

# High-Resolution Pulsed Field Ionization Photoelectron-Photoion Coincidence Study of CH<sub>4</sub>: Accurate 0 K Dissociation Threshold for CH<sub>3</sub><sup>+</sup>

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## INTRODUCTION

Since the introduction of the photoelectron-photoion coincidence (PEPICO) technique nearly 30 years ago, its development and applications have played a major role in providing accurate information on the energetics, kinetics, and dynamics of ionic reactions. The resolution of the PEPICO technique depends critically on the accompanying photoelectron spectroscopic method. With respect to the latter, a recent important advance was the development of zero-kinetic-energy photoelectron spectroscopy based on the pulsed field ionization (PFI) of high- $n$  ( $n \geq 100$ ) Rydberg states. Taking advantage of the high optical resolution capability of the Chemical Dynamics Beamline at ALS, we have recently developed PFI-PE detection schemes using monochromatized multibunch synchrotron radiation, achieving routinely resolutions of 1-5 cm<sup>-1</sup> (FWHM). Most recently, the PFI-PEPICO method has been further developed and perfected by us for use with both two-bunch and multibunch synchrotron radiation, attaining a resolution of 0.6 meV (FWHM), limited only by the PFI-PE measurement.

In this study, we report the first application of this high-resolution PFI-PEPICO technique to study the ion dissociation reaction of a polyatomic species, namely, the formation of methyl cation (CH<sub>3</sub><sup>+</sup>) from methane (CH<sub>4</sub>),  $\text{CH}_4 + h\nu \rightarrow \text{CH}_3^+ + \text{H} + e^-$ , which is known to be a prompt dissociation process. The analysis presented here establishes intrinsic features of the PFI-PEPICO breakdown curves, which can be used for accurate ion dissociation threshold determination.

## EXPERIMENT

The newly developed PFI-PEPICO apparatus and general procedures used for PFI-PEPICO measurements at the ALS have been described in detail elsewhere. In the present study, the sample is introduced into the photoionization/photoexcitation (PI/PEX) center of the apparatus as a skimmed supersonic beam. The CH<sub>4</sub> beam is excited at the PI/PEX center by dispersed synchrotron radiation. High- $n$  Rydberg states of CH<sub>4</sub> thus formed are ionized by the application of a delayed electric field pulse (height  $\approx 7$  V/cm, width  $\approx 160$  ns) in the dark gap existed in the ALS synchrotron ring period of 656 ns. The measurements described here have been performed using both the two-bunch mode and multibunch mode with a dark gap of 328 ns and 150 ns, respectively. The PI/PEX region is maintained at a dc electric field of 0-2 V/cm. The ion TOF is measured by a multichannel scalar, which is started by the detection of a PFI-PE. The photon energy ( $h\nu$ ) calibration is performed based on the field free ionization limits of various noble gases assuming that the energetic thresholds determined in this work correspond to the field free limits. The uncertainty introduced by this procedure is related to the difference between adiabatic and diabatic field ionization, and amounts to  $\approx 0.6$  meV for the current setup. The overall resolution of the experiment, including photon plus field contributions, was estimated to be 1.5 meV.

