to intriguing studies of the ionization, isomerization and breakup dynamics of acetylene ions. Fragmentation of the dication, $C_2H_2^{++}$, formed by direct UV photo-double ionization, was first studied by Thissen *et al.* [1] who measured yields into different channels and proposed structural configurations through which the fragmentation occurred. Of particular interest are the yields into the symmetric (CH^+/CH^+), deprotonation (HCC^+/H^+) and quasi-symmetric (HHC^+/C^+) channels, the latter involving isomerization from the neutral acetylene structure into the vinylidene configuration prior to breakup. It is to be expected that the products of dissociation, their kinetic energy releases (KER) and the isomerization times will depend on the particular initial electronic states of the dication involved, but such detailed information has heretofore not been available. In this work, the dication of acetylene is prepared by Auger decay following core-level X-ray photoionization. The energy and the angular distribution of the Auger electron is measured in coincidence with the kinetic energy of the fragments. We show that this experimental approach, in combination with *ab initio* quantum mechanical calculations, can yield a comprehensive map of the two-body dissociation pathways including transition through different electronic energy surfaces, barriers to direct dissociation and the associated rearrangement channels as well as information on core-hole localization at one of the carbon atoms.

While the fragmentation and isomerization of the acetylene dication have been studied for a number of years, the only experimental information previously available on the energetic pathways has been measurements of appearance energies reported by Thissen *et al.* [1] and some information on the KER in the symmetric breakup channels [2, 3]. Osipov *et al.* [2] reported an upper limit of 60 fs on the isomerization time when the dication is formed by K-shell photoionization followed by Auger decay, but did not control the electronic state from which the isomerization occurred.

We produce the dication by using 310 eV photons to remove one of the carbon K-shell electrons; the system then promptly (6 fs) Auger decays to the dication [4]. The process is $C_2H_2 + h\nu \rightarrow C_2H_2^{+*} + e^- (\sim 20 \text{ eV}) \rightarrow C_2H_2^{++} + e^-$ (Auger$\sim$ 250 eV). The Auger decay can leave the dication in any of a number of electronic states. If such a state has sufficient energy, through either vibrational or electronic energy or both, to dissociate into two charged fragments, we measure the momenta of the positively charged ions in coincidence with Auger electrons. A related experiment was performed by Osipov *et al.* [2]. The present experiment differs from that one in that we do not measure the photoelectron but instead measure the Auger electron with sufficient energy resolution to determine the electronic state of the dication which is fed. We can thus measure the fragmentation pattern for different electronic states of the dication and determine which ones fragment into the symmetric channel (Acetylene, A, $C_2H_2^{++} \rightarrow CH^+ + CH^+$), which to the quasi-symmetric channel (vinylidene, V, $C_2H_2^{++} \rightarrow CH_2^+ + C^+$) and which by ejection of a single proton (deprotonation, P, $C_2H_2^{++} \rightarrow C_2H^+ + H^+$). (In this paper we consider only these fully kinematically determined two-body channels, although others are fed as well.)

The experimental details are similar to those described in refs. [5–7]. A jet of acetylene gas was photoionized by
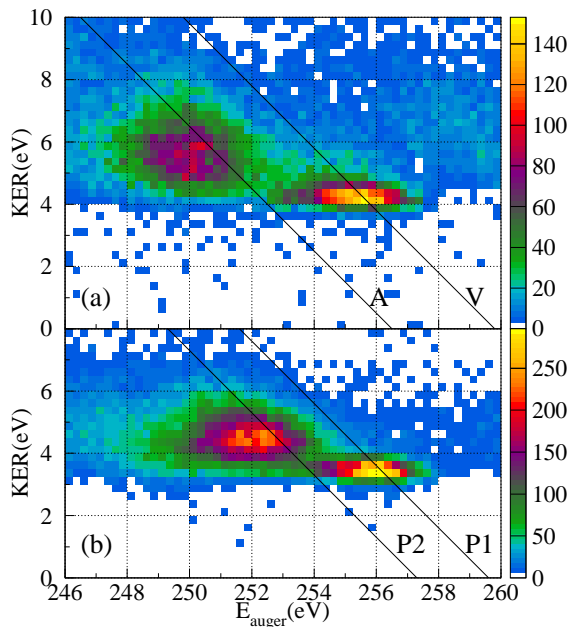
FIG. 1: (Color online) KER vs. Auger electron energy for **(a)** CH^+ + CH^+ and CH_2^+ + C^+ and **(b)** deprotonation C_2H^+ + H^+ break up channels. Diagonal lines are determined by energy conservation (KER + E_{Aug} = constant) with x-axis intercepts indicating the energy of the various product species at infinite separation (see text). The location of the curves was chosen approximately (± 0.5eV) through the peak position (not the midpoint) of the appropriate spots. The evidence of more density to the left of the diagonal lines than to the right is due to the presence of the rovibrationally excited product fragments

