

# 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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# 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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The formation of methyl cation (CH<sub>3</sub><sup>+</sup>) from methane (CH<sub>4</sub>) has been investigated in high resolution using the newly perfected pulsed field ionization photoelectron–photoion coincidence (PFI-PEPICO) scheme. The PFI-PEPICO data reveal that fragmentation of CH<sub>4</sub> in high-*n* Rydberg states occurs at energies above the dissociation threshold prior to pulsed field ionization. The crossover point of the breakdown curves is found to depend strongly on the Stark field in the ion source and thus traditional simulation procedures based on such a feature for ion dissociation energy determination are not appropriate in PFI-PEPICO studies. We show that for a prompt dissociation process, the disappearance energy of the parent molecule provides an accurate measure of the 0 K ion dissociation threshold, as that for CH<sub>3</sub><sup>+</sup> from CH<sub>4</sub> is 14.323±0.001 eV. © 1999 American Institute of Physics. [S0021-9606(99)01742-0]

Since the introduction of the photoelectron–photoion coincidence (PEPICO) technique<sup>1</sup> 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.<sup>2–4</sup> 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*≥100) Rydberg states.<sup>5–7</sup> Weitzel and Güthe<sup>8</sup> were the first to demonstrate the potential for performing PFI-photoelectron (PFI-PE) and PFI-PEPICO studies by employing synchrotron radiation in a single-bunch operation. Taking advantage of the high optical resolution capability of the Chemical Dynamics Beamline at the Advanced Light Source (ALS), we have recently developed novel PFI-PE detection schemes using monochromatized multibunch synchrotron radiation, routinely achieving resolutions in the range of 1–5 cm<sup>-1</sup> [full width at half maximum (FWHM)].<sup>9</sup> Most recently, we have further developed the PFI-PEPICO method 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.<sup>10</sup>

In this Communication, 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>), CH<sub>4</sub>+*hν*→CH<sub>3</sub><sup>+</sup>+H+*e*<sup>-</sup>, which is known to be a prompt dissociation process.<sup>11</sup> This experiment provides important insight into factors that must be considered in the analysis of PFI-PEPICO data. The analysis presented here establishes intrinsic features of the PFI-PEPICO breakdown curves, which can be used for accurate ion dissociation threshold determination. The breakdown data also shed light on the competing autoionization and fragmentation channels for the decay of CH<sub>4</sub> in high-*n* Rydberg states (CH<sub>4</sub><sup>\*</sup>).

In the present study, the CH<sub>4</sub> sample is introduced into the photoionization/photoexcitation (PI/PEX) center of the PFI-PEPICO apparatus<sup>10</sup> as a skimmed supersonic beam. The CH<sub>4</sub><sup>\*</sup> species formed by excitation of the CH<sub>4</sub> beam at the PI/PEX center by dispersed synchrotron radiation are ionized by the application of a delayed electric field pulse (height ≈7 V/cm, width ≈160 ns) in the dark gap of the ALS synchrotron ring period (656 ns). This experiment has been performed using both the two-bunch mode and multibunch mode with a dark gap of 328 and 144 ns, respectively. The PI/PEX region is maintained at a dc electric field in the range of ≈0–2 V/cm, which ensures that prompt electrons and ions are continuously deflected from the PI/PEX region toward their respective detectors.<sup>9</sup> The delay time (Δ*t*) for the application of the electric field pulse measured with respect to the light pulse was varied between 10 and 80 ns. Electrons formed by PFI in the dark gap are selected based on their time of flights (TOFs) through the application of a

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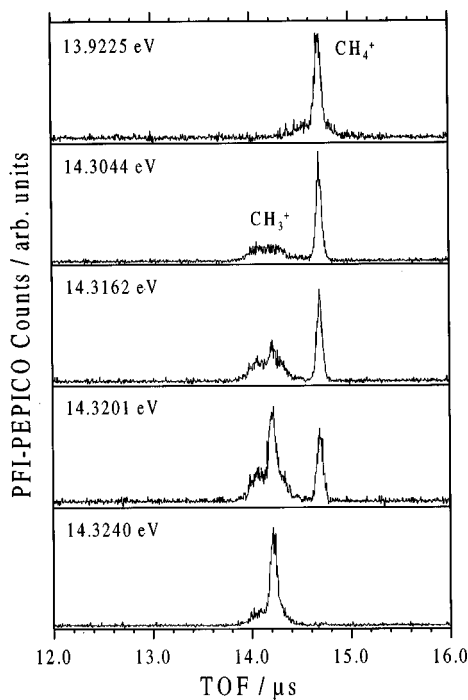


