

# High-resolution pulsed field ionization photoelectron-photoion coincidence study of $C_2H_2$ : Accurate 0 K dissociation threshold for $C_2H^+$

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By employing the newly developed pulsed field ionization photoelectron-photoion coincidence (PFI-PEPICO) apparatus of the Chemical Dynamics Beamline at the Advanced Light Source, we have examined the formation of ethynyl ion ( $C_2H^+$ ) from acetylene ( $C_2H_2$ ) at high resolution. The PFI-PEPICO time-of-flight spectra reveal that fragmentation of  $C_2H_2$  in high- $n$  Rydberg states occurs at energies above the dissociation threshold prior to pulsed field ionization. This study shows that for a prompt dissociation process, the disappearance energy of the parent molecule determined in PFI-PEPICO measurements provides an unambiguous measure of the 0 K ion dissociation threshold. For the formation of  $C_2H^+$  from  $C_2H_2$  this is found to be  $17.3576 \pm 0.0010$  eV.

Vacuum ultraviolet (VUV) photoionization mass spectrometry and photoelectron spectroscopy are major techniques for providing energetic,<sup>1</sup> spectroscopic,<sup>2,3</sup> and dynamical<sup>4,5</sup> information for cations. The VUV photoelectron-photoion coincidence (PEPICO) method<sup>4,6</sup> is the combination of these techniques, which involves the detection of correlated photoelectron-photoion pairs. The ion-internal-energy selection achieved in a PEPICO experiment depends critically on the photoelectron detection scheme used. Due to the efficient detection of threshold photoelectrons (TPEs) formed slightly above the ionization threshold,<sup>2,7</sup> the threshold-PEPICO (TPEPICO) technique has been widely used for the study of state- or energy-selected unimolecular<sup>4</sup> and bimolecular<sup>5</sup> reaction dynamics. Despite many successes in the application of the TPEPICO method, its full potential has not been realized due partly to the difficulty in eliminating the contamination of hot electrons. Hot electrons often manifest as a high-energy tail and are the main source of degradation in the TPE resolution.<sup>7</sup> This problem can be partially alleviated by using the electron time-of-flight (TOF) discrimination<sup>8</sup> and/or the penetration field technique<sup>9</sup> in a synchrotron experiment operating in a single or a two-bunch mode. However, due to the nature of the penetration field approach, it is not appropriate for PEPICO studies, especially for ion kinetic energy release measurements. We note that high-resolution TPEPICO studies of rare gas dimers have been reported recently using the penetration field technique.<sup>10</sup> Nevertheless, because of the very short ion flight path used in these studies, the ion TOF resolution was seriously compromised. Pulsed field ionization (PFI)-photoelectron (PFI-PE) spectroscopy,<sup>11,12</sup> which relies on the detection of electrons formed at