FIG. 2: (Color online) Potential energy curves in linear geometry for $C_2H_2^{++}$ (a) symmetric breakup and (b) deprotonation. All energies relative to neutral acetylene at equilibrium geometry. Note that the bond distances other than those displayed are fixed at the equilibrium geometry of neutral C_2H_2. Shaded portions indicate Franck-Condon regions and vertical lines mark the equilibrium geometry of the neutral.

a beam of circularly polarized photons from the LBNL Advanced Light Source. A COLTRIMS (cold target recoil ion momentum spectroscopy) spectrometer [5] was used to extract positively charged particles towards one side of the spectrometer and electrons towards the other side. RoentDek position sensitive delay line detectors [8] were placed at both ends of the spectrometer for measuring the position and the time-of-flight (TOF) of the charged particles. By using a weak magnetic field (~ 10 gauss) collinear with the spectrometer extraction field, we were able to collect all Auger electrons emitted within 15 degrees of the spectrometer axis (transverse to the photon beam) while all positive recoils of the reaction were measured with 4π solid angle efficiency. For each ionization event the vector momenta of both fragments and the Auger electron were determined by the times and positions of arrival of the particles on the detectors. From these the ion species, the Auger energies and the kinetic energy release were calculated for whichever channel (A,V or P) was populated in the event.

K-shell photoionization of C_2H_2 creates an energetic, singly-charged, quasi-degenerate state(s) of the core-
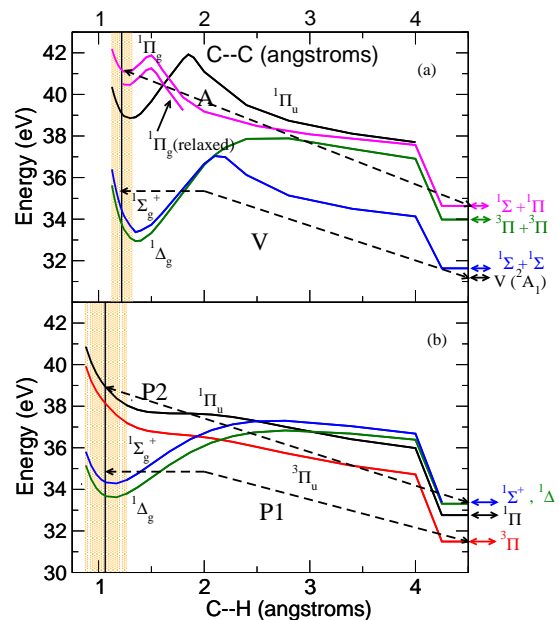
ionized molecule, $1\sigma_{g,u}^{-1}(^2\Sigma_{g,u}^+)$, with 291.1 eV energy relative to the neutral, which subsequently decays by filling the core vacancy and ejecting a fast electron. The Auger energy measurement determines the electronic state of the dication $C_2H_2^{++}$ from which the dissociation starts. The KER is a measure of the difference in energy between the starting point of the dissociation and the final state of the fragments. In Fig. 1 we display a density plot of Auger energy versus KER for the symmetric and quasi-symmetric channels A and V (Fig.1a) and the deprotonation channels (Fig.1b). The g/u splitting of the initial state(s) is of order ~ 100 meV [9], smaller than the Auger energy resolution of our apparatus (~ 0.5 eV) and of the same order of magnitude as the natural linewidths of the states (~ 90 meV), which means that they cannot be resolved in principle. The sum of the KER and the Auger energy represents the difference in energy between the initial core-hole state(s) and the final state of the fragments. This is shown as the x-axis intercepts of the solid lines in Fig. 1. Each intercept represents a different state of the fragments at the asymptotic limit.

Turning to Fig. 1a, we see two intense spots at Auger energies of 255.5 and 250 eV. Since the sum momentum of the fragment ions plus the recoil momentum must approximately add to zero (the photoelectron energy and photon momenta are much smaller) we were able to determine that the 255.5 eV peak corresponds almost ex-

TABLE I: Auger electron energies, vertical electronic energies and corresponding fragment energies for the symmetric (A), quasi-symmetric (V) and deprotonation (P1,P2) breakup channels. Energies in eV.

