Observation of Accurate Ion Dissociation Thresholds in Pulsed Field Ionization-Photoelectron Studies

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We report the first observation, together with a mechanism for such an observation, of a steplike feature in the pulsed field ionization photoelectron measurement of $CH_4(C_2H_2)$, marking the 0 K dissociation threshold for the formation of $CH_3{}^+ + H(C_2H^+ + H)$ from $CH_4(C_2H_2)$. The nonexistence of a step in the spectrum for C_2H_4 at its dissociation threshold for $C_2H_2{}^+$ formation provides strong support for the proposed mechanism. This experiment shows that, for a range of molecules, where the ion dissociation lifetimes near the dissociation thresholds are $<10^{-7}$ s, pulsed field ionization photoelectron measurements will yield not only highly accurate ionization energies, but also 0 K dissociation thresholds.

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Photoionization and photoelectron spectroscopy is a major technique for research in physical sciences. The most important data obtainable in a photoionization-photoelectron experiment are ionization energies (IEs) and ion dissociation thresholds or appearance energies (AEs), from which bond dissociation energies for neutrals and cations can be deduced [1]. The recent development in vacuum ultraviolet (VUV) lasers [2,3] and third generation synchrotron source [4,5], together with the introduction of pulsed field ionization (PFI) techniques [6–8], has revolutionized this field by significantly improving the energy resolution close to the optical bandwidth [9]. For many simple molecules, the PFI-photoelectron (PFI-PE) method allows the measurement of rotationally resolved photoelectron spectra, yielding definitive IEs with uncertainties limited only by the energy calibration [3,5–9]. The recent successful implementation of PFI schemes [10–13] using the high-resolution VUV synchrotron radiation at the Advanced Light Source (ALS) has made possible the routine examination of molecular dissociative photoionization processes employing PFI techniques [12,14–16]. Here, we show for the first time that highly accurate 0 K AE values [17] for a range of molecules can also be determined in PFI-PE studies.

The PFI-PE experiment presented here was conducted at the ALS utilizing the high-resolution monochromatized VUV source of the Chemical Dynamics Beam Line, which has demonstrated an optical resolution close to that of VUV lasers [4,5]. The greatest advantage of this source is its ease of tunability covering the full VUV range of 8–30 eV. The procedures for PFI-PE measurements using the photoelectron-photoion facility of the Chemical Dynamics Beam Line have been described previously [11]. Briefly, the gaseous samples (CH_4, C_2H_2, and C_2H_4) are introduced into the photoionization/photoexcitation (PI/PEX) region of the apparatus as a skimmed supersonic beam, achieving a temperature of ≈30 K [12]. The ALS light pattern in the present multibunch operation consists of 256 light pulses (duration of each light pulse = 50 ps) with a time separation of 2 ns between successive light pulses and a dark gap of 144 ns in one period (656 ns) [12]. Excited parent species in high-n ($n > 100$) Rydberg states, formed by excitation of the beam sample at the PI/PEX center by the dispersed synchrotron radiation, are field ionized by an electric field pulse (height ≈ 1.5 V/cm, width ≈ 40 ns) applied in the dark gap. This PFI pulse is delayed by 20 ns with respect to the beginning of the dark gap. Electrons formed by PFI in the dark gap are selected by a time-of-flight scheme using a detection time gate [11]. The photon energy calibration was achieved using rare gas PFI-PE bands recorded under the same experimental conditions. Previous experiments indicate that the accuracy of this calibration method is within ±0.5 meV [4,5,18].

The PFI-PE spectrum for $CH_4(C_2H_2)$ measured in the region of 14.25–14.40 eV (17.26–17.44 eV) is depicted in Fig. 1(a) [2(a)]. The most distinct feature discovered in the spectrum of Fig. 1(a) [2(a)] is the sharp steplike feature at 14.323 eV (17.358 eV). In recent PFI-PE-photoion coincidence (PFI-PEPICO) studies at the Chemical Dynamics Beam Line, we have examined the formation of $CH_3{}^+(C_2H^+)$ from $CH_4(C_2H_2)$ near its threshold [12,14,15]. The breakdown curves for $CH_3{}^+$ and $CH_4{}^+$ (C_2H^+ and $C_2H_2{}^+$) are depicted in Fig. 1(b) [2(b)] for comparison with the PFI-PE spectrum of $CH_4(C_2H_2)$. The 0 K AE for $CH_3{}^+(C_2H^+)$ has been determined as 14.323 ± 0.001 eV (17.3576 ± 0.0010 eV) by the disappearance energy of the parent $CH_4{}^+(C_2H_2{}^+)$ ion, i.e., the lowest energy at which the branching ratio for $CH_4{}^+(C_2H_2{}^+)$ becomes zero [14,15]. This 0 K AE value for $CH_3{}^+(C_2H^+)$ based on the analysis of the breakdown curves of Fig. 1(b) [2(b)] represents the most accurate experimental value in comparison with