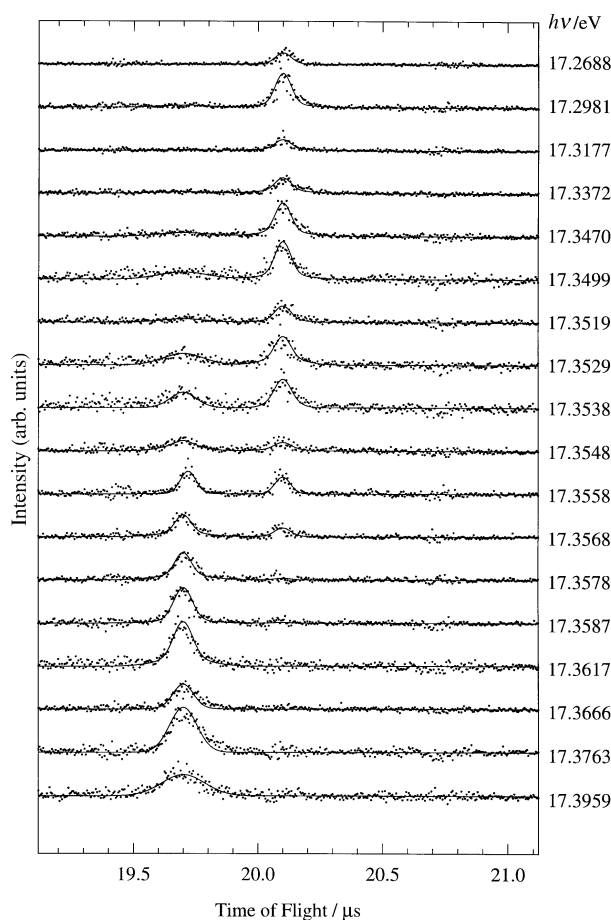
slightly below the true ionization threshold by PFI of high- $n$  ( $n \geq 100$ ) Rydberg species, is shown to be free from the hot-tail problem in previous laser-based studies. Weitzel and Güthe<sup>8</sup> were the first to demonstrate the potential for the PFI-PE and PFI-PEPICO measurements using synchrotron radiation in a single-bunch operation. Taking advantage of the high-resolution capability of the Chemical Dynamics Beamline at the Advanced Light Source (ALS), we have developed PFI-PE detection schemes for multibunch measurements,<sup>13,14</sup> routinely achieving resolutions in the range  $1\text{--}5\text{ cm}^{-1}$  (full-width-at-half-maximum, FWHM), as compared with  $0.3\text{--}4\text{ cm}^{-1}$  (FWHM) reported in VUV laser studies.<sup>3,15</sup> Most recently, we have further developed the PFI-PEPICO method for use with both two-bunch and multibunch synchrotron radiation at the ALS, attaining a resolution of  $0.6\text{ meV}$  ( $5\text{ cm}^{-1}$ , FWHM), limited only by the PFI-PE measurement.<sup>16</sup>

In this communication, we report on the application of this PFI-PEPICO method for the study of the formation of ethynyl ion ( $C_2H^+$ ) from acetylene ( $C_2H_2$ ),  $C_2H_2 + h\nu \rightarrow C_2H^+ + H + e^-$ , which is known to be a prompt dissociation process.<sup>17</sup> By analyzing the dissociation due to  $C_2H_2$  in the cold beam, we have obtained the dissociation threshold for  $C_2H^+$  to an accuracy of  $\leq 1.0\text{ meV}$  ( $8\text{ cm}^{-1}$ ). The elimination of the hot-tail in PFI-PE detection has made possible the use of the disappearance energy of the parent  $C_2H_2$  to determine the 0 K dissociation threshold of  $C_2H^+$ . Furthermore, this experiment provides evidence that  $C_2H_2^*$  fragments into  $C_2H^* + H$  prior to field ionization, where  $C_2H_2^*$  ( $C_2H^*$ ) represents  $C_2H_2$  ( $C_2H$ ) in high- $n$  Rydberg states. The  $C_2H$  radical is believed to play a significant role in soot formation in flames<sup>18</sup> and the hydrocarbon balance in planetary atmospheres.<sup>19</sup> For this reason, the accurate establishment of the thermochemical cycle for the  $C_2H/C_2H^+$  system is important.

All measurements were made using the newly developed PFI-PEPICO apparatus<sup>16</sup> and dispersed multibunch synchrotron radiation from the ALS. In the multibunch operation, the ALS period (656 ns) consists of 256 micro-VUV bunch (bunch width = 50 ps, separation of adjacent bunches = 2 ns) followed by a dark gap (light off period) of 144 ns. In this study, the PFI pulse (height =  $7.0\text{ V cm}^{-1}$ , width = 200 ns) was applied approximately 10 ns after the start of the dark gap. Since the dark gap was only 144 ns in duration, some overlap with the light occurs. However, only a small decrease in PFI-PEPICO signal is observed for this overlap and the long pulse

