Electron impact ionization of CD_x ($x = 1$–4)

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Abstract. We report measurements of absolute cross sections for the electron-impact ionization and dissociative ionization of the deuterated methane molecule CD_4 and the CD_x ($x = 1$–3) free radicals from threshold to 200 eV using the fast-neutral beam technique. We used the deuterated rather than the protonated target species to facilitate a better separation of the various product ions from a given parent molecule in our apparatus. Good agreement was found between our CD_4 results and the most recent measurements in CH_4. Our results for CD_3 and CD_2 agree well with earlier measurements carried out under different experimental conditions. The present results for the CD free radical are the first ionization cross section measurements for this target. A common feature of all four targets studied in this work was a dominant parent ionization cross section with essentially the same absolute value of 1.6–1.7×10^{-16} cm^2 at 70 eV. A comparison of the experimentally determined total single ionization cross sections with calculated cross sections using a modified additivity rule showed very good agreement for all four targets.

1. Introduction

Methane, CH_4, is an important constituent of the terrestrial atmosphere and of the atmospheres of the planets Jupiter, Saturn, Uranus, Neptune and Pluto and of some of their satellites, in particular Titan and Triton. Methane has also emerged as a frequently employed constituent of feedgas mixtures in technological processing plasmas used in deposition applications (diamond films, diamond-like carbon films, amorphous carbon films). In both environments, dissociation of CH_4, by collisional interaction and/or photodissociation, results in the formation of the free radicals CH_3, CH_2 and CH. Cross sections for the production of the various parent and fagment ions by electron collisional ionization and dissociative ionization of CH_x ($x = 1$–4) are important for the understanding and modelling of the chemistry in both planetary atmospheres and discharge plasmas. Most experimental studies to date have focused on the measurement of total and partial ionization cross sections for the stable CH_4 molecule (Tate and Smith 1932, Rapp and Englander-Golden 1965, Schramm *et al* 1966, Adamcyk *et al* 1966, Chatham *et al* 1984, Orient and Srivastava 1987). The only measured ionization cross sections for the free radicals are those of Baiocchi *et al* (1984) for the deuterated species CD_3 and CD_2 using the fast-beam technique, which were the first absolute measurements of electron-impact ionization cross sections for free radicals.

We present absolute partial cross sections for the electron-impact ionization and dissociative ionization of CD_x ($x = 1$–4) from the threshold to 200 eV. The cross sections for all four targets were measured in the same apparatus using the fast-beam technique. The deuterated rather than the protonated targets were used in the present experiments (as was done in the earlier work of Baiocchi *et al* (1984)) to facilitate a better separation of the

various product ions from a given parent molecule (see discussion later). Ionization cross sections are insensitive to isotope effects (Märk and Egger 1977, Märk *et al* 1977, Basner *et al* 1995). We can, therefore, compare our results for CD_4 to the most recent measurements of the partial ionization cross sections for CH_4 (Adamcyk *et al* 1966, Chatham *et al* 1984, Orient and Srivastava 1987). The present CD_3 and CD_2 results are compared to earlier measurements by Baiocchi *et al* (1984) carried out under different experimental conditions. The present CD results are the first ionization cross sections reported for this free radical. For each target, the measured partial ionization cross sections were combined to yield the total single ionization cross section of that target. A comparison with calculated total single ionization cross sections based on a modified additivity rule (Deutsch *et al* 1994) showed good agreement for all four targets.

