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Experimental observation of neutral radical formation from CH_4 by electron impact in the threshold region

C. Makochekanwa,[1,2,*] K. Oguri,[1] R. Suzuki,[1] T. Ishihara,[1] M. Hoshino,[1] M. Kimura,[2] and H. Tanaka[1]
[1]*Department of Physics, Sophia University, Tokyo 102-8554, Japan*
[2]*Graduate School of Sciences, Kyushu University, Fukuoka 812-8581, Japan*

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An apparatus combining the cross-beam and threshold-ionization techniques has been used to measure absolute cross sections for electron impact dissociation of CH_4 molecules into the CH_3 neutral radicals at energies from threshold up to 13 eV. The threshold energy for the lowest-lying ${}^3T_2$ state has been observed to be 7.5 ±0.3 eV, and attributed to neutral CH_3 formation. Peaks have been observed at ~9.6 and 11.5 eV, in agreement with electronic excitation and photon impact neutral dissociation literature data. The current results indicate that all excited states of CH_4 predominantly result in dissociation via the CH_3 neutral radical channel below 12.5 eV.

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I. INTRODUCTION

In addition to attracting research attention as a prototype for hydrocarbon physics and chemistry, industrial applications of methane (CH_4) have continued to widen from, among others, chemical vapor deposition for artificial diamond production [1,2] in the early 1980s, to developments in carbon nanotubes and nanocrystalline diamond films [3]. The controllability of bonding configurations of the hydrocarbon species during the deposition of the thin films is invaluable, and it has been established that this depends on the production rates for CH_x radical species from the CH_4 plasma, and particularly on the rate for the CH_3 [4].

In view of the above, it is important to correctly understand the fragmentation channels for CH_4. The best probe for this is by electron impact. This is because electron impact, unlike photon collisions limited by dipole interaction rules, can excite any dissociative state of the molecule and reduce it to these required fragment species. Indeed a number of experimental and theoretical works have been carried out to study the fragmentation of CH_4 into the various ionic fragments, with smaller number of studies of the neutrals. The abundances have been found to be in decreasing order from CH_3, CH_2, CH, C, to H for both the neutral and ionic decay pathways (see Ref. [5]).

The rather extensive photoabsorption and photoionization cross sections for CH_4 have recently been comprehensively reviewed by Kameta *et al.* [6]. However, as for electron impact, while there have been a significant number of experimental and theoretical works on the CH_4 fragmentation into the various ions, there is a paucity of data on the dissociation to neutral fragment channels. The reason for this is the difficulty associated with the detection of these uncharged fragments; since (i) they are nonemissive and (ii) one has to deal with very weak signal intensities, especially near the threshold. See a comprehensive review of the available ionization data by Janev *et al.* [7]. Important experimental works not covered by Janev *et al.* include the electron impact threshold ionization [8] and kinetic energy distribution [9] studies carried out for each fragment ion.

There are only two measurements available in the literature which studied the dominant neutral fragmentation decay channels of CH_4, i.e., CH_3 and CH_2. These were done by Nakano *et al.* [10], using the threshold ionization method in conjunction with a collision cell and a quadrupole mass spectrometer (QMS), and Motlagh *et al.* [11], who studied CH_3 formation cross sections using the so-called chemical getter technique. However, these results differ significantly in both energy dependence and magnitude over the energy range of overlap for the most dominant channel CH_3. Also, both measurements were only down to 10 eV. Thus there is an urgent need for (i) an independent accurate determination of the production rates for this channel to resolve the discrepancy above and (ii) investigation of the threshold behavior of this species, i.e. cross sections for energies below 10 eV. Other relevant experimental studies are those of Winters [12] who measured total electron impact dissociation cross sections for CH_4.

Although earlier theoretical studies [13,14] and photodissociation experiments [15] had indicated that the lowest excited state of CH_4 dissociated primarily via the CH_2 and H_2 pathway no experimental work had been done to either prove or discredit this important physics phenomenon for electron impact. In this work we seek to tackle this challenge and also establish the threshold and near-threshold behavior of the lowest-lying ${}^{1,3}T_2$ excited states of CH_4.