aids in ion extraction, which occurs in a pseudo-continuous fashion. A dc field of  $0.2 \text{ V cm}^{-1}$  is maintained across the interaction region to sweep prompt electrons from the ionization region prior to the application of the electric field pulse for Stark ionization. The PFI-PE selection was achieved by employing the electron TOF scheme.<sup>14</sup> The ion PFI-PEPICO TOF spectra were recorded using a multichannel scaler triggered by the detection of an electron. The current setup is sensitive to the ion kinetic energy.<sup>16</sup> Thus, the FWHM of the PFI-PEPICO TOF peak for  $\text{Ar}^+(^2\text{P}_{3/2})$  observed using an Ar supersonic beam (translational temperature = 20 K) is significantly narrower than that using an Ar effusive beam (temperature = 298 K). The analysis of the Ar TOF peak obtained using a supersonic Ar beam reveals that the thermal background of Ar in the photoionization chamber contributes  $\approx 15\%$  to the experimental Ar sample.<sup>16</sup> This thermal background contribution is roughly consistent with the estimated densities for the molecular beam and thermal background gas sample at the photoionization/photoexcitation region. The photon energy ( $h\nu$ ) calibration was achieved using the PFI-PE bands for  $\text{Ne}^+(^2\text{P}_{3/2})$  and  $\text{Ar}^+(^2\text{P}_{3/2})$  recorded under the same experimental conditions before and after each scan.<sup>13,14</sup> This calibration procedure assumes that the Stark shift for ionization thresholds of  $\text{C}_2\text{H}_2$  and the rare gases are identical. On the basis of the measured PFI-PE band for  $\text{Ar}^+(^2\text{P}_{3/2})$ , we estimate that the ion-energy selection achieved here is  $\approx 1.0 \text{ meV}$  (FWHM).

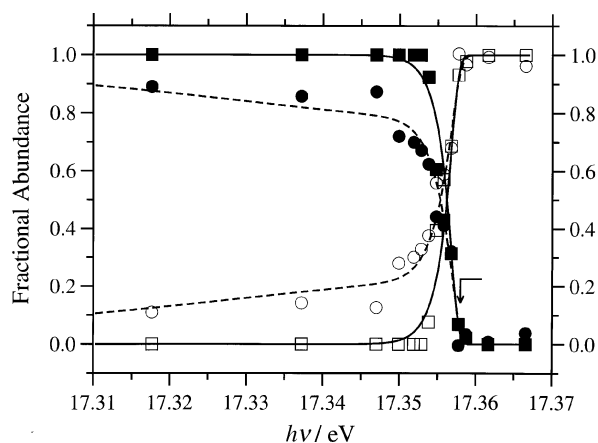
We have obtained PFI-PEPICO TOF spectra for  $\text{C}_2\text{H}^+$  and  $\text{C}_2\text{H}_2^+$  in the  $h\nu$  region of 17.2688–17.3959 eV (see Fig. 1), which is near the  $\text{C}_2\text{H}^+$  dissociation threshold. At  $h\nu = 17.2688\text{--}17.3373 \text{ eV}$ , the parent  $\text{C}_2\text{H}_2^+$  peak dominates



**Fig. 1** PFI-PEPICO TOF spectra for  $\text{C}_2\text{H}^+$  and  $\text{C}_2\text{H}_2^+$  in the  $h\nu$  range 17.2688–17.3959 eV. The TOF peaks centered at 19.7 and 20.1  $\mu\text{s}$  are due to  $\text{C}_2\text{H}^+$  and  $\text{C}_2\text{H}_2^+$ , respectively. The  $h\nu$  values associated with individual spectra are indicated on the right hand side of the spectra.

