High-resolution pulsed field ionization photoelectron–photoion coincidence study of CH$_4$: Accurate 0 K dissociation threshold for CH$_3^+$

Karl-Michael Weitzel and Marcus Malow
Freie Universität Berlin, Institut für Chemie, Physikalische und Theoretische Chemie, Takustrasse 3, 14195 Berlin, Germany

G. K. Jarvis
Lawrence Berkeley National Laboratory, Chemical Science Division, Berkeley, California 94720

Tomas Baer
Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290

Y. Song and C. Y. Ng[a]
Ames Laboratory, USDOE and Iowa State University, Department of Chemistry, Ames, Iowa 50011

The formation of methyl cation (CH$_3^+$) from methane (CH$_4$) 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$_4$ 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$_3^+$ from CH$_4$ 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[1] 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.[2–4] 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.[5–7] Weitzel and Güthe[8] 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^{-1} [full width at half maximum (FWHM)].[9] Most recently, we have further developed the PFI-PEPICO method for use with both two-bunch and multibunch synchrotron radiation, attaining a solution of 0.6 meV (FWHM), limited only by the PFI-PE measurement.[10]

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$_3^+$) from methane (CH$_4$), CH$_4 + h\nu \rightarrow$ CH$_3^+ +$ H $+ e^-$, which is known to be a prompt dissociation process.[11] 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$_4$ in high-n Rydberg states (CH$_4^*$).

In the present study, the CH$_4$ sample is introduced into the photoionization/photoexcitation (PI/PEX) center of the PFI-PEPICO apparatus[10] as a skimmed supersonic beam. The CH$_4^*$ species formed by excitation of the CH$_4$ 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.[9] The delay time (Δt) 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

[a]Author to whom correspondence should be addressed; electronic mail: cyng@ameslab.gov
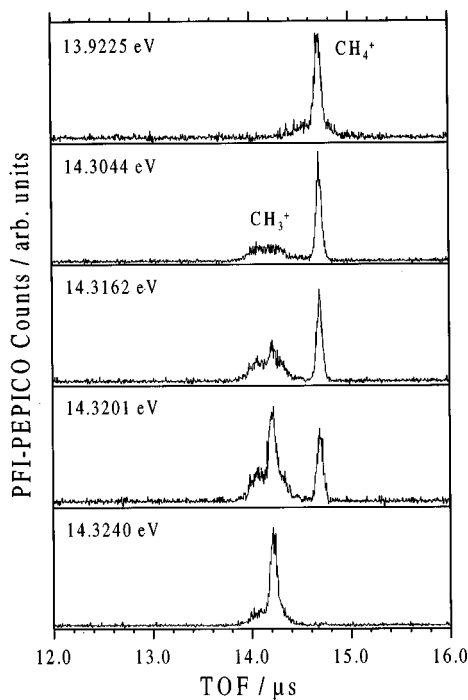
FIG. 1. PFI-PEPICO TOF spectra of CH_4 at $h\nu=13.9225$, 14.3044, 14.3162, 14.3201, and 14.3240 eV obtained using a dc electric background field of 1.3 V/cm. The TOF peaks centered at 14.10 and 14.35 μs are due to CH_3^+ and CH_4^+, respectively.

FIG. 2. Breakdown curves of CH_3^+ and CH_4^+ in the $h\nu$ range of 14.300–14.325 eV. The experimental fractional abundances for CH_3^+ and CH_4^+ obtained based on the entire daughter ion signal are ($\bigcirc$) 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.

detection time gate.[9] The ion TOF is measured by a multichannel scaler, which is started by the detection of an electron. The photon energy ($h\nu$) calibration was achieved using the $Ne^+(^2P_{3/2})$, and $Ar^+(^2P_{3/2})$ PFI-PE bands recorded under the same experimental conditions before and after each scan.[9] This calibration procedure assumes that the Stark shift for ionization thresholds of CH_4 and the rare gases are identical. On the basis of the measured PFI-PE band for $Ar^+(^2P_{3/2})$, we estimate that the ion-energy selection achieved in present study is ≈ 1.0 meV (FWHM).

The PFI-PEPICO TOF spectra of CH_4 have been recorded in the $h\nu$ range of 13.9–14.5 eV, near the dissociation threshold for CH_3^+ from CH_4.[11] 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 CH_4^+ ions are observed, whereas only daughter CH_3^+ ions are found at 14.3240 eV. The current setup is sensitive to the ion kinetic energy.[10] At 13.9225 eV, the CH_4^+ TOF peak is found to be composed of a narrow and a broad component due to photoionization of cold (temperature ≈ 30 K) CH_4 in the supersonic beam and thermal (298 K) background CH_4 in the photoionization chamber, respectively. The ratio of these intensities for the cold and thermal CH_4 is found to be $\approx 85:15$, which roughly corresponds to the ratio of the estimated number density of the CH_4 beam and that of the thermal background CH_4 at the PI/PEX region. As the $h\nu$ is increased to 14.3044 eV, a broad TOF peak for CH_3^+ was observed, concomitant with the disappearance of the broad thermal component for the CH_4^+ TOF peak. The average vibrational energy of CH_4 at 298 K is negligible. It was demonstrated in the previous threshold-PEPICO study that the entire rota-

