LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2001 issue.

NOTES

Production of positive ion pairs by electron-impact ionization of CH_4

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Accurate cross sections for electron-impact ionization of CH_4 are of importance for understanding the physics and chemistry of planetary atmospheres and for plasma processing. Consequently there have been quite a few measurements of the methane partial and total cross sections, including one from this laboratory.[1] However, there appear to be no prior observations of positive ion pair formation in methane. This note reports cross sections for formation of (CH_2^+, H^+), (CH^+, H^+), and (C^+, H^+) ion pairs for electron energies from threshold to 1000 eV via the following processes:

$$e + CH_4 \rightarrow CH_2^+ + H^+ + \cdots, \quad (1)$$

$$e + CH_4 \rightarrow CH^+ + H^+ + \cdots, \quad (2)$$

$$e + CH_4 \rightarrow C^+ + H^+ + \cdots. \quad (3)$$

The basic experimental technique employed, which has been thoroughly described in the literature,[2] involves passing a pulsed electron beam through a static gas target, then extracting, mass analyzing, and counting the ions formed along a known path length. It embodies the simplicity of the parallel plate arrangement used by Rapp and Englander-Golden[3] coupled with an extremely short path length mass spectrometer together with a detector with which it is possible to demonstrate complete collection of all fragment ions. The possibility of using a slight variation on this basic technique to determine cross sections for ion pair production was recently demonstrated by Sieglaff *et al.*[4] It was shown that cross sections for production of positive ion pairs may be determined by taking advantage of the fact that the counting electronics used can only process one event at a time and therefore when two ions are created in the same collision the first to arrive at the detector will, if detected, preclude detection of any subsequent ions and thus lead to underestimation of their cross sections. In order to measure the true cross section for production of C^+ ions, for example, a gate must be applied to the timing signal to suppress detection of the lighter H^+ ions which arrive at the detector earlier than the C^+ ions. If no gate is applied to the timing signal the apparent cross section for the heavier ion will be reduced slightly due to the presence of pair production events. Thus, if a light ion Y and a heavier ion X, are formed in the same collision and the timing electronics is limited to recording only the first ion detected, then the apparent cross section for production of the heavier ion X, $\sigma_{app}(X)$, is given by

$$\sigma_{app}(X) = \sigma(X) - \epsilon\sigma(X,Y), \quad (4)$$

where $\sigma(X)$ is the true cross section for production of X ions, $\sigma(X,Y)$ is the cross section for production of both an X and a Y ion in the same event, and ϵ is the detection efficiency of

TABLE I. Absolute cross sections for the production of (CH_2^+, H^+), (CH^+, H^+), and (C^+, H^+) ion pairs by electron-impact ionization of CH_4. The uncertainties in $\sigma(CH_2^+, H^+)$, $\sigma(CH^+, H^+)$, and $\sigma(C^+, H^+)$ are $\pm 15\%$, $\pm 15\%$, and $\pm 20\%$, respectively, unless otherwise indicated.

Energy (eV)	$\sigma(CH_2^+, H^+)$ $(10^{-18}\,cm^2)$	$\sigma(CH^+, H^+)$ $(10^{-18}\,cm^2)$	$\sigma(C^+, H^+)$ $(10^{-19}\,cm^2)$
40		0.32±0.18	
45		0.45±0.20	
50		0.72±0.20	
60	0.63±0.33	0.97±0.20	3.49±1.29
70	1.15±0.31	1.31±0.23	4.30±1.45
80	1.34±0.28	1.48	5.95
90	1.95	1.42	6.12
100	2.27	1.53	6.27
110	2.61	1.41	7.23
125	2.85	1.55	6.82
150	2.43	1.50	7.06
175	2.37	1.36	6.24
200	2.06	1.27	5.45
250	1.71	1.05	4.28
300	1.42	0.93	3.91
400	1.12	0.76	2.49
500	0.94	0.53	2.15
600	0.69	0.45	1.74
700	0.52±0.10	0.39	1.35
800	0.44±0.09	0.30±0.05	1.04±0.25
900	0.36±0.08	0.22±0.05	0.88±0.24
1000	0.21±0.07	0.16±0.04	0.63±0.24