FIG. 1. PFI-PEPICO TOF spectra of  $\text{CH}_4$  at  $h\nu=13.9225$ ,  $14.3044$ ,  $14.3162$ ,  $14.3201$ , and  $14.3240$  eV obtained using a dc electric background field of  $1.3$  V/cm. The TOF peaks centered at  $14.10$  and  $14.35$   $\mu\text{s}$  are due to  $\text{CH}_3^+$  and  $\text{CH}_4^+$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

detection time gate.<sup>9</sup> The ion TOF is measured by a multi-channel scaler, which is started by the detection of an electron. The photon energy ( $h\nu$ ) calibration was achieved using the  $\text{Ne}^+(^2P_{3/2})$ , and  $\text{Ar}^+(^2P_{3/2})$  PFI-PE bands recorded under the same experimental conditions before and after each scan.<sup>9</sup> This calibration procedure assumes that the Stark shift for ionization thresholds of  $\text{CH}_4$  and the rare gases are identical. On the basis of the measured PFI-PE band for  $\text{Ar}^+(^2P_{3/2})$ , we estimate that the ion-energy selection achieved in present study is  $\approx 1.0$  meV (FWHM).

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  $\text{CH}_4$ .<sup>11</sup> Selected PFI-PEPICO TOF spectra measured at  $h\nu=13.9225$ – $14.3240$  eV are depicted in Fig. 1. At  $13.9225$  eV, only parent  $\text{CH}_4^+$  ions are observed, whereas only daughter  $\text{CH}_3^+$  ions are found at  $14.3240$  eV. The current setup is sensitive to the ion kinetic energy.<sup>10</sup> At  $13.9225$  eV, the  $\text{CH}_4^+$  TOF peak is found to be composed of a narrow and a broad component due to photoionization of cold (temperature  $\approx 30$  K)  $\text{CH}_4$  in the supersonic beam and thermal ( $298$  K) background  $\text{CH}_4$  in the photoionization chamber, respectively. The ratio of these intensities for the cold and thermal  $\text{CH}_4$  is found to be  $\approx 85:15$ , which roughly corresponds to the ratio of the estimated number density of the  $\text{CH}_4$  beam and that of the thermal background  $\text{CH}_4$  at the PI/PEX region. As the  $h\nu$  is increased to  $14.3044$  eV, a broad TOF peak for  $\text{CH}_3^+$  was observed, concomitant with the disappearance of the broad thermal component for the  $\text{CH}_4^+$  TOF peak. The average vibrational energy of  $\text{CH}_4$  at  $298$  K is negligible. It was demonstrated in the previous threshold-PEPICO study that the entire rota-

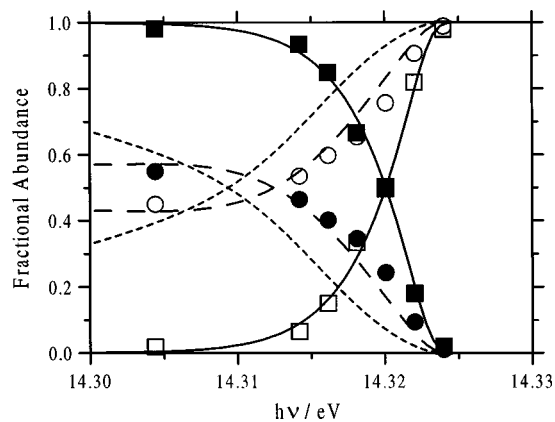


FIG. 2. Breakdown curves of  $\text{CH}_3^+$  and  $\text{CH}_4^+$  in the  $h\nu$  range of  $14.300$ – $14.325$  eV. The experimental fractional abundances for  $\text{CH}_3^+$  and  $\text{CH}_4^+$  obtained based on the entire daughter ion signal are  $(\circ)$  and  $(\bullet)$ , whereas those obtained using only the cold daughter ion signal are indicated as  $(\square)$  and  $(\blacksquare)$ , 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. See the text.

tional energy (average rotational energy  $\approx 39$  meV) of  $\text{CH}_4$  is available to the dissociation reaction.<sup>11</sup> The TOF peak structures resolved in Fig. 1 unambiguously show that  $\text{CH}_3^+$  formed at  $14.3044$  eV are mostly produced by dissociation of rotationally excited  $\text{CH}_4^+$  formed in the photoionization of thermal  $\text{CH}_4$ . The narrow components of the TOF peaks for  $\text{CH}_3^+$  resulting from the dissociation of cold  $\text{CH}_4^+$  are observed with increasing intensity as the  $h\nu$  is increased from  $14.3162$  to  $14.3201$ , and to  $14.3240$  eV.

