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To cite this article: Casten Makochekanwa et al 2007 J. Phys.: Conf. Ser. 86 012004

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Electron-Impact Induced Neutral Radical Fragmentation of CH₄

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Abstract. A new apparatus combining the crossed-beam method and the threshold-ionization technique has been developed to measure absolute cross sections for electron impact dissociation of CH₄ into neutral fragments. A Continuum Multiple Scattering code has also been developed and used to study the neutral radical decay pathways in these molecules. Details of the two methods and results obtained so far are presented in this paper.

1. Introduction

Electron impact excitation, fragmentation and ionization of methane (CH₄) are processes that have invited a lot of research interest owing to their various industrial applications. In particular, fragmentation becomes the most important channel. This is because electron impact, unlike photon collisions limited by dipole interaction rules, can excite any dissociative state of a molecule and reduce it to fragments; a key mechanism by which radicals and molecular ions are produced in the many fields of industrial applications, including aspects of the atmosphere and space science [1-3].

The fragmentation of a molecule, e.g. XY, (CH₄ inclusive) by electron impact can proceed in any of the following four pathways:

(1) \[ e + XY \rightarrow (XY) \rightarrow X^* + Y + 2e, \quad \text{dissociative ionisation} \]
(2) \[ \rightarrow X + Y, \quad \text{negative ion formation} \]
(3) \[ \rightarrow X + Y + e, \quad \text{non-radiative neutral fragmentation} \]
(4) \[ \downarrow \rightarrow X + hv \quad \text{radiative fragmentation} \]

In general, and mostly for experiments, studies of processes (i) and (ii) are more abundant in literature than those of (iii) and (iv). The reason for this is because of the difficulty associated with the detection of these uncharged fragments, compared to their ionic counterparts. However, a few experimental and theoretical works have been carried out to study the electron impact fragmentation of CH₄ into the various neutral and ionic fragments; whose abundances have been found to be in decreasing order from CH₃, CH₂, CH, C and H for both the neutral and ionic decay pathways (see Ref. [4], and references therein). On the contrary, a rather intensive literature database exists for photon impact with CH₄ molecules, i.e. mainly photoabsorption and photoionization and some derived photon impact neutral dissociation cross sections for CH₄ fragments. See Kameta et al. for a comprehensive
review on the photon impact [5], and Janev et al. [6] and Shirai et al. [7] for reviews on electron impact studies.

There are only two measurements available in literature which measured cross sections for the dominant neutral fragmentation decay channels of CH\textsubscript{4}, i.e. CH\textsubscript{3} and CH\textsubscript{2}. These were done by Nakano et al. [8]; using the threshold ionization method in conjunction with a collision cell and a quadrupole mass spectrometer (QMS), and Motlagh and Moore [9]; using the so-called chemical getter technique. However as shown in Fig. 1, the results by these two groups differ significantly in both energy dependence and magnitude over the energy range of overlap, which worrying since this is observed for the most dominant channel CH\textsubscript{3}. Besides, both measurements were only down to 10 eV, and thus there was need to for (i) an independent approach for accurate studies to determine the production rates for this channel and (ii) the threshold behavior of this species, i.e. cross sections for energies below 10 eV. In related experiments, Winters [10] measured total electron impact dissociation cross sections for CH\textsubscript{4}.

![Absolute cross sections (10^{-16} cm^2) vs Impact energy (eV)](image)

**Fig. 1 Literature data for CH\textsubscript{3} neutral radical formation cross sections from CH\textsubscript{4} by electron impact.**

In this project a new experimental method combining the crossed-beam method and the threshold ionisation technique has been developed for studying neutral fragmentation of molecules by electron impact. CH\textsubscript{4} is used as the test-bed, and CH\textsubscript{3} neutral radical formation cross sections are studied both to solve the above-mentioned controversy due to the two literature results, and also to establish the threshold behaviour of this species. The use of the crossed-beam method brings with it the advantage of reducing the surface area for which the (i) produced CH\textsubscript{3} can stick before detection and (ii) the parent CH\textsubscript{4} molecules can stick to resulting in increased noise signals, i.e. a problem which Nakano et
2. Experimental method