in the TOF spectra, whereas at  $h\nu \geq 17.3578 \text{ eV}$  only the daughter  $\text{C}_2\text{H}^+$  peaks are discernible. Since the internal energy distribution for  $\text{C}_2\text{H}_2^+$  ions is expected to be similar to that of their neutral  $\text{C}_2\text{H}_2$  precursors, the broad  $\text{C}_2\text{H}^+$  peaks observed at  $h\nu \leq 17.3548 \text{ eV}$  can be attributed to fragmentation of  $\text{C}_2\text{H}_2^+$  formed in the photoionization of thermal (298 K) background  $\text{C}_2\text{H}_2$ . At  $h\nu = 17.3558\text{--}17.3617 \text{ eV}$ , the  $\text{C}_2\text{H}^+$  TOF peaks also possess a narrower component, indicating that the main contribution is due to fragmentation of  $\text{C}_2\text{H}_2^+$  produced by photoionization of internally cold  $\text{C}_2\text{H}_2$  in the molecular beam. We have simulated the individual TOF spectra using two Gaussian functions with FWHMs of 75 and 240 ns to account for the respective contributions due to the cold beam and thermal background  $\text{C}_2\text{H}_2$  sample. The kinetic energy release for  $\text{C}_2\text{H}^+$  due to fragmentation is expected to be small around the dissociation threshold region because the H atom should carry away most of the energy release. Therefore, to a good approximation, we have treated both daughter  $\text{C}_2\text{H}^+$  and parent  $\text{C}_2\text{H}_2^+$  similarly in the analysis. However, for TOF spectra at 17.3666, 17.3763, and 17.3959 eV (Fig. 1), it is necessary to increase the FWHMs of the 'cold' Gaussian fits to 96, 130, and 200 ns, respectively, to account for kinetic energy released in fragmentation. The least-squared Gaussian fits (solid lines) to the TOF spectra are shown in Fig. 1.

Since the PFI-PEPICO TOF spectra resolve the dissociation due to cold  $\text{C}_2\text{H}_2$  from that of thermal  $\text{C}_2\text{H}_2$ , we have analyzed the TOF spectra by taking into account only the 'cold'  $\text{C}_2\text{H}^+$  ion signal based on the narrow TOF component. Due to the efficient rotational cooling of  $\text{C}_2\text{H}_2$  achieved by the supersonic expansion, the 'cold' breakdown curves thus obtained are very sharp as indicated by open and solid squares for the respective fractional abundances of  $\text{C}_2\text{H}^+$  and  $\text{C}_2\text{H}_2^+$  shown in Fig. 2. These breakdown curves show that the complete dissociation of  $\text{C}_2\text{H}_2^+$  to  $\text{C}_2\text{H}^+ + \text{H}$  occurs in an internal energy interval of  $< 5 \text{ meV}$  with the cross-over point located at 17.3562 eV. We have also constructed the breakdown curves for  $\text{C}_2\text{H}^+$  and  $\text{C}_2\text{H}_2^+$  [see open and solid circles, respectively, in Fig. 2] by including the total 'hot' and 'cold'  $\text{C}_2\text{H}^+$  signals. As expected, the variation of these breakdown curves is more gradual with a lower cross-over energy at 17.3550 eV, reflecting the nominally higher temperature of the  $\text{C}_2\text{H}_2$  sample. We have performed simulation of the breakdown curves using similar procedures described previously.<sup>20</sup> All calculations were based on rovibronic densities of states taking into account one two-dimensional rotor. The vibrational densities of states were calculated by the Beyer–

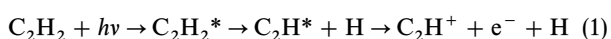


**Fig. 2** Breakdown curves of  $\text{C}_2\text{H}^+$  and  $\text{C}_2\text{H}_2^+$  in the  $h\nu$  range 17.31–17.37 eV. The experimental fractional abundances for  $\text{C}_2\text{H}^+$  and  $\text{C}_2\text{H}_2^+$  obtained based on the entire daughter ion signal are (○) and (●), whereas those obtained using only the cold daughter ion signal are indicated as (□) and (■), respectively. The lines are simulations curves: (—) 20 K ensemble and (---) 20 K ensemble with 15% thermal background and with an energy dependent loss. See text.