The apparatus used in these experiments implements a combination of the crossed-beam method [16] and the threshold ionization technique [17]. It has already been described in detail in our preliminary report [18], and thus only summarized here. It consists of the primary electron gun (hereafter referred to as the primary gun), a collision region with an effusive gas nozzle, a differentially pumped ionization region and the ionizing electron gun (hereafter referred to as the ionization gun), a QMS and the detection and counting electronics. The primary beam current could be varied with impact energy between 0.8 and 3.0 μA over the energy range 5 to 13 eV, and the energy resolution was about 0.6 eV full-width-half-maximum (FWHM). This rather large

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[*] Email address: casten@yamaguchi-u.ac.jp

resolution was a compromise in order to get higher signal intensities. The gas pressure in the collision region was $\sim 2 \times 10^{-4}$ Pa during the measurements while the background pressures were as good as $\sim 2.5 \times 10^{-5}$ Pa. The energy calibration of the primary beam was done using the well known 2.4 eV electron-N_2 $^2\Pi_g$ resonance [19].

Electron-CH_4 interactions in the collision region produce the neutral, as well as ionic, fragments. The QMS is fixed in a position at 90° to the primary electron beam direction, which itself can be rotated on a turntable. The reason for choosing this differential angle is to reduce noise signals coming from fragmentation of CH_4 at the lens and chamber surfaces that would inevitably come in if the QMS was set in line with the primary beam. A 2 mm aperture separates the collision region from the QMS ionization region. This rather large diameter for the aperture is chosen in order to maximize the collision volume in the ionization region and thus enhance signal intensities. Just behind this aperture, however, ion deflector lenses are inserted so that only neutral fragments are allowed into the ionization chamber. Based on the threshold ionization technique and the known threshold energies for CH_4 molecules and CH_3 radicals (see the tables in Refs. [18,20]), the ionization gun energy was set at 10.5 eV for the CH_3 detection, i.e., an energy carefully chosen between 14.3 eV (threshold for $e + CH_4 \rightarrow CH_3^+ + H + 2e$) and 9.8 eV (threshold for $e + CH_3 \rightarrow CH_3^+ + 2e$) to reduce the background contributions from ions coming from thermal fragmentation of the neutrals and parent CH_4 molecules. The background noise was subtracted after a comparison between spectra obtained with the primary and ionization gun beams in ON and OFF conditions (see Ref. [18] for details).

The radical signal S is directly proportional to the primary beam current, the gas pressure in the collision region, the partial dissociation cross section (i.e., for CH_3 production) and integration time for pulse counting. With integration over time the radical signal increases linearly, with the slope being equivalent to the fragmentation cross section.

In the analysis of the obtained raw data, lines are drawn through the rising time integrated signal curves using least-squares fits. Whereas measurements at impact energies of 10 eV and above require about 7.5 h for good statistics, an average 25 hours or more was needed at energies towards the threshold, making these experiments extremely difficult and time consuming. However, these experiments were repeated about six times with good qualitative reproducibility of the structures discussed in the following sections.

II. RESULTS

For conversion of these slopes, or intensities, into absolute cross sections the following equation was used: $S = \sigma V n (I_Q / e) C_Q k$, where S is the signal detection rate, n is the radical number density, σ is the CH_3 radical ionization cross section, I_Q is the ionization gun current (i.e., fixed at 100 μA), e is the electronic charge, V is the radical-electron beam collision volume (assumed equal to the ionization gauge geometrical volume), C_Q is the drift function for CH_3 radicals moving from the ionization region to the detector, and k is the detection rate for the channeltron and other signal detection electronics. The data used for σ for CH_3 are those from Janev *et al.* [7]. If C_a is the drift function for CH_3 radials between the collision and ionization regions, then $n = \sigma' V' n' (I_0 / e) C_a$, where I_0 is the primary gun current, n' is the collision region CH_4 gas density, V' is the collision volume in the fragmentation region, and σ' the required cross section. Except for C_Q, C_a, k, and V', all the parameters are measurable directly during the experiments.