The contribution to the  $\text{CH}_3^+$  signal due to thermal background  $\text{CH}_4$  is also evident from the breakdown curves. Figure 2 shows the experimental breakdown data in the  $h\nu$  range of  $14.300$ – $14.325$  eV obtained at a  $1.3$  V/cm dc field. The open and closed circular symbols in Fig. 2 show the respective fractional abundances of  $\text{CH}_3^+$  and  $\text{CH}_4^+$  derived by taking into account the cold and thermal components of  $\text{CH}_3^+$ . These breakdown data exhibit a considerable amount of fragmentation between  $14.30$  and  $14.32$  eV. Qualitatively, the main origin of this fragmentation signal arises from  $298$  K  $\text{CH}_4^+$  formed by photoionization of thermal  $\text{CH}_4$ . However, the amount of fragmentation is significantly higher than the estimated thermal  $\text{CH}_4$  breakdown of  $\approx 15\%$ . All our attempts failed to simulate these breakdown data (the circular symbols of Fig. 2) by just assuming a combination of cold beam and thermal background molecules as in earlier work.<sup>11</sup>

Since the PFI-PEPICO TOF spectra resolve the dissociation due to cold  $\text{CH}_4$  from that of thermal  $\text{CH}_4$ , 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  $\text{CH}_4$ . By assuming a temperature of  $33$  K for  $\text{CH}_4^+$  and all three internal rotations being energetically active, we are able to obtain excellent simulation (solid lines in Fig. 2) of breakdown curves.<sup>11</sup> The  $0$  K dissociation energy for  $\text{CH}_3^+$

from  $\text{CH}_4$  determined in this simulation is 14.323 eV.

Although the dissociation due to the cold  $\text{CH}_4$  beam can be rationalized, the question remains why the amount of thermal  $\text{CH}_3^+$  signal is so high in the  $h\nu$  range below the 0 K threshold. For example, at 14.316 eV (see Fig. 1), the broad thermal  $\text{CH}_3^+$  component accounts for nearly 50% of the total  $\text{CH}_3^+$  signal. 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, which have survived autoionization and fragmentation for 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 with a lifetime shorter than the  $\Delta t$ , prompt dissociation of  $\text{CH}_4^*$  will occur to form  $\text{CH}_3^* + \text{H}$ ,<sup>6</sup> 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.<sup>12</sup>

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 that of  $\text{CH}_4^*$ .

On the basis of the above picture for the decay of  $\text{CH}_4^*$ , we have performed modified simulations for the breakdown data. We assumed that the effective energy distribution of neutral  $\text{CH}_4$  consists of a 33 K molecular beam with 15% thermal (298 K) background. In addition, we assumed that 90% of all  $\text{CH}_4^*$  molecules formed below the dissociation threshold are lost due to autoionization. Although this simulation (short-dashed lines in Fig. 2) represents a major improvement over all simulations neglecting this loss channel, the agreement with the experimental breakdown data including the entire ion signals (circles in Fig. 2) is by no means satisfying. Reasonable agreement between the experimental data and the simulation is obtained only if we assume that the amount of parent  $\text{CH}_4^*$  lost due to autoionization varies with excitation energy. The long-dashed lines in Fig. 2 have been obtained assuming that the amount of all parent  $\text{CH}_4^*$  lost decreases from  $\approx 92\%$  at 14.303 eV to  $\approx 68\%$  at 14.323 eV. Since the internal energy distribution of  $\text{CH}_4^*$  is basically identical to that for  $\text{CH}_4$  prior to photoexcitation, this assumption implies that the loss depends on the rotational angular momentum of  $\text{CH}_4$ . This variation of loss is most likely due to a variation of the autoionization lifetime of  $\text{CH}_4^*$ .

In traditional photoion studies,<sup>13,14</sup> the dissociation threshold is usually determined from the lowest  $h\nu$  at which the fragment ion is observed. However, the fragment ion threshold is not a sharp step but rather depends on the parent internal energy distribution and the Franck-Condon factors for photoionization transitions.<sup>13</sup> For sample molecules introduced as a molecular beam, the parent internal energy distri-

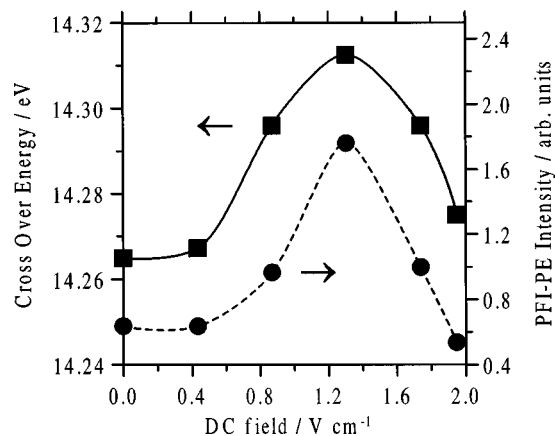


FIG. 3. The experimental crossover energy (■) and relative PFI-PE intensity (●) plotted as a function of the dc electric field.

bution is often difficult to account for accurately because of the unknown temperature. In the past, these problems have been overcome by the threshold-PEPICO approach.<sup>15</sup> There, the dissociation threshold is either derived from the crossover point, or from a simulation of the entire breakdown curve.