Channel	Auger energy	Vertical energy	Auger energy +KER	Fragment energy
A	250	41.1	256.5	34.6
V	255.5	35.6	259.75	31.35
P1	256	35.1	259.5	31.6
P2	252	39.1	257.3	33.8

FIG. 3: Auger electron angular distribution in the molecular frame for (a) symmetric $CH^+ + CH^+$ (250eV Auger) and (b) deprotonation $C_2H^+ + H^+$ (252eV Auger) break up channels

clusively to V fragmentation, while the 250 eV peak corresponds to A fragmentation. The details of this separation are similar to those discussed in ref. [2, 10]. Fig. 1b exhibits two intense spots labeled P1 and P2 which were determined to correlate with the deprotonation channel.

The initial step is to extract the relevant energetics information associated with the A, V, P1 and P2 dissociation channels from Fig. 1. This information is summarized in Table I. To assist in the interpretation of the measured data, we have carried out multi-reference configuration-interaction calculations on the electronic states of the dication. Fig. 2 shows two cuts in linear geometry through the potential surfaces of the states relevant to this study, corresponding to symmetric breakup and deprotonation, respectively. Note that the bond distances other than the one being plotted are fixed at the equilibrium geometry of neutral acetylene.

It is well established that Auger decays from closed-shell molecules populate triplet states only weakly. In the simplest spin-restricted theory, the Auger decay probability is determined by a two-electron Coulomb integral involving a core orbital, a continuum orbital and two valence orbitals. For triplet states, where the two valence orbitals must necessarily be different, the transition matrix element involves the antisymmetric combination of two spatial integrals, which tend to cancel for high energy continuum orbitals [11]. This feature of Auger spectra for similar molecules is well established [12] and leads us to hereafter eliminate triplet states from consideration.

Both the experimental data and theory show that the A (acetylene) and P2 (deprotonation) channels originate from higher excited states of the dication. We find that fragmentation of the A channel is occurring along the $1\pi_u^{-1}2\sigma_u^{-1},^1\Pi_g$ state, which was seen in the Auger spectrum of Kivimaki et al. [13], but was not considered in earlier theoretical studies [1, 14, 15]. Figure 2 shows that this state intersects the FC distance of 1.2 Å near an energy of 41 eV and dissociates to $CH^+(^1\Sigma)+CH^{+*}(^1\Pi)$ near 34.5 eV, which is consistent with the observed data. Although Fig. 2a shows that there is a barrier to dissociation when the CH distances are constrained to their initial values, optimization of these distances (shown as
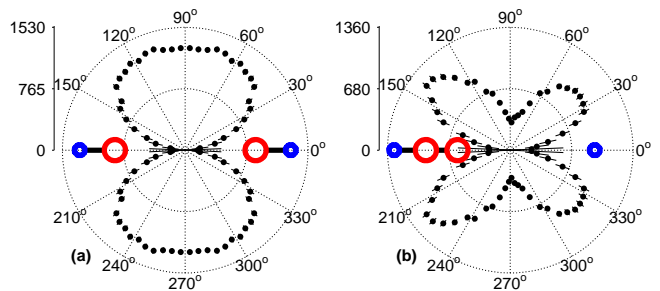
the "relaxed" curve in Fig. 2a) reveals that dissociation is possible with essentially no barrier.

We now turn our attention to the P2 deprotonation channel in Fig.1b. Close examination shows that the Auger energy in this channel, at 252 eV, is slightly higher than the 250 eV Auger energy in the A channel of Fig. 1a. Kivimaki et al. [13] also see two peaks in this region, and the one at 252 eV is interpreted as $1\pi_u^{-1}3\sigma_g^{-1},^1\Pi_u$. On energetic grounds, the $^1\Pi_u$ assignment is consistent with our calculations as well as the other theoretical studies [1, 14, 15] and, as shown in Fig. 2b, there is no barrier to dissociation in this channel. It is also noteworthy that the observed KER of 5.3 eV for this channel indicates that C_2H^+ is evidently being formed in its $^1\Delta$ or $^1\Sigma^+$ excited state.

We have measured the Auger angular distributions in the molecular frame for each of the features discussed above. These are shown in Fig. 3. They provide a valuable consistency check on the deduced state identifications and, as we show below, give additional insight into the dissociation dynamics. K-shell photoionization will eject electrons from either the $1\sigma_g$ or $1\sigma_u$ orbitals. Whether Auger decay populates the even parity $1\pi_u^{-1}2\sigma_u^{-1},^1\Pi_g$ final state at 250 eV or the odd parity $1\pi_u^{-1}3\sigma_g^{-1},^1\Pi_u$ state at 252 eV, the Auger electrons would be ejected into $k\pi_g$ or $k\pi_u$ continua, so we would expect to find a node in the Auger angular distribution along the axis of the molecule. The Auger angular distributions for the P2 and A channels shown in Fig. 3 support this expectation.