2. Experimental details

The fast-beam apparatus and the experimental procedure employed to obtain absolute partial ionization cross sections have been described in detail in previous publications (Wetzel *et al* 1987, Freund *et al* 1990, Tarnovsky and Becker 1992, 1993). Briefly, a DC discharge operated at a positive bias of typically 2–3 kV through CD_4 served as a primary ion source. The primary ions after mass selection in a Wien filter were neutralized by near-resonant charge transfer in a cell filled with Xe. Xe with an ionization energy of 12.14 eV (Lias *et al* 1988) was found to be an appropriate charge neutralization target for all four CD_x ($x = 1–4$) targets whose ionization energies range from 9.85 eV (CD_3) to 12.51 eV (CD_4). Similar to what was observed in previous studies (Tarnovsky and Becker 1993, Tarnovsky *et al* 1993, 1994, Basner *et al* 1994), efficient charge transfer was not critically dependent on an exact match of the ionization energies of the charge-transfer partners. The residual ions were removed from the beam by electrostatic deflection and most target species in Rydberg states were quenched in a region of high electric field. The neutral beam was subsequently crossed at right angles by a well characterized electron beam (5–200 eV beam energy, 0.5 eV FWHM energy spread, 0.03–0.4 mA beam current). The product ions were focused in the entrance plane of an electrostatic hemispherical analyser which separates ions of different charge-to-mass ratios (i.e. singly from multiply charged ions and parent ions from fragment ions). The ions leaving the analyser were detected by a channel electron multiplier (CEM). As discussed previously (Freund *et al* 1990, Tarnovsky and Becker 1992, 1993), the well established Kr or Ar absolute ionization cross sections served as a convenient normalization standard to put the relative cross section functions on an absolute scale. Even though the apparatus is capable of determining absolute ionization cross sections without any normalization and without fitting the measured data to theory (Wetzel *et al* 1987), experience has proved that it is advantageous to use the Kr or Ar benchmark cross sections to calibrate the pyroelectric crystal (Freund *et al* 1990). The calibrated detector, in turn, is then used to determine the flux of the neutral target beam in absolute terms. This procedure avoids the frequent and prolonged exposure of the sensitive pyroelectric crystal to fairly intense ion beams and thus enhances significantly the stability and useful lifetime of the crystal.

We carried out a series of experimental studies supported by ion trajectory modelling calculations (for details, see Tarnovsky *et al* 1993) to establish for each target that all molecular fragment ions with an excess kinetic energy of less than 2–2.5 eV per fragment ion are collected and detected with 100% efficiency. Furthermore, careful threshold studies revealed little evidence of the presence of excited target species (vibrationally excited species, metastables, and species in high-lying Rydberg states) in the incident neutral beams for CD_3, CD_2 and CD. On the other hand, we observed a shift of almost 2 eV
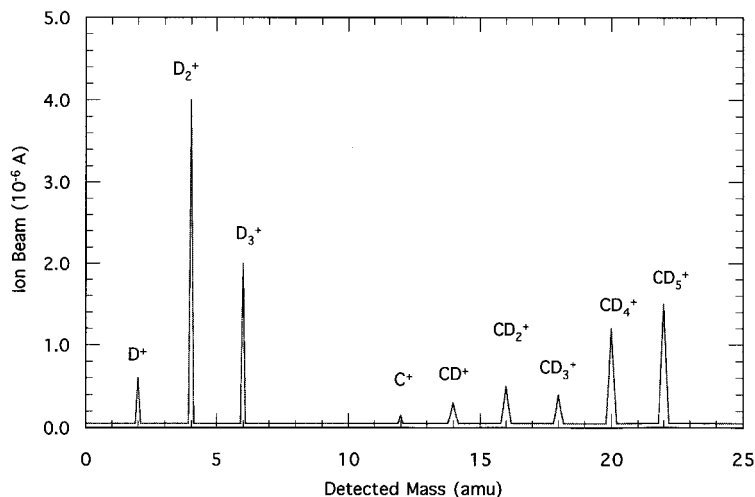
Figure 1. Production ion mass spectrum after the Wien filter obtained for primary ions extracted from the Colutron discharge operated through CD_4 at a beam energy of 2 keV. The absolute ion current in 10^{-6} A is plotted as a function of the mass number in amu.

in the appearance energy of CD_4^+ ions to lower energies compared to the ionization energy of CD_4 in its ground vibrational state (Lias *et al* 1988). This is a result of the well known fact that the charge neutralization from the ground state of the CD_4^+ ion produces a significant amount of vibrationally excited neutral CD_4 molecules (Hariharan and Pople 1974, Baiocchi *et al* 1984). The influence of the presence of vibrationally excited CD_4 molecules in the target beam on the measured CD_4 ionization cross sections will be discussed later. The experimental checks described above are necessary for any target to be studied using the fast-beam technique in order to ensure that the measured cross sections are free from systematic uncertainties to the maximum extent possible (Tarnovsky and Becker 1992, 1993, Tarnovsky *et al* 1993). Additional experimental considerations pertain specifically to hydrogen-containing targets studied in our fast-beam apparatus. This is due to the fact there is a mass difference of only 1 amu (2 amu for the deuterated target species) between the various primary ions extracted from the discharge source and between the various product ions produced from a given parent in the interaction region.