The apparatus used in these experiments consists of a combination of the crossed-beam method [11] and the threshold ionization technique [12]. It consists of a primary electron gun, a collision region with an effusive gas nozzle, an ionization region and the ionizing electron gun, a quadrupole mass spectrometer (QMS) and the detection and counting electronics. In these experiments, the primary beam current varied with impact energy between 0.8 and 3 µA over the energy range 5 to 15 eV, and the energy resolution was about 0.6 eV at full-width-half-maximum (FWHM). The gas pressure in the collision region was $2 \times 10^{-4}$ Pa during the measurements while the base pressures were as good as $2.5 \times 10^{-5}$ Pa. The energy calibration of the primary beam was done using the well-known 2.4 eV electron-N$_2$ $^2\pi_g$ resonance [13]. A schematic diagram of the apparatus is shown in Fig. 2.

![Schematic diagram of the apparatus](image)

**Fig. 2.** Schematic diagram of the new method combining the crossed-beam method and the threshold ionization technique for neutral radical detection.

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$_4$ from the lens and chamber surfaces that would inevitably come in if the QMS was set in line with the primary beam. Only those ionic and neutral fragments produced with initial velocities in the directions covered by the 13° view-cone angle can drift towards the QMS via a 2 mm aperture separating the collision region from the ionization region. Just behind this aperture however, ion deflector lens are inserted so that only neutral fragments are allowed into the ionization chamber. The neutrals are then ionized using the ionization electron gun, in the ionization region, for detection by the QMS. Based on the threshold ionization technique and the known threshold energies for CH$_4$ molecules and CH$_3$ radicals (see tables in Ref. [14]), the ionization gun energy was set at 10.5 eV for CH$_3$ detection, while its current was fixed at 100 µA. Background noise was subtracted after a comparison between spectra obtained at four different experimental conditions; (i) with both the primary and ionization guns turned ON, (ii) with the primary gun ON, but the ionization gun OFF, (iii) with the primary gun OFF, but the ionization gun ON, and (iv) both guns OFF, i.e. with the true signal given by the subtraction of signals (ii), (iii) and (iv) from (i).
The detected radical signal, \( S \), is directly proportional to the primary beam current, gas pressure in collision region, the neutral dissociation cross section (i.e. for \( \text{CH}_3 \) production from \( \text{CH}_4 \)), the impact energy and integration time for pulse counting. Thus, we measure the radical signal (= signal (i) - (ii) - (iii) - (iv)) accumulatively while alternating at 60 seconds intervals between the primary beam ON and OFF conditions. With integration of time the radical signal increases linearly, with the slope being equivalent to the fragmentation cross section. Typical results are shown in Fig. 3. In the analysis of the obtained raw data, straight lines are drawn through the rising time integrated signal curves using least-squares fits. Whereas measurements at impact energies 10 eV and above require about 150 sweeps (7.5 hours) and we already have enough statistics, more time is needed for measurements below 10 eV, i.e. so much that as impact energies decrease towards the threshold about 500 sweeps (25 hours) or more become necessary for better statistics. This makes 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.

For conversion of these slopes, or intensities, into absolute cross sections the following equation was used.

\[
S = \sigma V n(I_0/e)C_Qk; \quad (1)
\]

where \( S \) is the signal detection rate, \( n \) is the radical number density, \( \sigma \) is the \( \text{CH}_3 \) radical ionization cross section, \( I_0 \) is the ionization gun current (i.e. fixed at 100 \( \mu \)A), \( e \) 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 \( \text{CH}_3 \) 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 \( \sigma \) for \( \text{CH}_3 \) are those from Janev et al. [6].

