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Fragmentation pathways for selected electronic states of the acetylene dication

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Abstract
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 for certain breakup channels show evidence of core–hole localization.

(Some figures in this article are in colour only in the electronic version)

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 led 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 (A, CH^+/CH^+), deprotonation (P, HCC^+/H^+) and quasi-symmetric (V, HHC^+/C^+) channels, the latter involving isomerization from the neutral acetylene structure into the vinylidene configuration prior to breakup. One expects 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 basic technique of Auger electron–ion fragment coincidence was pioneered by Eberhardt and coworkers with their study on N_2 [2]. In our work, 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

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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 are measurements of appearance energies reported by Thissen *et al* [1] and some information on the KER in the symmetric breakup channels [3, 4]. Osipov *et al* [3] reported an upper limit of 60 fs for 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. Adachi *et al* [5] have recently reported coincident measurements of K-shell photoelectron angular distributions with A, P and V breakup channels, but like earlier investigators, did not attempt to identify specific parent electronic states.

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 [6]. The process is $C_2H_2 + h\nu \rightarrow C_2H_2^{+*} + e^- (\sim 20\ \text{eV}) \rightarrow C_2H_2^{++} + 2e^-$ (Auger ~ 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 the Auger electrons. A related experiment was performed by Osipov *et al* [3]; however here 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 determine 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, $C_2H_2^{++} \rightarrow C_2H^+ + H^+$). (We consider only these fully kinematically determined two-body channels.)

The experimental details are similar to those described in [7–9]. A jet of acetylene gas was photoionized by a beam of circularly polarized photons from the LBNL advanced light source. A COLTRIMS (cold target recoil ion momentum spectroscopy) spectrometer [7] was used to extract positively charged ions to one side of the spectrometer and electrons to the other. RoentDek position-sensitive delay line detectors [10] 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 $15°$ of the spectrometer axis (transverse to the photon beam) while all positive ions were measured with 4π solid angle efficiency. For each ionization event the vector momenta of both ion 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.
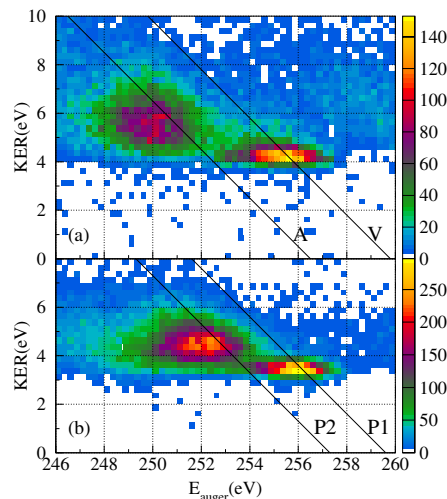
Figure 1. KER versus Auger electron energy for (a) $CH^+ + CH^+$ and $CH_2^+ + C^+$ and (b) deprotonation $C_2H^+ + H^+$ break-up channels. Diagonal lines are determined by energy conservation (KER + E_{Aug} = constant) with *x*-axis intercepts indicating the energy of the various product species at infinite separation (see the text). The location of the curves was chosen approximately (± 0.5 eV) 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.

K-shell photoionization of C_2H_2 creates an energetic, singly-charged, quasi-degenerate state(s) of the core-ionized molecule, $1\sigma_{g,u}^{-1}(^2\Sigma_{g,u}^+)$ 291.1 eV above the neutral, which then 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 energy difference between the starting point of the dissociation and the final state of the fragments. In figure 1 we display a density plot of Auger energy versus KER for the symmetric and quasi-symmetric channels A and V (figure 1(a)) and the deprotonation channels (figure 1(b)). The g/u splitting of the initial state(s) is ~ 100 meV [11], 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), thus they can barely be resolved in principle. The sum of the KER and the Auger energy is 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 figure 1. Each intercept represents a different asymptotic state of the fragments.

Turning to figure 1(a), we see two intense spots at Auger energies of 255.5 and 250 eV. Since the sum momentum of the fragment ions must be approximately zero (the photoelectron energy and photon momenta are much smaller) we were able to determine that the 255.5 eV peak corresponds almost exclusively to V fragmentation (with possibly small contributions from A fragmentation), while the 250 eV peak corresponds exclusively to A fragmentation. The details of this separation are similar to those discussed in [3, 12]. Figure 1(b) exhibits two intense spots labelled P1 and P2 which were determined to correlate with the deprotonation channel.