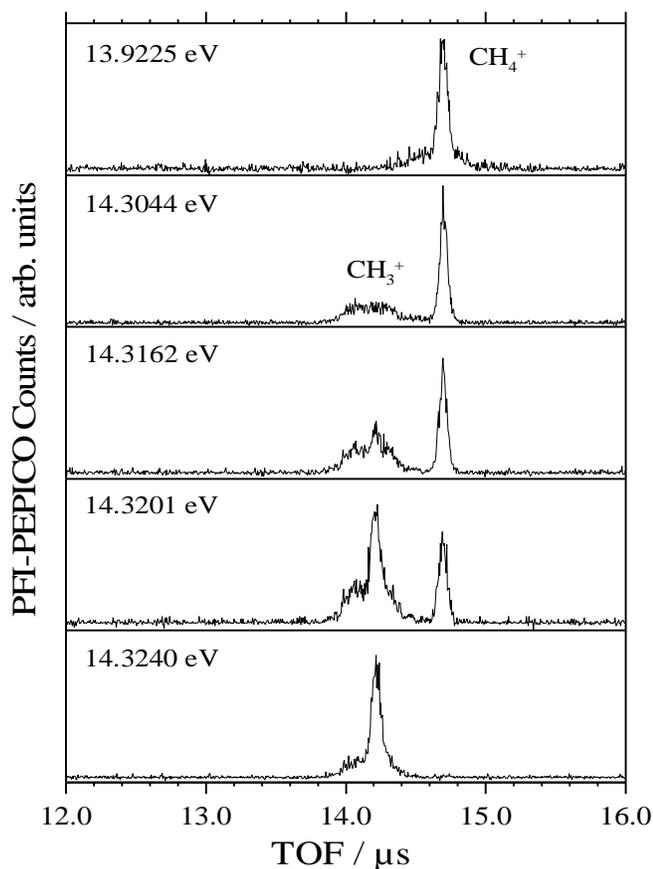


Figure 1. PFI-PEPICO TOF spectra of  $\text{CH}_4$  at  $h\nu=13.9225$ ,  $14.3044$ ,  $14.3162$ ,  $14.3201$ , and  $14.3240$  eV obtained using a static electric background field of  $1.3$  V/cm. The TOF peaks centered at  $14.10$  and  $14.35$   $\mu\text{s}$  are due to  $\text{CH}_3^+$  and  $\text{CH}_4^+$ , respectively.

## RESULTS AND DISCUSSION

The PFI-PEPICO TOF spectra of  $\text{CH}_4$  have been recorded in the  $h\nu$  range of  $13.9$ - $14.5$  eV, near the dissociation threshold for  $\text{CH}_3^+$  from  $\text{CH}_4$ . Selected PFI-PEPICO TOF spectra are depicted in Fig. 1. Figure 2 shows the experimental breakdown data in the  $h\nu$  range of  $14.300$ - $14.323$  eV obtained at a  $1.3$  V/cm dc field. We have analyzed the TOF spectra by taking into account only the cold  $\text{CH}_3^+$  ion signal based on the narrow TOF component. As expected, these data form much steeper breakdown curves (rectangles in Fig. 2), which represent the dissociation of cold  $\text{CH}_4^+$  formed by photoionization of supersonically cooled  $\text{CH}_4$ . For these breakdown curves, almost perfect agreement is observed with the simulation (solid lines in Fig. 2) based on the approach described previously. More specifically, this simulation assumed a temperature of  $33$  K for  $\text{CH}_4^+$  and all three internal rotations being energetically active. The  $0$  K dissociation energy for  $\text{CH}_3^+$  from  $\text{CH}_4$  determined in this simulation is  $14.323$  eV.

For the decay of  $\text{CH}_4^*$ , there are two important competing decay channels, i.e., autoionization and fragmentation. Clearly, in our PFI experiment only those  $\text{CH}_4^*$  molecules survived autoionization and fragmentation up to a time longer than  $\Delta t$  can be observed by PFI. Autoionization of  $\text{CH}_4^*$  is accessible in the entire energy range studied since the energies are far above the ionization energy (IE) of  $\text{CH}_4$ . If the  $\text{CH}_4^+$  core is dissociative, prompt