If \( C_a \) is the drift function for \( \text{CH}_3 \) radicals between the collision and ionization regions, then

\[
n = \sigma' V'n'(I_o/e)C_Qk; \quad (2)
\]

where \( I_o \) is the primary gun current, \( n' \) is the collision region \( \text{CH}_4 \) gas density, \( V' \) is the collision volume in the fragmentation region and \( \sigma' \) the required cross section. Except for \( C_Q, C_a, k \) and \( V' \), all the other 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. Ions produced from the fragmentation of \( \text{CH}_4 \) in the collision region were detected using the QMS. These ionization signals must be equal to the literature ionization cross sections for \( \text{CH}_4 \) fragmentation into the \( \text{CH}_3 \) ions. Thus by normalizing the so-measured signals to these literature cross sections one determines the normalization factor at each energy.

This normalization factor 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. [6] were used here. The fragmentation region collision volume \( V' \) was determined in separate experiments by measuring the elastically scattered electrons, using a second Faraday cup (not shown in Fig. 2) positioned diametrically opposite to the QMS entrance, and normalizing the intensities to the known differential cross sections for \( \text{CH}_4 \) for each energy. This \( V' \) did not show any noticeable change with energy. Though these cross sections are measured at the differential angle of 90°, because of the geometrical symmetry of this molecule we assume isotropic production of these radicals and thus multiply by the factor of \( 4\pi \) for the integral cross sections.
Fig. 3. Typical CH$_3$ neutral radical formation signal intensity integration over time. Here a sweep is 180 seconds, i.e. consisting of 60 seconds of signal + background and 60 seconds of background measurements, and 60 seconds of waiting time for the ionization gun current to rise and stabilize before the next signal + background measurement.

3. Results and discussion

Fig. 4 shows the results obtained using the current method in comparison with part of the two literature results shown in Fig. 2. Our results presented here were earlier published and thus reproduced here just to put into perspective the presentation of the experimental method, which could not be published earlier [15]. The errors shown in the data in Figs. 4 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.

Though our method is completely different from that of Motlagh and Moore, we clearly observe similarity in magnitude of the cross sections, with little though to talk about with respect to similarity in energy dependence since they only have two data points in this energy region of overlap. However, our data point almost falls on top of their 10.5 eV data, and their 12 eV data point is within our experimental error at this energy. On the other hand, our result is about 5.7 times and 4.8 times greater than the Nakano et al. data at 12 eV and 13 eV, respectively. For the first time by this method, the threshold for CH$_3$ neutral radical formation from CH$_4$ by electron impact was established at 7.5 ± 0.3 eV. Because our measurements are at intervals of 0.5 eV, peaks are observed at 9.6 and 11.5 eV, and a shoulder at 10.5 eV, which could not be observed in these previous two results. As discussed in our earlier publication [15], the 9.6 eV peak and the 10.5 eV shoulder are have been observed in a number
of photoabsorption studies and assigned to the $^1T_2$ state (9.6 eV) and its Jahn-Teller distortion pair peak, respectively. The 11.5 eV peak has been assigned to the lowest 4s Rydberg state. See Refs. [14-18] for full discussion of these features and their assignments. However, the current result makes it clear that below the 8.5 eV optical excitation threshold [16-18], CH$_3$ neutral radical production is only accessible via electron impact and that it should be nonemissive.

![Graph](image)

Fig. 4 Electron-CH$_4$ impact induced CH$_3$ neutral radical formation cross sections; the result by this method [15] compared to those by Nakano et al. [8] and Motlagh and Moore [9].

4. Conclusion
In this paper we report on a new method for measurement of electron impact induced neutral radical formation from molecules. CH$_4$ has been studied as a rather well known molecule for easy instrument characterization and calibration. Absolute cross sections have been measured for the most abundant neutral radical, CH$_3$, formation over the energy range 5 to 13 eV. Agreement has been observed between the results by this group and that one by Motlagh and Moore [9], but significant difference, in both magnitude and energy dependence with the result of Nakano et al. [8].

Acknowledgements
This work was supported by the Grant-in-Aid for Science Research (C) from the Ministry of Education, Science, Sports, Culture and Technology, National institute for Fusion Science, the Japan Atomic Energy Agency (JAEA) and the Japan Society for the Promotion of Science. This work was also done under the International Atomic Energy Agency (IAEA) project for C.M., M.H., M.K. and H.T.

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