Swinehardt algorithm<sup>21</sup> based on known harmonic frequencies.<sup>22</sup> By assuming a temperature of 20 K for  $C_2H_2$  in the molecular beam, we have obtained an excellent simulation (solid lines) of the 'cold' breakdown curves, yielding a value of  $17.3576 \pm 0.0010$  eV for the 0 K dissociation threshold of  $C_2H^+$  from  $C_2H_2$ . We note that this value is identical to the disappearance energy for the parent  $C_2H_2^+$  at 17.3578 eV as marked by the arrow in Fig. 2. The dashed lines in Fig. 2 are calculated breakdown curves assuming 15% thermal background in addition to the 20 K cold beam discussed above. As in the case of the methane dissociation<sup>23</sup> to form  $CH_3^+$ , in order to obtain good fit to the breakdown curves, which include the dissociation of thermal  $C_2H_2$ , we need to take into account the loss of parent  $C_2H_2^*$  due to spontaneous autoionization. Here, we assume that the percentage lost depends on energy, which decreased from 77% at 17.320 eV to 50% at 17.356 eV. Compared to the methane dissociation reaction,<sup>23</sup> the total fraction of parent  $C_2H_2^*$  molecules lost is smaller and its energy dependence is less pronounced.

As expected, although the shapes and cross-over points of the two sets of break down curves obtained by including and excluding the dissociation of 'hot'  $C_2H_2$  sample are quite different, the disappearance energies for the parent  $C_2H_2^+$  are identical. With increasing  $h\nu$ , an increasing part of the energy distribution of the neutral molecules is shifted above the dissociation threshold. The disappearance energy of the parent molecule is the energy at which even the coldest part of the neutral energy distribution reaches above the dissociation threshold. Thus, the disappearance energy of the parent molecule is an intrinsic feature in a PFI breakdown diagram and can be used to give an unambiguous determination of the 0 K fragmentation threshold independent of the internal energy distribution of parent molecules. We emphasize that in order for this feature to serve as a true measure of the ion dissociation threshold, the dissociation reaction must be prompt, i.e., the dissociation lifetime of the excited parent species is much shorter than the time scale  $\approx 10^{-7}$  s) of the experiment. Furthermore, it is worth noting that in TPEPICO experiments, where the TPE measurement suffers from the hot-tail problem, the fractional abundance for the parent molecule is not zero at the 'true' dissociation threshold. As a result, the disappearance energy for the parent molecule cannot be used for the determination of the ion dissociation threshold in such cases.<sup>17</sup>

A most interesting observation is that the fraction of fragmentation due to the 'hot'  $C_2H_2$  sample is considerably higher than the estimated 15–25% for the thermal background contribution to the experimental  $C_2H_2$  sample. This estimation is based on the fractional abundance of 'hot' signal at 17.2688 eV, which is entirely associated with the parent  $C_2H_2^+$  and has a value of  $\approx 19\%$ . The TOF spectra at 17.3529–17.3548 eV, which are slightly lower than the ion dissociation threshold for 'cold'  $C_2H^+$ , reveal a broad TOF peak for  $C_2H^+$ , indicating a 'hot'  $C_2H^+$  fractional abundance of 40–50%. At photon energies ( $> 17.3578$  eV) above the dissociation threshold for 'cold'  $C_2H^+$ , the fractional abundance for the 'hot' signal has a value of  $\approx 10$ –30%. In summary, the 'hot'  $C_2H^+$  signal increases from zero at well below the dissociation threshold to a maximum of  $\approx 50\%$  near the dissociation threshold and drops sharply to  $\approx 10$ –30% once the threshold has passed. The observation of this effect can be rationalized by a competition between autoionization and fragmentation of  $C_2H_2^*$  at energies below and above the dissociation threshold. If the ion core  $C_2H_2^+$  of  $C_2H_2^*$  is dissociative with a lifetime shorter than the delay time between the excitation micro-VUV pulse for the formation of  $C_2H_2^*$  and the electric field pulse for PFI, a viable mechanism for the formation of  $C_2H^+$  from  $C_2H_2^*$  is