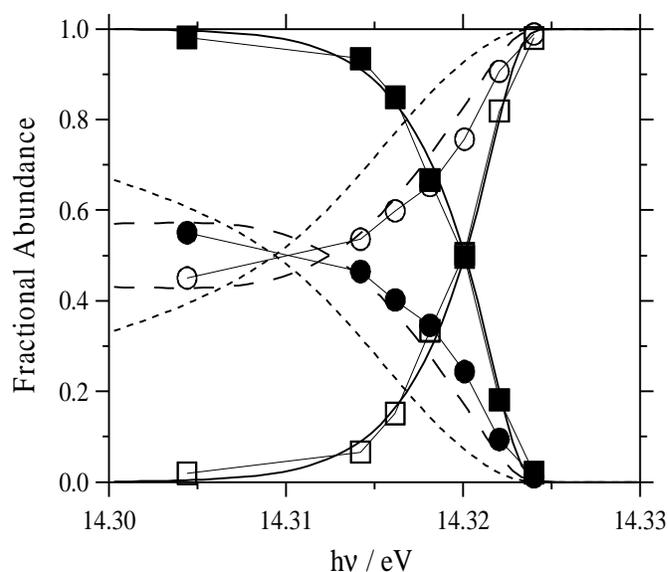


Figure 2. Breakdown curves of  $\text{CH}_3^+$  and  $\text{CH}_4^+$  in the  $h\nu$  range of  $14.300$ - $14.325$  eV derived based on the PFI-PEPICO TOF data. The experimental branching ratios for  $\text{CH}_3^+$  and  $\text{CH}_4^+$  obtained based the entire daughter ion signal are (O) and (●), whereas those obtained using only the cold daughter ion signal are indicated as (□) and (■), respectively. The lines are simulation curves: (—)  $33$  K ensemble; (---)  $33$  K ensemble with  $15\%$  thermal background and  $90\%$  loss of parent ions; and (- -)  $33$  K ensemble with  $15\%$  thermal background and with an energy dependent loss.

dissociation of  $\text{CH}_4^*$  will occur to form  $\text{CH}_3^* + \text{H}$  via an ‘inverse Born-Oppenheimer’ process, where  $\text{CH}_3^*$  represents  $\text{CH}_3$  in a high- $n$  Rydberg state. The occurrence of such a process is supported by previous PFI-PE studies of  $\text{O}_2$  in high- $n$  Rydberg states converging to a dissociative ion core.

We note that any high- $n$  Rydberg species, which have spontaneously autoionized before  $\Delta t$ , are lost to the PFI detection. The pivotal point is that the  $\text{CH}_3^*$  radicals formed by fragmentation of  $\text{CH}_4^*$  near the dissociation threshold are preferentially formed below the IE of  $\text{CH}_3$ . Thus, we may conclude that autoionization is not readily accessible for  $\text{CH}_3^*$  and is predominantly operative for  $\text{CH}_4^*$ . We note that for  $\text{CH}_3^*$  formed slightly above the dissociation threshold, it can also autoionize. However, the autoionization of this  $\text{CH}_3^*$  may still be less probable than  $\text{CH}_4^*$ .

From Fig. 2, we derive a 0 K threshold of  $14.323 \pm 0.001$  eV for the formation of  $\text{CH}_3^+$  from  $\text{CH}_4$ . From previous photoion studies, Chupka derived  $14.320 \pm 0.004$  eV and McCulloh and Dibeler reported  $14.324 \pm 0.003$  eV. The optical resolution in both experiments was 0.007 eV. The threshold-PEPICO experiments of Weitzel et al. yielded a 0 K threshold of  $14.327 \pm 0.01$  eV. Additional data are available in the literature for the reaction threshold at 298 K. This comparison shows that the present experiment is compatible with previous studies. However, it is characterized by a higher accuracy. The reference data book on ion energetics suggests a 0 K threshold of 14.312 eV. However, the current internet version of Ref. 18 leads to a value of 14.281 eV. The adiabatic IE of  $\text{CH}_3$  ( $9.8357 \pm 0.00037$  eV) and  $\text{CH}_4$  ( $12.618 \pm 0.004$  eV) have been accurately determined recently from rotationally resolved PFI-PE measurements. Combining these values with the present dissociation threshold for  $\text{CH}_3^+$  leads to accurate 0 K dissociation energies ( $D_0$ ) for  $\text{CH}_4$  and  $\text{CH}_4^+$  as  $D_0(\text{H}-\text{CH}_3) = 4.487 \pm 0.001$  eV and  $D_0(\text{H}-\text{CH}_3^+) = 1.705 \pm 0.004$  eV, respectively.

In summary, we have investigated the formation of  $\text{CH}_3^+$  from  $\text{CH}_4$  in high resolution using the PFI-PEPICO method. The PFI-PEPICO TOF spectra and the breakdown curves provide evidence that dissociation of  $\text{CH}_4^*$  occurs prior to pulsed field ionization in an inverse Born-Oppenheimer process. Simulations indicate that a large fraction of  $\text{CH}_4^*$ , which do not dissociate are lost due to autoionization and the amount lost depends on the internal energy and thus on the rotational angular momentum of  $\text{CH}_4^*$ . The cross-over energy in the PFI-PEPICO breakdown curves is found to change dramatically with the Stark field in the PI/PEX region and thus, this quantity is not well suited to derive the dissociation threshold. Most importantly, we have established that the disappearance energy of the parent molecule observed in PFI-PEPICO TOF measurements is an unambiguous feature for the determination of the 0 K ion dissociation threshold of a prompt dissociation process.

## REFERENCE

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