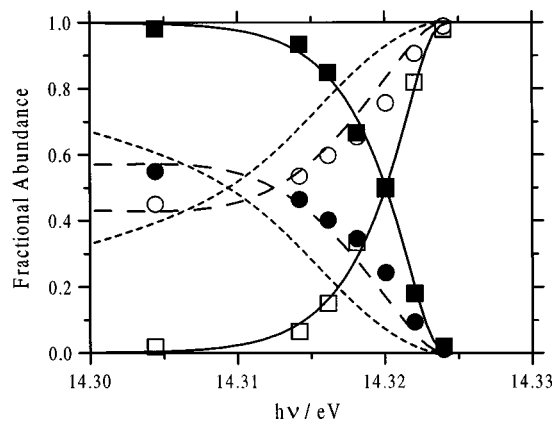tional energy (average rotational energy ≈ 39 meV) of CH_4 is available to the dissociation reaction.[11] The TOF peak structures resolved in Fig. 1 unambiguously show that CH_3^+ formed at 14.3044 eV are mostly produced by dissociation of rotationally excited CH_4^+ formed in the photoionization of thermal CH_4. The narrow components of the TOF peaks for CH_3^+ resulting from the dissociation of cold 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 CH_3^+ signal due to thermal background 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 CH_3^+ and CH_4^+ derived by taking into account the cold and thermal components of 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 CH_4^+ formed by photoionization of thermal CH_4. However, the amount of fragmentation is significantly higher than the estimated thermal 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.[11]

Since the PFI-PEPICO TOF spectra resolve the dissociation due to cold CH_4 from that of thermal CH_4, we have analyzed the TOF spectra by taking into account only the cold 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 CH_4^+ formed by photoionization of supersonically cooled CH_4. By assuming a temperature of 33 K for 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.[11] The 0 K dissociation energy for CH_3^+

from CH_4 determined in this simulation is 14.323 eV.

Although the dissociation due to the cold CH_4 beam can be rationalized, the question remains why the amount of thermal 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 CH_3^+ component accounts for nearly 50% of the total CH_3^+ signal. For the decay of CH_4^*, there are two important competing decay channels, i.e., autoionization and fragmentation. Clearly, in our PFI experiment only those CH_4^* molecules, which have survived autoionization and fragmentation for a time longer than Δt, can be observed by PFI. Autoionization of CH_4^* is accessible in the entire energy range studied since the energies are far above the ionization energy (IE) of CH_4. If the CH_4^+ core is dissociative with a lifetime shorter than the Δt, prompt dissociation of CH_4^* will occur to form $CH_3^* + H$,[6] where CH_3^* represents CH_3 in a high-n Rydberg state. The occurrence of such a process is supported by previous PFI-PE studies of O_2 in high-n Rydberg states converging to a dissociative ion core.[12]

We note that any high-n Rydberg species, which have spontaneously autoionized before Δt, are lost to the PFI detection. The pivotal point is that the CH_3^* radicals formed by fragmentation of CH_4^* near the dissociation threshold are preferentially formed below the IE of CH_3. Thus, we may conclude that autoionization is not readily accessible for CH_3^* and is predominantly operative for CH_4^*. We note that for CH_3^* formed slightly above the dissociation threshold, it can also autoionize. However, the autoionization of this CH_3^* may still be less probable than that of CH_4^*.

On the basis of the above picture for the decay of CH_4^*, we have performed modified simulations for the breakdown data. We assumed that the effective energy distribution of neutral CH_4 consists of a 33 K molecular beam with 15% thermal (298 K) background. In addition, we assumed that 90% of all 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 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 CH_4^* lost decreases from $\approx 92\%$ at 14.303 eV to $\approx 68\%$ at 14.323 eV. Since the internal energy distribution of CH_4^* is basically identical to that for CH_4 prior to photoexcitation, this assumption implies that the loss depends on the rotational angular momentum of CH_4. This variation of loss is most likely due to a variation of the autoionization lifetime of CH_4^*.

In traditional photoion studies,[13,14] 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.[13] For sample molecules introduced as a molecular beam, the parent internal energy distri-
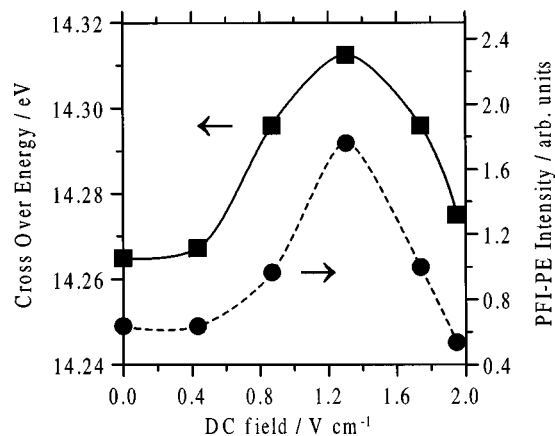

FIG. 3. The experimental crossover energy (■) and relative PFI-PE intensity (●) plotted as a function of the dc electric field.