The resolution of the Wien filter was sufficient to separate the various primary ions (CD_4^+, CD_3^+, CD_2^+, CD^+, and C^+) extracted from the ion source. Figure 1 shows the ion beam mass spectrum after the Wien filter obtained for primary ions extracted from the discharge source operated with CD_4 as the feedgas at a beam energy of 2 keV. The various primary ion peaks are well separated. Note the appreciable intensity of the CD_5^+ and D_3^+ peaks which correspond to species formed in the discharge by plasma chemical processes. Both ions are well known as abundant constituents in CD_4-containing discharge plasmas under a variety of operating conditions (see e.g. Sugai *et al* 1990). Also note that we observed only a weak signal corresponding to primary C^+ ions under most discharge operating conditions.

The electrostatic hemispherical analyser had a sufficient resolving power to separate the parent and the various fragment ions from a given neutral radical, e.g. CD_3^+, CD_2^+, CD^+, and C^+ ions from CD_3 were separated by the analyser. Fragment ions resulting from the dissociative ionization of the parent neutral are often produced with a certain amount of

excess kinetic energy. This results in slightly divergent fragment ion beams emerging from the interaction region compared to the spatially well collimated parent ion beam which, in turn, causes the fragment ions to spread out spatially in the hemispherical analyser. This makes the separation of the various product ion signals more difficult. In an effort to assess the capability of the hemispherical analyser to separate the various product ions for a given target, a fixed beam energy and a fixed amount of excess kinetic energy, we employed a variant of the experimental technique used by Hayes *et al* (1989a, b) and Shul *et al* (1989) in their studies of the ionization and dissociative ionization of the SiF_x ($x = 1$–3) free radicals. The procedure involves the use of a narrow moveable slit in front of the CEM entrance in order to separate the spatially well collimated parent ion signal from the spread-out fragment ion signal. The fragment ions signals were obtained by sweeping the spatially spread-out fragment ion signal across the CEM entrance cone and integrating the signal for a given fragment ion (after the narrow slit was removed). Since the dissociative ionization of CD_3, CD_2, and CD was dominated by a single channel (see below), the data acquisition was not complicated by the presence of several overlapping fragment ion signals from different fragment ions. In the case of CD_4, the partially overlapping CD_3^+, CD_2^+, and CD^+ fragment ion signals were deconvoluted with the help of extensive ion trajectory modelling calculations (Tarnovsky *et al* 1993).

3. Results and discussion

In a first step, we measured the absolute partial ionization cross sections for the formation of the parent CD_4^+ ion and of the most intense fragment ions, CD_3^+ and CD_2^+ from the CD_4. In a second step, we measured absolute partial ionization and dissociative ionization cross sections for the free radicals CD_3, CD_2, and CD. All measurements followed the previously described experimental procedure (Freund *et al* 1990, Tarnovsky and Becker 1993, Tarnovsky *et al* 1993). For a given target, relative ionization cross section functions were measured for all product ions from threshold to 200 eV. In all cases studied here, the
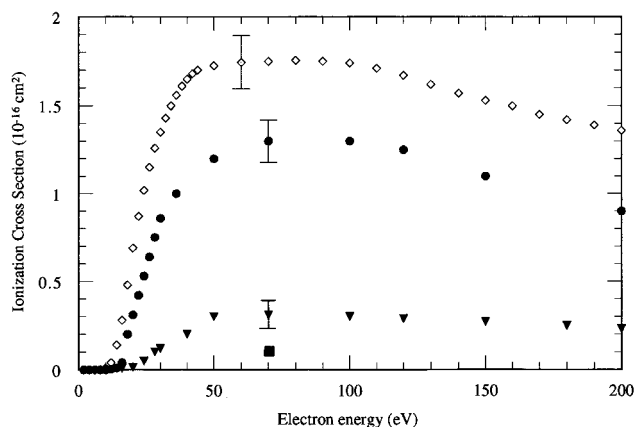