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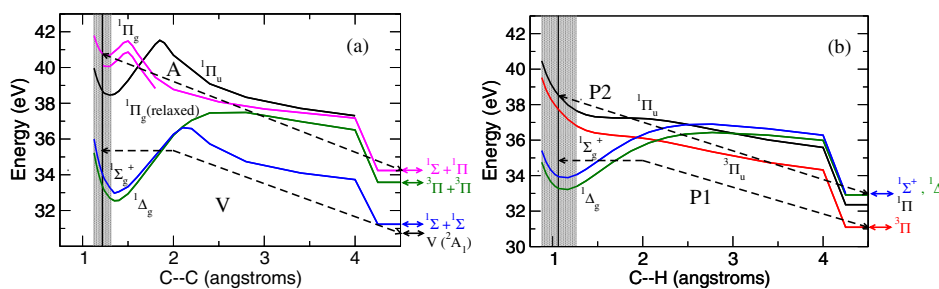
Figure 2. Potential energy curves in linear geometry for $C_2H_2^{++}$ (a) symmetric breakup and (b) deprotonation. All energies relative to neutral acetylene at equilibrium geometry. Note that the bond distances other than those displayed are fixed at the equilibrium geometry of neutral C_2H_2. Shaded portions indicate Franck–Condon regions and vertical lines mark the equilibrium geometry of the neutral. The dashed curves indicate the initial electronic and final fragment states for the four (P1, P2, A and V) observed channels.

Table 1. 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

We extracted the relevant energetics information associated with the A, V, P1 and P2 dissociation channels from figure 1. This information is summarized in table 1. To assist in the interpretation of these measured data, we carried out configuration-interaction calculations on the electronic states of the dication. The calculations included all single and double excitations from a ten-orbital complete active space, with the restriction that the carbon 1s core-orbitals remain doubly occupied. Our computed adiabatic double ionization energies are close to recent experimental determinations [13]. Figure 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 that being plotted are fixed at the equilibrium geometry of neutral acetylene.

It is well known 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 [14]. This feature of Auger spectra for similar molecules is well established [15] and leads us to eliminate triplet states from consideration.

The experiment and theory show that the A (acetylene) and P2 (deprotonation) channels originate from higher excited states of the dication. We find that the fragmentation of the A channel occurs 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* [16], but was not considered in earlier theoretical studies [1, 17, 18]. Figure 2

shows that this state intersects the Franck–Condon (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 figure 2(a) shows a barrier to dissociation when the CH distances are constrained to their initial values, optimization of these distances (shown as the 'relaxed' curve in figure 2(a)) reveals that dissociation is possible with essentially no barrier.

Turning next to the P2 deprotonation channel in figure 1(b), close examination shows that the Auger energy, at 252 eV, is slightly higher than the 250 eV Auger energy in the A channel of figure 1(a). Kivimaki *et al* [16] also saw two peaks in this region, and that 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, 17, 18] and, as shown in figure 2(b), 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 formed in its $^1\Delta$ or $^1\Sigma^+$ excited state.

We have measured the Auger angular distributions for each of the features discussed above. These distributions are shown in figure 3. If the axial recoil approximation is valid, i.e. if the axis along which the departing fragments fly is approximately that of the original acetylene molecule, then these molecular frame angular distributions can 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 a node in the Auger angular distribution along the axis of the molecule. The Auger angular distributions for the A and P2 channels shown in figures 3(a) and (d), respectively, clearly support this expectation. The distributions associated with the P1 and V channels are more difficult to interpret and will be discussed further below.