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.[15] 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 ≈ 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 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 CH_3 and CH_4 involved in the Stark ionization are different, resulting in different dc field dependencies for the PFI-PE intensities for CH_3^+ and CH_4^+.[10] We note that this effect is general for most molecules[7] and may give rise to irregular structures of the
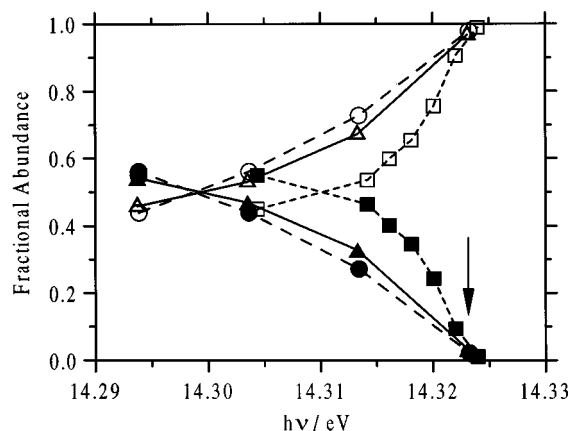

FIG. 4. Experimental breakdown data CH_3^+/CH_4^+ based on total ion signals, which are measured at dc fields of 0.87 V/cm (△/▲), 1.30 V/cm (□/■), and 1.74 V/cm (○/●). Note that the disappearance energies for CH_4^+ are identical.

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.[11] 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 ± 0.001 eV for the formation of CH_3^+ from CH_4. From previous photoion studies, Chupka[13] derived 14.320 ± 0.004 eV and McCulloh and Dibeler[14] reported 14.324 ± 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 ± 0.01 eV.[12] This comparison shows that although the present experiment is compatible with previous studies, it is characterized by a higher accuracy. The reference data[16] book on ion energetics suggests a 0 K threshold of 14.312 eV. However, the current internet version leads to a value[17] of 14.281 eV. The adiabatic IE of CH_3 (9.8357 ± 0.00037 eV)[18] and CH_4 (12.618 ± 0.004 eV)[19] have re-

cently been accurately determined from rotationally resolved PFI-PE measurements. Combining these values with the present dissociation threshold for CH_3^+ leads to accurate 0 K dissociation energies (D_0) for CH_4 as $D_0(H-CH_3) = 4.487 \pm 0.001$ eV and $D_0(H-CH_3^+) = 1.705 \pm 0.004$ eV, respectively.

[1] E. v. Puttkammer, Z. Naturforsch. A **25**, 1062 (1970).
[2] T. Baer, J. A. Booze, and K.-M. Weitzel, in *Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters*, edited by C. Y. Ng (World Scientific, Singapore, 1991), p. 259.
[3] W. Kamke, in *Cluster Ions*, edited by C. Y. Ng, T. Baer, and I. Powis (Wiley, Chichester, 1993), p. 1.
[4] C. Y. Ng, in *Techniques for the Study of Ion-Molecule Reactions*, edited by J. M. Farrar and W. H. Saunders (Wiley, New York, 1988), p. 417.
[5] K. Müller-Dethlefs, M. Sander, and E. W. Schlag, Z. Naturforsch. A **39**, 1089 (1984).
[6] E. W. Schlag, *ZEKE Spectroscopy* (Cambridge University Press, Cambridge, 1998).
[7] *High Resolution Laser Photoionization and Photoelectron Studies*, edited by I. Powis, T. Bear, and C. Y. Ng, Wiley Series in Ion Chemistry & Physics (Wiley, Chichester, 1995).
[8] K.-M. Weitzel and F. Güthe, Chem. Phys. Lett. **251**, 295 (1996).
[9] C.-W. Hsu *et al.*, Rev. Sci. Instrum. **68**, 1694 (1997); G. K. Jarvis, Y. Song, and C. Y. Ng, *ibid.* **70**, 2615 (1999).
[10] G. K. Jarvis *et al.*, Rev. Sci. Instrum. (in press).
[11] K.-M. Weitzel, J. Mähnert, and H. Baumgärtel, Ber. Bunsenges. Phys. Chem. **97**, 134 (1993).
[12] M. Evans *et al.*, J. Chem. Phys. **110**, 315 (1999); C.-W. Hsu *et al.*, *ibid.* **109**, 1285 (1998).
[13] W. A. Chupka, J. Chem. Phys. **48**, 2337 (1968).
[14] K. E. McCulloh and V. H. Dibeler, J. Chem. Phys. **64**, 4445 (1976).
[15] K.-M. Weitzel, Trends Chem. Phys. Suppl. Research Trends **6**, 143 (1997).
[16] S. G. Lias *et al.*, J. Phys. Chem. Ref. Data Suppl. **17**, 1 (1998).
[17] The NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/.
[18] J. A. Blush *et al.*, J. Chem. Phys. **98**, 3557 (1993).
[19] R. Signorell and F. Merkt, J. Chem. Phys. **110**, 2309 (1999).