Figure 2. Absolute cross sections for the formation of the CD_4^+ parent ions ($\Diamond$) and the CD_3^+ ($\bullet$) and CD_2^+ ($\blacktriangledown$) fragment ions from CD_4 as a function of electron impact energy. The error bars indicate the total uncertainty (statistical + systematic) of the measured cross sections. The single data point at 70 eV ($\blacksquare$) indicates the absolute value of the CD^+ fragment ionization cross section at this energy.

investigations were limited to singly charged ions, since cross sections for the formation of doubly charged ions were found to be at or below the detection sensitivity of our technique (peak cross sections of less than 0.05×10^{-16} cm^2). The parent ionization cross sections were put on an absolute scale by normalization to the well known Kr or Ar benchmark cross sections as discussed before. All dissociative ionization cross sections were subsequently normalized to the parent ionization cross section for a given target. In all cases, careful threshold studies were carried out to check for the presence of excited species in the incident neutral beam and to determine the appearance energies for the various product ions. This is particularly crucial for dissociative ionization processes, since the appearance energy when compared to thermochemical and spectroscopic data for the formation of a particular fragment ion provides information about the (minimum) excess kinetic energy with which the fragment ion is formed.

The absolute cross sections were determined with uncertainties of $\pm 15\%$ for the parent ionization cross sections and $\pm 18\%$ for the dissociative ionization cross sections. These error margins, which are similar to what we quoted previously for ionization cross sections measured for other molecules and free radicals in the same apparatus (Freund *et al* 1990, Tarnovsky and Becker 1993, Tarnovsky *et al* 1993), include statistical uncertainties and all known sources of systematic uncertainties.

3.1. Ionization cross sections for the CD$_4$ molecule

The results of our ionization cross section measurements for CD$_4$ are depicted in figure 2. We show the absolute parent CD$_4^+$ ionization cross section and the CD$_3^+$ and CD$_2^+$ fragment ionization cross sections from threshold to 200 eV. The measured CD$^+$ fragment ionization cross section is indicated by a single data point representing its absolute value of $0.10 \pm 0.02 \times 10^{-16}$ cm^2 at 70 eV. Its energy dependence is similar to that of the other cross section functions displayed in figure 2. Good agreement was found between our absolute partial ionization cross sections for CD$_4$ in terms of the absolute values and the cross section shapes for impact energies above 30 eV with the results of the most recent measurements for CH$_4$ (Adamcyk *et al* 1966, Chatham *et al* 1984, Orient and Srivastava 1987; see table 1 for absolute cross section values at 70 eV). Our CD$_4^+$/CD$_4$ parent ionization cross section has a value of $1.70 \pm 0.28 \times 10^{-16}$ cm^2 eV which lies within the range of the reported CH$_4^+$/CH$_4$ ionization cross sections of 1.65–1.82×10^{-16} cm^2 at this energy (Adamcyk *et al* 1966, Chatham *et al* 1984, Orient and Srivastava 1987). The energy dependences of the cross section functions in all four measurements are essentially the

Table 1. Comparison of the parent and dissociative ionization cross section for CD$_4$ measured in this work with recent measurements of parent and dissociative ionization cross sections for CH$_4$. All cross section values (in units of 10^{-16} cm^2) are given at an electron impact energy of 70 eV.

Target	CH$_4^+$/CH$_4$	CH$_3^+$/CH$_4$	CH$_2^+$/CH$_4$	CH$^+$/CH$_4$
CH$_4$[a]	1.65	1.42	0.22	0.11
CH$_4$[b]	1.75	1.31	0.22	0.10
CH$_4$[c]	1.82	1.81	0.26	0.11
CD$_4$ (this work)	1.70	1.38	0.35	0.10

[a] Adamcyk *et al* (1966).
[b] Chatham *et al* (1984).
[c] Orient and Srivastava (1987).