Using the same experimental conditions mentioned above for the neutral radical measurements, the ionization gun and ion repulsion lens voltages were turned off. CH_3 ions produced from the fragmentation of CH_4 in the collision region were detected using the QMS and the signals were normalized to the literature ionization cross section values at each energy. The normalization factor at each energy contains all the needed information on the transmission and detection coefficients C_Q, C_a, and k. Once again the ionization cross section data from Janev *et al.* [7] were used here. It is important to note that the Janev *et al.* data used here are not theoretical results but recommended values derived from a wide range of consistent experimental results. In addition, our experience shows that it is of ultimate importance that any calibration for coefficients such as the above be done using the exact ionic species, and mass numbers, because the setting of a QMS can have a huge bearing on these coefficients even for neighboring mass numbers. Thus the calibration using N from N_2 for both CH_3 and CH_2 by Nakano *et al.* [10] might have affected their results. The fragmentation region collision volume V' was determined in separate experiments by measuring the elastically scattered electrons and normalizing the intensities to the known differential cross sections for CH_4 for each energy. Though these cross sections are measured at the differential angle of 90°, we assume isotropic production of these radicals for this symmetrical molecule, and thus multiply by the factor of 4π for the integral cross sections.

The errors shown in the data in Figs. 1 and 2 were estimated to be up to 20%. This value is made up of contributions from the ~15% errors quoted for the Janev *et al.* data used for the above normalization process, with the remainder coming from the combined errors due to the variation in the gas pressure, electron gun currents and the least-squares fitting.

Figure 1 shows the present absolute cross sections for the CH_3 neutral radical formation, together with the CH_4 photoabsorption and photon impact neutral dissociation cross sections of Kameta *et al.* [6]. Also included are the similar photoabsorption cross sections of Au *et al.* [21] since they extend down to the photoexcitation threshold of 8.5 eV. Figure 2 shows the neutral CH_3 formation cross sections in comparison with the previous results by Nakano *et al.* [10] and Motlagh *et al.* [11].

III. DISCUSSION

Threshold behavior. From our lowest energy results (Fig. 1) we estimate the threshold for the CH_3 production from CH_4 to be 7.5 ± 0.3 eV. This result agrees well with the earlier result of 7.5 eV from the two trapped-electron experi-

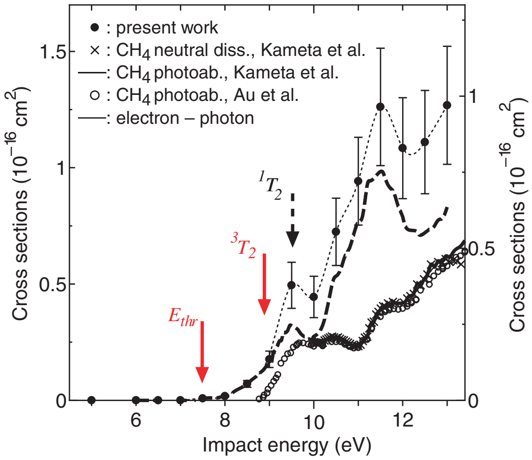

FIG. 1. (Color online) Present absolute cross sections for CH_3 radical production. Also included are the photon impact results from literature. The arrows show the threshold energy E_{thr} and the $^3T_2$ and $^1T_2$ state peaks. The dashed curve is the difference between the current neutral CH_3 and the photon impact total neutral dissociation cross sections.

ments [22,23], while differing from the high-energy electron impact and optical spectra results where the threshold has been consistently observed to be at 8.5 eV (e.g., Refs. [23,24]). The difference between the electron and photon impact excitation spectra below 10 eV has been associated with the optically forbidden $^3T_2$ state [23]. In Fig. 1, the broken line shows the "current CH_3 values – Kameta *et al.* photon impact total neutral dissociation values," i.e., the significance of optically forbidden transitions in this energy range is obvious. Spectral decomposition of this broken line shows that the observed change of slope at ~8.8 eV can be ascribed to (i) the CH_3 (or $^3T_2$state) intensities below 10 eV having a gaussian distribution with a peak at ~8.8 eV and (ii) the rapidly rising $^1T_2$ (and other optically forbidden) states with a threshold at ~8.52 eV [13,20]. The $^1T_2$ state is observed to peak at ~9.6 eV. This is in agreement with previous results which locate this peak at about 9.7 eV, together with its Jahn-Teller distortion pair peak at 10.5 eV (see Refs. [13,20,25,26]). It is clear that below the 8.5 eV optical excitation threshold, CH_3 neutral radical production is only accessible via electron impact and that it should be nonemissive.