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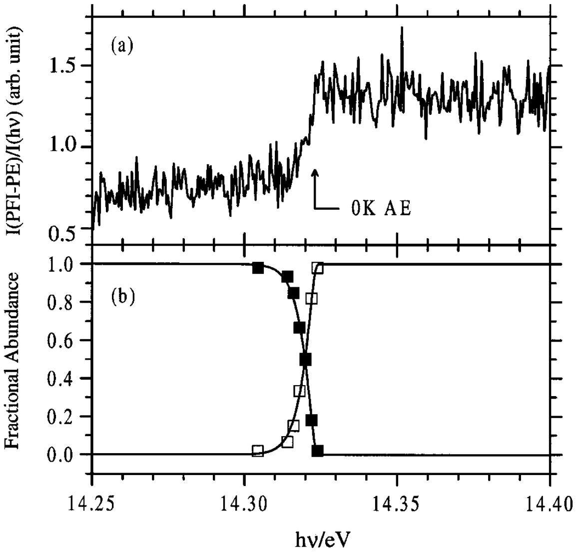

FIG. 1. Comparison of the PFI-PE spectrum and breakdown diagram for CH_4 in the energy range of 14.25–14.44 eV. (a) PFI-PE spectrum for CH_4. I(PFI-PE) and $I(h\nu)$ represent the PFI-PE and VUV intensity, respectively. The arrow marks the 0 K AE for CH_3^+. (b) The breakdown curves for CH_3^+ (open squares) and CH_4^+ (solid squares) [14].

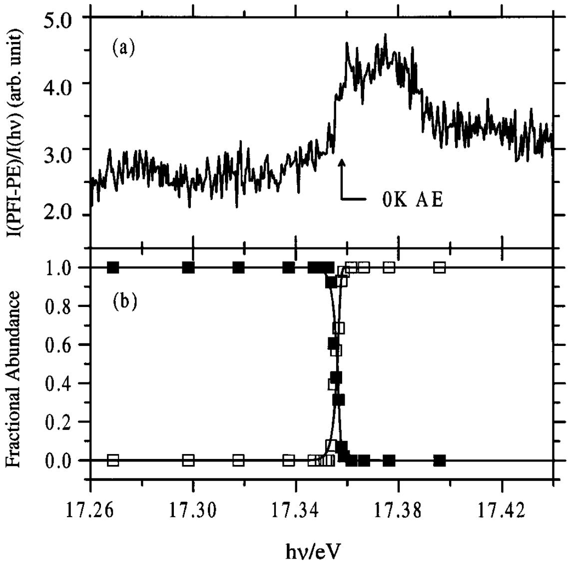

FIG. 2. Comparison of the PFI-PE spectrum and breakdown diagram for C_2H_2 in the energy range of 17.26–17.40 eV. (a) PFI-PE spectrum for C_2H_2. I(PFI-PE) and $I(h\nu)$ represent the PFI-PE and VUV intensity, respectively. The arrow marks the 0 K AE for C_2H^+. (b) The breakdown curves for C_2H^+ (open squares) and $C_2H_2^+$ (solid squares) [15].

previous measurements [1], which fall in the range of 14.23–14.33 eV (17.22–17.36 eV).