same above about 30 eV. Our CD_3^+/CD_4 dissociative ionization cross section with a value of $1.38 \pm 0.25 \times 10^{-16}$ cm^2 at 70 eV agrees well with the cross section values of Adamcyk *et al* (1966), 1.42×10^{-16} cm^2, and Chatham *et al* (1984), 1.31×10^{-16} cm^2, at this energy. All three measurements are lower than the 70 eV cross section value reportd by Orient and Srivastava (1987), 1.82×10^{-16} cm^2, but the four values are consistent with each other within their combined error margins. Our CD_2^+/CD_4 cross section has an absolute value at 70 eV of $0.35 \pm 0.07 \times 10^{-16}$ cm^2 which is somewhat larger than the CH_2^+/CH_4 values reported by the other three groups (0.22–0.26×10^{-16} cm^2). This discrepancy could be due to the fact that the open design of our apparatus enables a more complete collection of energetic fragment ions. For both fragment ions, CD_3^+ and CD_2^+, our measured cross section shapes are essentially identical to those reported in the CH_4 measurements above 30 eV. Our CD^+/CD_4 cross section with a 70 eV value of $0.10 \pm 0.02 \times 10^{-16}$ cm^2—indicated by a single data point in figure 2—is identical to the values reported by the other three groups for CH^+/CH_4.

Similar to what was observed by Baiocchi *et al* (1984), the appearance energy for CD_4^+ ions from CD_4 measured in this work was found to be shifted to lower energies by almost 2 eV compared to the well known ionization energy of the CD_4 molecule in its vibrational ground state (Lias *et al* 1988). This is a consequence of the fact that the charge neutralization of ground state CD_4^+ produces a significant fraction of vibrationally excited CD_4 molecules as the result of geometry differences between CD_4 and CD_4^+ at their potential minima (Hariharan and Pople 1974). The generally good agreement between the present absolute partial ionization cross sections for CD_4 measured with a fast beam of CD_4 molecules containing a significant fraction of vibrationally excited species and the well established ionization and dissociative ionization cross section of CH_4 resulting from experiments, in which no vibrationally excited target molecules were present (Adamcyk *et al* 1966, Chatham *et al* 1984, Orient and Srivastava 1987), indicates that vibrational excitation of the target has little effect on the measured ionization cross sections except for impact energies close to the ionization threshold, i.e. below about 30 eV in our case. This observation is supported by other recent experimental and theoretical studies which support the notion that vibrational excitation of the target molecule affects the ionization cross section primarily in the near-threshold region, but has little impact on the cross section shape at energies above about twice the ionization threshold in most cases (Cacciatore *et al* 1982, Celiberto and Rescigno 1993, Capitelli and Celiberto 1995, Kühn *et al* 1995).

We found little evidence of D^+ fragment ions from CD_4. Previous studies in CH_4 reported a cross section for H^+/CH_4 of about 0.1×10^{-16} cm^2 at 100 eV (Chatham *et al* 1984). Great care should be exercised when reporting H^+/CH_4, D^+/CD_4 or D^+/CD_x ($x = 1$–3) cross sections, since H^+/D^+ fragment ions from CH_4/CD_4 are formed with a wide distribution of kinetic energies which peaks at a value of several electronvolts per fragment and which extends to maximum kinetic energies of more than 10 eV per H^+ fragment (Appell and Kubach 1971, Furuya *et al* 1994). Ion trajectory modelling indicates that light D^+ fragments from CD_x ($x = 1$–4) are lost in our apparatus, if their excess kinetic energies are above about 1 eV per fragment (in the worst case of D^+/CD_4). Therefore, no quantitative data for D^+ formation from any of the CD_x target species are reported in this paper.

3.2. Ionization cross sections for the CD_x (x = 1–3) free radicals

Figure 3 shows the absolute cross sections for the formation of CD_3^+ and CD_2^+ ions from the CD_3 free radical from threshold to 200 eV. The peak cross sections for the formation