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* [16] and were identified as $1\pi_u^{-2}$ states, where the vacuum state is neutral acetylene with

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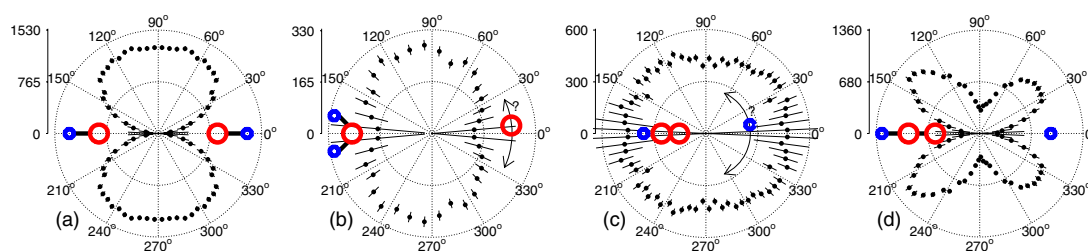
Figure 3. Auger electron angular distribution in the molecular frame for (a) symmetric $CH^+ + CH^+$ (250 eV Auger), (b) vinylidene $CH_2^+ + C^+$ (255.5 eV Auger), (c) deprotonation (P1) $C_2H^+ + H^+$ (256 eV Auger) and (d) deprotonation (P2) $C_2H^+ + H^+$ (252 eV Auger) break-up channels.

configuration $1\sigma_g^2$, $1\sigma_u^2$, $2\sigma_g^2$, $2\sigma_u^2$, $3\sigma_g^2$, $1\pi_u^4$. 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 expected to be major gateways into the A channel because the barrier along the CC bond, seen in figure 2(a), is too high. We note that the location of this barrier has been the subject of considerable controversy [17, 18], since it does not seem to be consistent with the low appearance energy for the A channel seen by Thissen *et al* [1]. Indeed, we cannot rule out the possibility, based on the examination of the Auger angular distributions, that some contribution to symmetric breakup originates from the $^1\Delta_g$ state. We argue below, however, 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 an FC process, which is insufficient to overcome the barriers seen in figure 2(a). However, previous theoretical calculations [17, 18] show that dissociation to the V or P1 configuration is expected to pass through much lower barriers, low enough that even an FC process could supply the required vibrational energy. The Auger intensity plots in figure 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 figure 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 FC allowed, previous theory [18] 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 the P1 and V channels are fed by the $^1\Sigma_g^+$ state. For the P1 channel, the measured KER indicates that C_2H^+ ion is produced in its ground $^3\Pi$ state. As the potential curves in figure 2(b) 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. We must also point out that the 35.35 eV barrier position we deduce for V formation on

the $^1\Sigma_g^+$ surface is very close to the barrier for A formation on the $^1\Delta_g$ surface calculated by Zyubina *et al* [18]. Since the ground-state asymptotes for the V and A channels only differ by a fraction of an eV, we must consider the possibility that, in addition to quasi-symmetric (V) breakup via the $^1\Sigma_g^+$ state, symmetric breakup via the $^1\Delta_g$ state also contributes to the fragmentation in the 255.5 eV channel. This hypothesis is supported by the Auger angular distributions for this channel (figure 3(b)).

Returning to a discussion of the Auger angular distributions, we see that the distribution shown in figure 3(d), which is associated with the P2 deprotonation channel, shows a clear 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 work of Adachi *et al* [5], who observed asymmetry in the photoelectron angular distributions associated with deprotonation, and leads us to believe that we are seeing an indication of proton dynamics induced by core–hole creation [19]. Note that, in contrast to the P2 angular distribution, the Auger angular distribution associated with the lower P1 deprotonation channel (figure 3(c)) is essentially isotropic, indicating that there is substantial rearrangement of the molecule prior to dissociation in this channel. This rearrangement also washes out any left/right asymmetry in the Auger angular distributions for this channel. Turning finally to the distribution in figure 3(b), we again find some left/right asymmetry, consistent with hole localization in the quasi-symmetric V breakup channel. But the elongated shape of the distribution relative to the molecular axis is what one would expect from Auger decay into the $^1\Delta_g$ dication state, so we believe that the measured Auger distribution for this channel contains a superposition of Auger electrons corresponding to two different parent states.

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

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by a K core–hole created through photoionization. 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 and the other through the $1\pi_u^{-1}3\sigma_g^{-1}, {}^1\Pi_u$ state. For the latter, the Auger angular distribution shows an asymmetry that gives clear evidence of hole localization in the initial core-ionized state. There is also evidence of hole localization in the quasi-symmetric V break-up channel, which is partially obscured by a competing symmetric break-up channel into ground-state CH^+ + CH^+ products. 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.

Acknowledgments

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