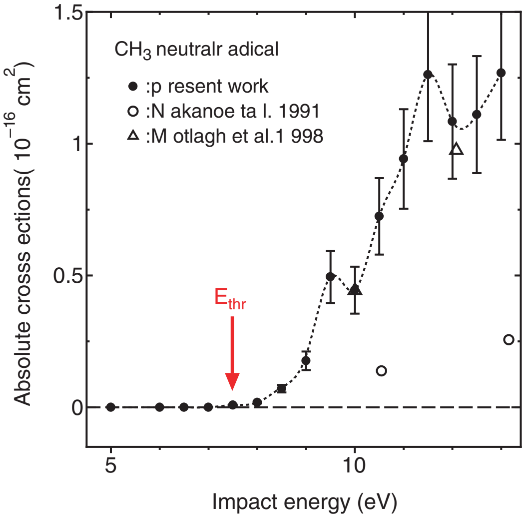

FIG. 2. (Color online) Quantitative comparison of the current CH_3 results with previous experimental results. Note that the 10 eV value of Motlagh *et al.* falls on top of our 10 eV value.

Indeed, photoabsorption results thus far have consistently observed the above Jahn-Teller pair at these energies (e.g., Refs. [6,21]), in agreement with the high-energy electron energy loss spectra (e.g., Refs. [23,26]). It is worth noting that although the Kameta *et al.* photon impact total neutral dissociation data are only measured down to 10 eV (see Fig. 2), the 10.5 eV $^1T_2$ component is clearly visible. In addition, the cross sections in this region are equal to the photoabsorption cross sections. Thus, since it has long been established that all the excited states of CH_4 are dissociative [20], it follows that all photoabsorption transitions lead to fragmentation via neutral radicals in this region.

Qualitative agreement is clear between the positions of the ~9.6 and ~11.5 eV peaks in the current data with those in the photoabsorption, and also photon impact neutral dissociation, cross sections shown in Fig. 1. This suggests that the same transitions are involved for both electron and photon impact, despite the magnitude differences. The ~11.5 eV peak has been assigned to the lowest 4*s* Rydberg state [21,26]. Based on these similarities between electron and photon impact, we infer the above conclusion that, at these energies below the CH_4 ionization threshold, all excited states of CH_4 molecules result in decay into neutral fragments, to be true also for electron impact.

Absolute values. As shown in Fig. 2, the current results for CH_3 agree both qualitatively and quantitatively with the Motlagh *et al.* data, but disagree with the Nakano *et al.* results. Both groups, however, only had two data points in the current energy region, and thus could not resolve the finer structures observed in the current results. We also note that the Nakano *et al.* results have magnitudes approximately half of those of the photoabsorption data shown in Fig. 1. The agreement with the Motlagh *et al.* results gives invaluable information about the dissociation dynamics of CH_4 below 12.5 eV. This is because Motlagh *et al.* assumed the cross sections for production of neutral CH_2, CH, C, and H radicals to be negligible in the absolute value conversion process for their CH_3 results. Since we do not make any such assumption in our data analysis, this agreement thus implies that even the next significant decay channel, i.e., CH_2 [5], is, within experimental errors, extremely marginal or nonexistent in this energy range. This result, however, contradicts the results of Nakano *et al.*, who reported CH_2 cross sections which are comparable to CH_3 below 15 eV, and earlier theoretical (e.g., Refs. [13,14]) and photodissociation experiments [15] that attributed the lowest-lying excited state as dissociating primarily into $CH_2$and H_2. Furthermore, this leads us to infer that the CH_3 decay channel almost solely produces the cross sections for all excited states of CH_4 in this region below 12.5 eV. Therefore, we conclude that we observe the Jahn-Teller component at 9.6 eV and the 4*s* Rydberg state at 11.5 eV, in agreement with the abovementioned earlier observations and assignments. However, we do not clearly observe the 10.5 eV peak in our data, except for a rather washed out shoulder.

IV. CONCLUSIONS

In conclusion, a method has been used to study the threshold behavior of the lowest-lying excited states of CH_4 molecules. Cross sections for the neutral CH_3 radicals have been studied from threshold up to 13 eV. The threshold energy for the lowest-lying $^3T_2$ state has been observed to be 7.5 ± 0.3 eV and attributed to CH_3 neutral radical formation, in disagreement with earlier results that attributed it to neutral CH_2 radical formation. The peaks for the $^3T_2$ and $^1T_2$ states have been observed at ~ 8.8 and ~ 9.6 eV, respectively. In the future, experiments will be done on CH_3 for the energy range between 13 and 100 eV, where the current two literature experimental results also significantly differ with each other. Neutral CH_2 radical cross sections will also be studied.

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