of CD$^+$ fragment ions from CD$_3$ was found to be less than 0.1×10^{-16} cm^2. Cross sections for the other singly charged fragment ions (D$^+$, C$^+$) and cross sections for multiply charged ions were even smaller. There is generally good agreement between the present data and the results of the earlier CD$_3^+$/CD$_3$ and CD$_2^+$/CD$_3$ measurements of Baiocchi *et al* (1984) carried out at a neutral beam energy of 1 keV. We find cross sections at 70 eV of $1.73 \pm 0.30 \times 10^{-16}$ cm^2 for CD$_3^+$ and $1.10 \pm 0.19 \times 10^{-16}$ cm^2 for CD$_2^+$. The good agreement between our data and the earlier measurements is even more apparent from the tabulated cross section values in table 2 which show excellent agremeent between the two independent measurements over the entire range of impact energies from threshold to 200 eV. The cross section tables (with particlar emphasis on the low energy regime) are presented for the convenience of practitioners who use these cross section data for modelling purposes or other applications (e.g. in the quantitative analysis of threshold ionization mass spectroscopic studies for plasma diagnostics purposes (Robertson *et al* 1983)). The measured appearance energies of the CD$_3^+$ parent ions and the CD$_2^+$ fragment ions is close to the minimum values expected based on spectroscopic and thermochemical considerations (Chase *et al* 1985, Lias *et al* 1988, Wagman *et al* 1982) which indicates that the CD$_2^+$ fragment ions are formed with little excess kinetic energy.
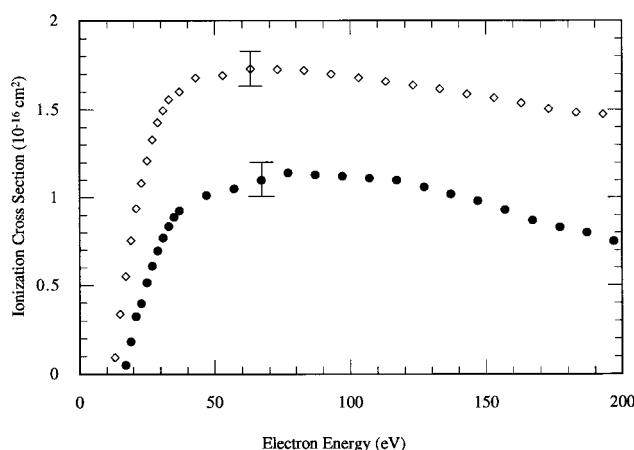

Figure 3. Absolute cross sections for the formation of the CD$_3^+$ parent ions ($\Diamond$) and the CD$_2^+$ ($\bullet$ fragment ions from CD$_3$ as a function of electron energy. The error bars indicated represent typical error bars for the total uncertainty (statistical + systematic) of the measured cross sections (see text for further details).

Figure 4 shows the absolute cross sections for the formation of CD$_2^+$ and CD$^+$ ions from the CD$_2$ free radical from threshold to 200 eV. The peak cross sections for the formation of other singly charged fragment ions (D$^+$, C$^+$) and the cross sections for multiply charged ions were estimated to be less than 0.1×10^{-16} cm^2. Again the earlier results of Baiocchi *et al* (1984) for CD$_2$ are in good agreement with the present results. We find cross sections at 70 eV of $1.67 \pm 0.30 \times 10^{-16}$ cm^2 (CD$_2^+$) and $0.67 \pm 0.09 \times 10^{-16}$ cm^2 (CD$^+$). Table 3 presents our measured CD$_2$ ionization cross sections data along with selected data from the earlier measurements of Baiocchi *et al* (1984) in tabulated form for convenient quantitative reference. The measured appearance energies of the CD$_2^+$ parent ions and the CD$^+$ fragment ions is close to the minimum values expected based on spectroscopic and thermochemical considerations (Chase *et al* 1985, Lias *et al* 1988, Wagman *et al* 1982) which indicate that the CD$^+$ fragment ions are formed with little excess kinetic energy.

Table 2. Absolute cross sections for the formation of CD_3^+ and CD_2^+ ions from CD_3 by electron impact. The cross sections are given in units of 10^{-16} cm^2. Given are the partial cross sections measured in the present work together with a few selected values from the earlier work of Baiocchi *et al* (1984).