The comparison of the PFI-PE spectrum and the breakdown diagram of $CH_4(C_2H_2)$ reveals excellent correlation between the step observed and the 0 K AE for $CH_3^+(C_2H^+)$. The analysis of the PFI-PEPICO data for CH_3^+ and CH_4^+ (C_2H^+ and $C_2H_2^+$) has suggested that the formation of $CH_3^+(C_2H^+)$ from $CH_4(C_2H_2)$ in PFI proceeds via processes 1(a), 1(b), and 1(d) at energies slightly above the AE, while $CH_4^+(C_2H_2^+)$ ions are produced by processes 1(a) and 1(c) below the AE:

$$\begin{array}{llcl}
CH_4(C_2H_2) + h\nu & \xrightarrow{(a)} CH_4^*(C_2H_2^*) & \xrightarrow{(b)} & CH_3^*(C_2H^*) + H \\
 & \quad\downarrow (c) & & \quad\downarrow (d) \\
 & CH_4^{+*}(C_2H_2^{+*}) + e^- & & CH_3^+(C_2H^+) + e^- .
\end{array} \tag{1}$$

Here, $CH_4^*(C_2H_2^*)$ and $CH_3^*(C_2H^*)$ represent excited $CH_4(C_2H_2)$ and $CH_3(C_2H)$, respectively, in long-lived high-n Rydberg states, and $CH_4^{+*}(C_2H_2^{+*})$ stands for excited $CH_4^+(C_2H_2^+)$. The formation of fragment neutrals in high-n Rydberg states from dissociation of parent species in high-n Rydberg states as shown in process 1(b) has been documented previously [19]. Processes 1(c) and 1(d) are PFI processes. This mechanism, which indicates that $CH_4^*(C_2H_2^*)$ fragments into $CH_3^* + H(C_2H^* + H)$ at energies above the AE prior to PFI, is also consistent with the step at the 0 K AE observed in the PFI-PE spectrum. The dominant decay channels for $CH_4^*(C_2H_2^*)$ are autoionization and fragmentation. At energies below the AE for $CH_3^+(C_2H^+)$, the PFI-PE signal is due to process 1(c) and is proportional to the concentration of $CH_4^*(C_2H_2^*)$ species that have survived the decay for a time longer than the delay (Δt) of the PFI pulse relative to the excitation light pulse. For $CH_4^*(C_2H_2^*)$ species that have spontaneously autoionized faster than Δt are lost to PFI detection. Assuming that all $CH_4^*(C_2H_2^*)$ species are destroyed by the PFI pulse, we estimate Δt to be in the range of 20–552 ns.

The $CH_3^*(C_2H^*)$ species formed at the AE are expected to be in high-n Rydberg levels converging to the ground state of $CH_3^+(C_2H^+)$, i.e., below the IE of $CH_3(C_2H)$. Consequently, autoionization is not accessible to these $CH_3^*(C_2H^*)$ fragments. The $CH_3^*(C_2H^*)$ fragments produced at energies slightly above the AE can autoionize only by rotational autoionization. The latter process is expected to be slower than vibrational and electronic autoionization for the case of $CH_4^*(C_2H_2^*)$, which lies well above the IE of $CH_4(C_2H_2)$. Assuming that the decay rates via fragmentation for $CH_4^*(C_2H_2^*)$ and $CH_3^*(C_2H^*)$ are similar, we expect that a larger fraction of $CH_3^*(C_2H^*)$ survives the decay than that of $CH_4^*(C_2H_2^*)$. Thus, the PFI-PE signal derived from process 1(d) slightly above the AE is higher than that obtained from process 1(c) below the

AE. The step marking the 0 K AE in the PFI-PE spectrum can be attributed to the lifetime switching effect at the AE, where $CH_4^*(C_2H_2^*)$ species with shorter lifetimes are converted into $CH_3^*(C_2H^*)$ fragments with longer lifetimes. The observation of the sharp steplike feature in the PFI-PE spectrum is consistent with the conclusion that the conversion from $CH_4^*(C_2H_2^*)$ to $CH_3^*(C_2H^*)$ is complete prior to process 1(d) and that the dissociation process has a rate constant $\gg 1/\Delta t$ ($\approx 10^7$ s^{-1}) [14,15]. The observation of a sharp step at the 0 K AE in the PFI-PE spectrum is a sufficient condition for observing sharp breakdown curves as shown in Figs. 1(b) and 2(b).

For a slow dissociation reaction that the dissociation lifetimes for excited high-n Rydberg species for parent species are longer than Δt, the PFI-PE signal should originate entirely from PFI of excited parent species at energies both below and above the AE. Hence, the PFI-PE spectrum should be smooth across the AE. However, if excited parent ions thus formed completely dissociate within the time scale of the PFI-PEPICO experiment ($\approx 10^{-5}$ s) [12], we still expect to observe complete dissociation at the AE, such that the disappearance energy of the parent ion can still be used to identify the 0 K AE [14,15]. This can be considered as an intermediate case, in which the 0 K AE can be determined in a PFI-PEPICO experiment, but not in a PFI-PE study.