According to this mechanism,  $C_2H_2^*$  first undergoes prompt dissociation to form  $C_2H^* + H$ . The subsequent PFI of  $C_2H^*$  results in the formation of  $C_2H^+$  and a PFI-PE. The recent lifetime measurements<sup>24</sup> of  $O_2$  in high- $n$  Rydberg states ( $O_2^*$ ) converging to dissociative  $O_2^+$  states provide strong support for process (1) as the major process for  $C_2H^+$  formed in the PFI of  $C_2H_2^*$ . We note that any high- $n$  Rydberg species, which have spontaneously autoionized before the application of the pulsed electric field, are lost to the PFI detection. The  $C_2H^*$  radicals formed by fragmentation of  $C_2H_2^*$  at the dissociation threshold are expected to form below the ionization energy (IE) of  $C_2H$ . Thus, autoionization is not readily accessible for  $C_2H^*$  and is predominantly operative for  $C_2H_2^*$ , which lies at energies far above the IE of  $C_2H_2$ . For  $C_2H^*$  formed slightly above the dissociation threshold, it can also autoionize. However, the autoionization of this  $C_2H^*$  may still be less probable than that of  $C_2H_2^*$ . The higher than expected PFI-PEPICO intensity for  $C_2H^+$  from thermal  $C_2H_2$  observed below the dissociation threshold can thus be accounted for by a longer autoionization lifetime for  $C_2H^*$  than that for  $C_2H_2^*$ . Since the (15–25%) thermal sample has a large distribution of energies, as the dissociation threshold is approached, the formation of  $C_2H^+$  from  $C_2H^*$  will be favored for the thermal  $C_2H_2$  sample over  $C_2H_2^+$  from the supersonically cooled  $C_2H_2$  sample. Due to the magnification of the  $C_2H^+$  intensity from thermal  $C_2H_2$ , the breakdown diagram will reveal a lower cross-over point if  $C_2H^+$  ions from both thermal and cold  $C_2H_2$  are included in the data analysis. This effect of increasing the fragment ion signal relative to the parent ion signal is equivalent to a nominally higher temperature for the parent molecules.

Taking into account the experimental uncertainties, the dissociation threshold ( $17.3576 \pm 0.0010$  eV) for  $C_2H^+$  from  $C_2H_2$  determined here is consistent with values obtained in previous photoion<sup>25</sup> and PEPICO studies,<sup>17,26–28</sup> which fall in the range 17.300–17.360 eV. However, the value obtained here is characterized by a significantly higher accuracy. The IE( $C_2H_2$ ) has been determined in a recent PFI-PE study to be  $11.4006 \pm 0.0006$  eV.<sup>29</sup> The combination of the latter value and the 0 K dissociation threshold for  $C_2H^+$  from  $C_2H_2$  determined here yields  $D_0(H-C_2H^+) = 5.9570 \pm 0.0012$  eV. Although an accurate value for the H- $C_2H$  bond dissociation energy at 0 K [ $D_0(H-C_2H) = 5.7125 \pm 0.0010$  eV] and the heat of formation at 0 K ( $\Delta_f H^\circ$ ) for  $C_2H$  have been determined in recent high-resolution photodissociation experiments,<sup>30</sup> to our knowledge the IE for  $C_2H$  has not been measured. By combining the 0 K dissociation threshold for process (1) and this  $D_0(H-C_2H)$  value, we calculate a value of  $11.6451 \pm 0.0014$  eV for IE( $C_2H$ ). Using the well-established  $\Delta_f H^\circ$  values<sup>1</sup> for  $C_2H_2$  ( $235.76 \pm 0.79$  kJ mol<sup>-1</sup>) and H ( $216.035 \pm 0.006$  kJ mol<sup>-1</sup>), we also obtain  $\Delta_f H^\circ(C_2H^+) = 1694.44 \pm 0.80$  kJ mol<sup>-1</sup>. We note that the accuracy of the latter value is now limited by the  $\Delta_f H^\circ(C_2H_2)$ . A high-resolution PFI-PE study of  $C_2H$  is timely to check the consistency of the  $D_0(H-C_2H)$  and 0 K dissociation threshold for  $C_2H^+$ . The self-consistency of these values forming the thermochemical cycle will provide confirmation for the accuracy of the experimental  $\Delta_f H^\circ(C_2H)$  value.

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