Electron energy (eV)	Ionization cross section (in 10^{-16} cm^2)			
	CD_3^+/CD_3 This work	CD_3^+/CD_3 Biaocchi *et al* (1984)	CD_2^+/CD_3 This work	CD_2^+/CD_3 Baiocchi *et al* (1984)
10.0	< 0.01			
11.0	0.04			
12.0	0.14			
13.0	0.26			
14.0	0.39			
15.0	0.50	0.60	0.01	
16.0	0.57		0.02	0.04
17.0	0.64		0.09	
18.0	0.70		0.18	
19.0	0.76		0.25	
20.0	0.80	0.89	0.33	0.30
22.0	0.93		0.50	
24.0	1.08		0.59	
26.0	1.19		0.68	
28.0	1.29		0.77	
30.0	1.40	1.33	0.78	0.73
35.0	1.51		0.86	
40.0	1.60	1.47	0.92	0.82
45.0	1.65		0.96	
50.0	1.70	1.58	1.01	0.97
60.0	1.72		1.04	
70.0	1.73	1.64	1.10	1.05
80.0	1.72		1.12	
90.0	1.72		1.11	
100.0	1.70	1.59	1.10	1.05
120.0	1.63		1.05	
140.0	1.59		0.97	
160.0	1.52		0.92	
180.0	1.49		0.89	
200.0	1.43	1.35	0.80	0.89

Figure 5 shows the absolute cross sections for the formation of CD^+ and C^+ ions from the CD free radical from threshold to 200 eV. The peak cross sections for the formation of D^+ fragment ions was estimated to be less than 0.1×10^{-16} cm^2. Cross sections for multiply charged ions were even smaller. No data from other groups are available for comparison in the case of CD. We find cross sections at 70 eV of $1.58 \pm 0.30 \times 10^{-16}$ cm^2 (CD^+) and $0.45 \pm 0.07 \times 10^{-16}$ cm^2 (C^+). Table 4 presents all measured CD ionization cross sections in tabulated form for convenient quantitative reference. The measured appearance energies of the CD^+ parent ions and the C^+ fragment ions are close to the minimum values expected based on spectroscopic and thermochemical considerations (Chase *et al* 1985 Lias *et al* 1988, Wagman *et al* 1982) which indicate that the C^+ fragment ions are formed with little excess kinetic energy.

In summary, two observations should be noted: (i) the parent ionization cross section for all four targets CD_x ($x = 1-4$) has essentially the same maximum value of 1.6–1.7×10^{-16} cm^2 at 70 eV and (ii) for all four targets, parent ionization is the dominant

Table 3. Absolute cross sections for the formation of CD$_2^+$ and CD$^+$ ions from CD$_2$ by electron impact. The cross sections are given in units of 10^{-16} cm^2. Given are the partial cross sections measured in the present work together with a few selected values from the earlier work of Baiocchi *et al* (1984).

| Electron energy (eV) | Ionization cross section (in 10^{-16} cm^2) | | | |
	CD$_2^+$/CD$_2$ This work	CD$_2^+$/CD$_2$ Biaocchi *et al* (1984)	CD$^+$/CD$_2$ This work	CD$^+$/CD$_2$ Baiocchi *et al* (1984)
11.0	0.02			
12.0	0.09			
13.0	0.20			
14.0	0.31			
15.0	0.40	0.49		
16.0	0.51		0.02	0.04
17.0	0.60		0.04	
18.0	0.70		0.08	
19.0	0.78		0.11	
20.0	0.85	0.88	0.15	0.13
22.0	0.96		0.23	
24.0	1.08		0.30	
26.0	1.21		0.35	
28.0	1.30		0.40	
30.0	1.40	1.34	0.45	0.42
35.0	1.49		0.51	
40.0	1.52	1.55	0.56	
45.0	1.58		0.60	
50.0	1.61	1.61	0.63	0.54
60.0	1.64		0.66	
70.0	1.67	1.67	0.67	0.64
80.0	1.67		0.66	
90.0	1.65		0.65	
100.0	1.62	1.66	0.64	0.62
120.0	1.57		0.62	
140.0	1.52		0.60	
160.0	1.49		0.58	
180.0	1.45		0.55	
200.0	1.40	1.51	0.52	0.60

process and the most prominent dissociative ionization channel is the one in which one D atom is removed, i.e. CD$_x$ → CD$_{x-1}^+$ + D. The cross section for this dissociative channel becomes progressively weaker as one goes from CD$_4$ (where the CD$_3^+$/CD$_4$ cross section amounts to 80% of the parent ionization cross section at 70 eV) to CD$_3$ (65%) to CD$_2$ (40%) to CD (30%).