Experiment and theory show that the P1(256 eV) and V(255.5 eV) channels originate from lower states of the dication. Peaks at these energies appear in the non-coincident Auger spectra of Kivimaki et al. [13] and were identified as $1\pi_u^{-2}$ states, where the vacuum state is neutral acetylene with configuration $1\sigma_g^2, 1\sigma_g^2, 2\sigma_g^2, 2\sigma_g^2, 3\sigma_g^2, 1\pi_u^4$. Removal of two π_u electrons from this configuration gives the lowest three electronic states of the double cation, $^3\Sigma_g^-,^1\Delta_g,$ and$^1\Sigma_g^+$ [1]. As mentioned above, the triplet state is not (or only weakly)

fed by the Auger process. Moreover, these states are not gateways into the A channel because the barrier along the CC bond, seen in Fig. 2a, is too high. We note that the location of this barrier has been the subject of considerable controversy [14, 15], since it does not seem to be consistent with the low appearance energy for the A channel seen by Thiessen *et al.* [1]. We argue below that both the V and P1 channels originate from the $^1\Sigma_g^+$ dication state.

The equilibrium separation of the C atoms in the neutral, 1.2 Å, allows the $^1\Sigma_g^+$ state to be fed with only about 2 eV of vibrational energy in a Franck-Condon (FC) process, which is insufficient to overcome the barriers seen in Fig. 2a. However, previous theoretical calculations [14, 15] show that dissociation to the V or P1 configuration are expected to pass through much lower barriers, low enough that even a FC process could supply the required vibrational energy. The Auger intensity plots in Fig. 1 show that the P1 and V KERs are clipped from below, indicating that the intensities are determined by energy barriers, which can be deduced from the measured data. The KER values and corresponding Auger energies where the intensities are clipped indicate that the barriers for the P1 and V channels lie at 34.85 and 35.35 eV, respectively, as shown by the flat portion of the broken lines in Fig. 2. Excitation energies between 34.85 and 35.35 eV lead to the deprotonation P1. For energies above 35.35 eV, where the KER intensity for P1 is again clipped, the V channel opens up and overtakes deprotonation. Although the $^1\Delta_g$ and $^1\Sigma_g^+$ states are both Franck-Condon allowed, previous theory [15] finds that the V barrier is lower than the P barrier on the $^1\Delta_g$ surface. Since we observe the opposite order, we are led to believe that both channels are fed by the $^1\Sigma_g^+$ state. For the P1 channel, the measured KER indicate that C_2H^+ ion is produced in its ground $^3\Pi$ state. As the potential curves in Fig. 2b show, the dissociation may begin with the $^1\Sigma_g^+$ state, but the excited $1\pi_u^{-1}3\sigma_g^{-1},^3\Pi_u$ state, which crosses the $^1\Sigma_g^+$ state and correlates with the observed products, is evidently involved in the dissociation dynamics of P1.

The Auger angular distribution in Fig. 3 associated with the P2 deprotonation channel shows a left/right asymmetry, which we believe to be evidence of a localized core-hole in the initial ionized state. Such a localized hole could impart different initial momenta to the two H atoms and break the $g-u$ symmetry of the ion in the ~6 fs before the hole is filled. In this way, the memory of the initial core-hole is reflected in the dissociation dynamics following Auger decay, leading in turn to the observed left/right asymmetry. This explanation is also consistent with the recent observations of Adachi *et al.* [16] and leads us to believe that we are seeing an indication of proton dynamics induced by core-hole creation [17]. We

should also mention here that the Auger angular distribution associated with the lower P1 deprotonation channel (not shown) is essentially isotropic, indicating that there is substantial rearrangement of the molecule prior to dissociation in this channel.

In conclusion, we have measured the fragmentation patterns of the acetylene dication prepared in different electronic states. The identification of these states is consistent with the measured Auger angular distributions and is supported by our theoretical calculations. The states were prepared by identifying the Auger decay channels fed by a K core-hole created through photoionization. The production of the vinylidene-like fragmentation is found to proceed mainly through the $^1\Sigma_g^+$ $(1\pi_u^{-2})$ dication state while symmetric fragmentation occurs when the system is prepared in the excited $1\pi_u^{-1}2\sigma_u^{-1},^1\Pi_g$ state. We find two deprotonation channels, one through the $^1\Sigma_g^+$ state, the other through the $1\pi_u^{-1}3\sigma_g^{-1},^1\Pi_u$ state. For the latter channel, the Auger angular distribution shows an asymmetry that gives evidence of hole localization in the initial core-ionized state. It is noteworthy that only in the A channel does the dissociation lead directly to the expected correlated products. In all other channels, the fragmentation appears to involve curve crossings and/or conical intersections.

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