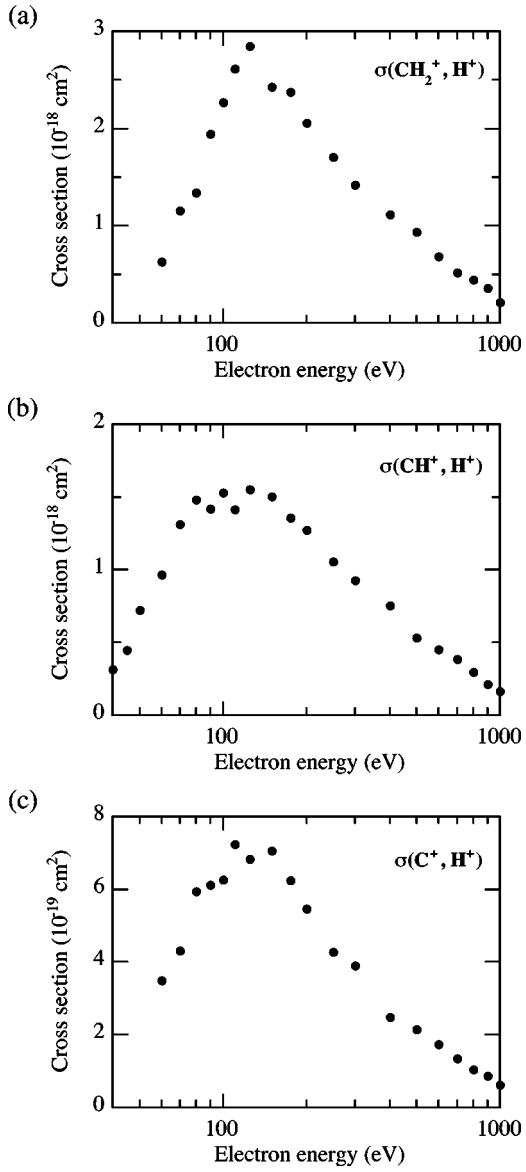

FIG. 1. Cross sections for the production of (a) (CH_2^+, H^+) ion pairs; (b) (CH^+, H^+) ion pairs; and (c) (C^+, H^+) ion pairs.

the system. By measuring both the true and the apparent cross sections for production of C^+ ions, for instance, and then applying Eq. (4) it is possible to determine the cross sections for production of (C^+, H^+) ion pairs.[5]

The cross sections for the various ion pair production channels are given in Table I and plotted in Fig. 1. The quoted uncertainties are primarily due to counting statistics and the mean energy of the electron beam was established to within ± 0.5 eV. The magnitudes of the (CH_n^+, H^+) pair production cross sections are roughly 10% of those for production of the CH_n^+ ions themselves.[1,6] Although no other experimental or theoretical data exist with which to directly compare these measurements, they are roughly consistent with previous observations of similar processes in CF_4 (Refs. 4 and 7) and SF_6.[8] It is worth noting that the experimental technique used here is not optimally suited to the measurement of pair production cross sections. One consequence of this is that the uncertainties in these measurements are relatively large; another is that pair production processes involving CH_3^+ ions are below the sensitivity of the apparatus. It is hoped that the present data will prompt further work using more sophisticated approaches to address these issues.

This study demonstrates that when single particle counting techniques are used to determine electron-impact ionization cross sections the occurrence of ion pair production processes may materially affect the results. A case in point is our previous measurement of the partial cross sections for electron-impact ionization of methane.[1] At that time the possibility that ion pair production could play a significant role in the experiment was not fully appreciated, and consequently some of the cross sections reported there were slightly lower than the true values. Fortunately, the magnitude of the effect in that particular case, less than 5%, was smaller than the uncertainties ascribed to the data.

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