We have recorded experimental breakdown curves at different dc fields in the range of  $\approx 0$ –2 V/cm. The most striking observation is that the crossover energy depends on this dc Stark field as shown in Fig. 3 (closed rectangles). The actual crossover energy is lowest at zero dc field and approaching 2 V/cm. It runs through a maximum for a dc field of 1.3 V/cm. A similar dc field dependence is observed for the relative PFI-PE intensity (see the closed rectangles in Fig. 3). The dramatic dc field effect observed on the crossover energy indicates that the patterns of low- $n$  interloper Rydberg states for  $\text{CH}_3$  and  $\text{CH}_4$  involved in the Stark ionization are different, resulting in different dc field dependencies for the PFI-PE intensities for  $\text{CH}_3^+$  and  $\text{CH}_4^+$ .<sup>10</sup> We note that this effect is general for most molecules<sup>7</sup> and may give rise to irregular structures of the

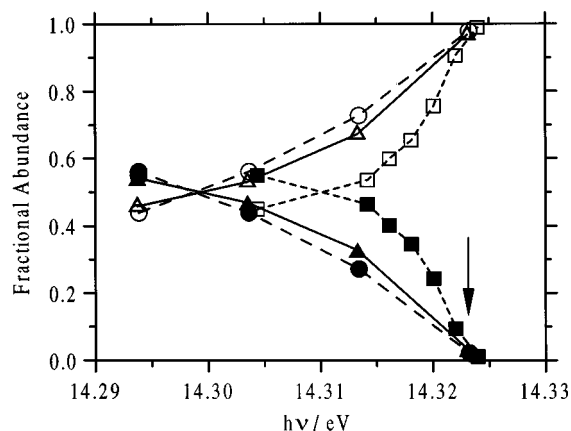


FIG. 4. Experimental breakdown data  $\text{CH}_3^+/\text{CH}_4^+$  based on total ion signals, which are measured at dc fields of 0.87 V/cm ( $\Delta/\blacktriangle$ ), 1.30 V/cm ( $\square/\blacksquare$ ), and 1.74 V/cm ( $\circ/\bullet$ ). Note that the disappearance energies for  $\text{CH}_4^+$  are identical.

experimental breakdown curves based on PFI-PEPICO TOF measurements.

Since the crossover energy depends on the dc electric field, this does not appear to be a good property for deriving 0 K ion dissociation thresholds. However, there is a unique feature, namely the disappearance energy of the parent molecule, in the PFI breakdown curve, which can be used to characterize the 0 K fragmentation threshold. Figure 4 shows the experimental breakdown data obtained at dc electric fields of 0.87, 1.30, and 1.74 V/cm. Here, although the shapes and crossover points of the breakdown curves observed at different dc fields are different, the disappearance energy (marked by the arrow in Fig. 4) is an intrinsic feature. 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 that energy at which even the coldest part of the neutral energy distribution reaches above the dissociation threshold. We emphasize that in order for the parent disappearance energy 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. In threshold-PEPICO studies, where the threshold photoelectron measurement were affected by the hot-tail problem, the fractional abundance for the parent is not zero at the dissociation threshold.<sup>11</sup> Thus, the disappearance energy for the parent molecule observed in such studies cannot be used for the determination of ion dissociation thresholds.

From Fig. 4, 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<sup>13</sup> derived  $14.320 \pm 0.004$  eV and McCulloh and Dibeler<sup>14</sup> 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  $14.33 \pm 0.01$  eV.<sup>12</sup> This comparison shows that although the present experiment is compatible with previous studies, it is characterized by a higher accuracy. The reference data<sup>16</sup> book on ion energetics suggests a 0 K threshold of 14.312 eV. However, the current internet version leads to a value<sup>17</sup> of 14.281 eV. The adiabatic IE of  $\text{CH}_3$  ( $9.8357 \pm 0.00037$  eV)<sup>18</sup> and  $\text{CH}_4$  ( $12.618 \pm 0.004$  eV)<sup>19</sup> have re-

cently been accurately determined 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  $\text{CH}_4$  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.

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