According to a previous coincidence study [20], the reaction $C_2H_4 + h\nu \rightarrow C_2H_2^+ + H_2 + e^-$ has dissociation rates of 10^3–10^5 s^{-1} near its 0 K AE (13.135 eV). Thus, the dissociation lifetime of excited $C_2H_4^{+*}$ formed at the AE should be significantly longer than the time scale of the PFI-PEPICO experiment. Figures 3(a) and 3(b) compare the PFI-PE and PFI-PEPICO data of C_2H_4 in the energy range of 13.10–13.18 eV. The slow varying breakdown curves observed for $C_2H_4^+$ (solid squares) and $C_2H_2^+$ (open squares) are characteristic of the metastable decay of parent $C_2H_4^{+*}$ ions. The fractional abundance for parent $C_2H_4^+$ remains very high (0.7) at the 0 K AE for $C_2H_2^+$ as marked in Fig. 3(b). We have simulated these breakdown curves [solid lines of Fig. 3(b)] employing a similar procedure described in previous studies [14,15] and using the known 0 K AE and dissociation rate constants [20]. The simulation has taken into account contributions from the dissociation of excited $C_2H_4^{+*}$ and a competition between autoionization and fragmentation of excited neutral species. As expected, the PFI-PE spectrum for C_2H_4 shown in Fig. 3(a) is smooth across the 0 K AE for $C_2H_2^+$.

As pointed out above, the requirement for observing a step at the 0 K AE in the PFI-PE spectrum is that the dissociation lifetimes of high-n Rydberg parent species are shorter than Δt, which is in the range of 20–552 ns in the present experiment. We note that the Δt value can be extended by a multiple of 656 ns, i.e., the synchrotron ring period, to a range from 20 ns to several μs [5]. Thus, the 0 K AE values for dissociation reactions with rate constants $\approx 10^6$ s^{-1} can be determined in PFI-PE measurements.

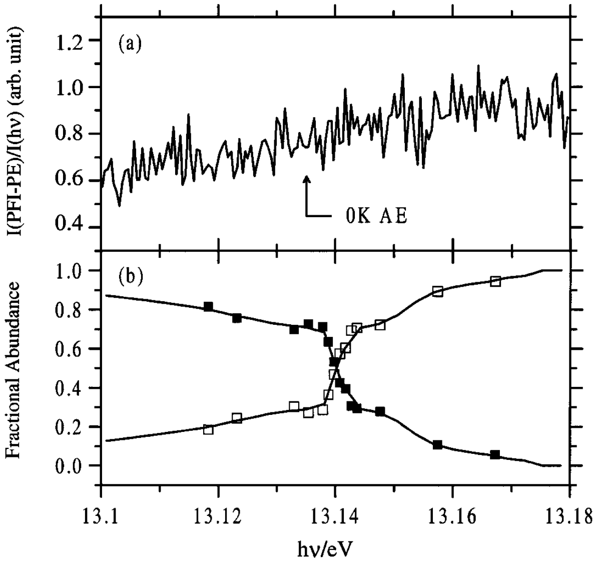

FIG. 3. Comparison of the PFI-PE spectrum and breakdown diagram for C_2H_4 in the energy range of 13.10–13.18 eV. (a) PFI-PE spectrum for C_2H_4. I(PFI-PE) and $I(h\nu)$ represent the PFI-PE and VUV intensity, respectively. The arrow marks the 0 K AE for $C_2H_2^+$. (b) The breakdown curves for $C_2H_2^+$ (open squares) and $C_2H_4^+$ (solid squares).

In summary, we report here the first observation of a step at the 0 K AE for $CH_3^+(C_2H_2^+)$ in the PFI-PE spectrum of $CH_4(C_2H_2)$ and have established the mechanism for such an observation. Similar observations have now been found for other dissociative photoionization reactions [21], which lend further support of this mechanism. For diatomic and triatomic species that have a lower density of states, a discrete peak instead of a step should be discernible at the 0 K AE. This observation in PFI-PE measurements, together with the breakdown curves obtained in PFI-PEPICO studies, can provide unambiguous 0 K AE values for the dissociation reactions involved, which in turn can yield highly accurate energetic information for simple neutrals and cations.

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