3.3. Total single ionization cross sections and comparison with calculations

Figures 6(*a*)–(*d*) show a comparison between the calculated total single ionization cross section for CH$_x$ and the experimentally determined single ionization cross section for CD$_x$ (*x* = 1–4) derived from the present data. In all cases, the experimental CD$_x$ cross section was determined by summing the measured partial ionization cross sections, CD$_4^+$ + CD$_3^+$ + CD$_2^+$ for CD$_4$, CD$_3^+$ + CD$_2^+$ for CD$_3$, CD$_2^+$ + CD$^+$ for CD$_2$, and CD$^+$ + C$^+$ for CD. No allowance was made for the unobserved channels or for channels with peak cross sections of 0.1×10^{-16} cm^2 or less. The calculated total single ionization cross sections
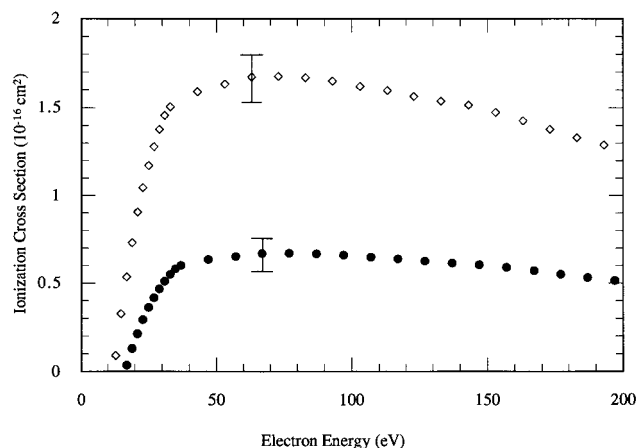
Figure 4. Absolute cross sections for the formation of the CD_2^+ parent ions ($\Diamond$) and the CD^+ ($\bullet$ fragment ions from CD_2 as a function of electron energy. The error bars indicate the total uncertainty (statistical + systematic) of the measured cross sections.
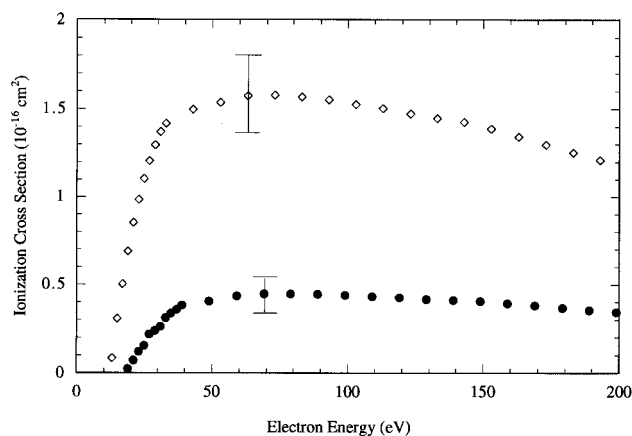

Figure 5. Absolute cross sections for the formation of the CD^+ parent ions ($\Diamond$) and the C^+ ($\bullet$ fragment ions from CD as a function of electron energy. The error bars indicate the total uncertainty (statistical + systematic) of the measured cross sections.

were obtained from a modified additivity rule (Deutsch *et al* 1994) which incorporates weighting factors in order to account for molecular bonding. The level of agreement between experimentally determined and calculated cross sections is generally very good. The agreement in the case of CD_4 (figure 6(*a*)) is satisfactory in terms of the absolute cross section value, notwithstanding some minor differences in the cross section shapes. The lower experimental cross section in the energy region below 100 eV is most likely due to the fact that we did not include the CD^+/CD_4 and D^+/CD_4 cross sections in our experimental curve—their inclusion would increase the experimental cross section by about 0.2×10^{-16} cm^2 at 70 eV. The more rapid decline of the calculated cross section towards higher impact energies compared to the experimental cross section has also been observed before in the case of SO (Tarnovsky *et al* 1995) and for the CF_x and NF_x radicals (Deutsch *et al* 1994). The agreement in the case of CD_3 and CD_2 (figures 6(*b*) and 6(*c*)) is excellent over
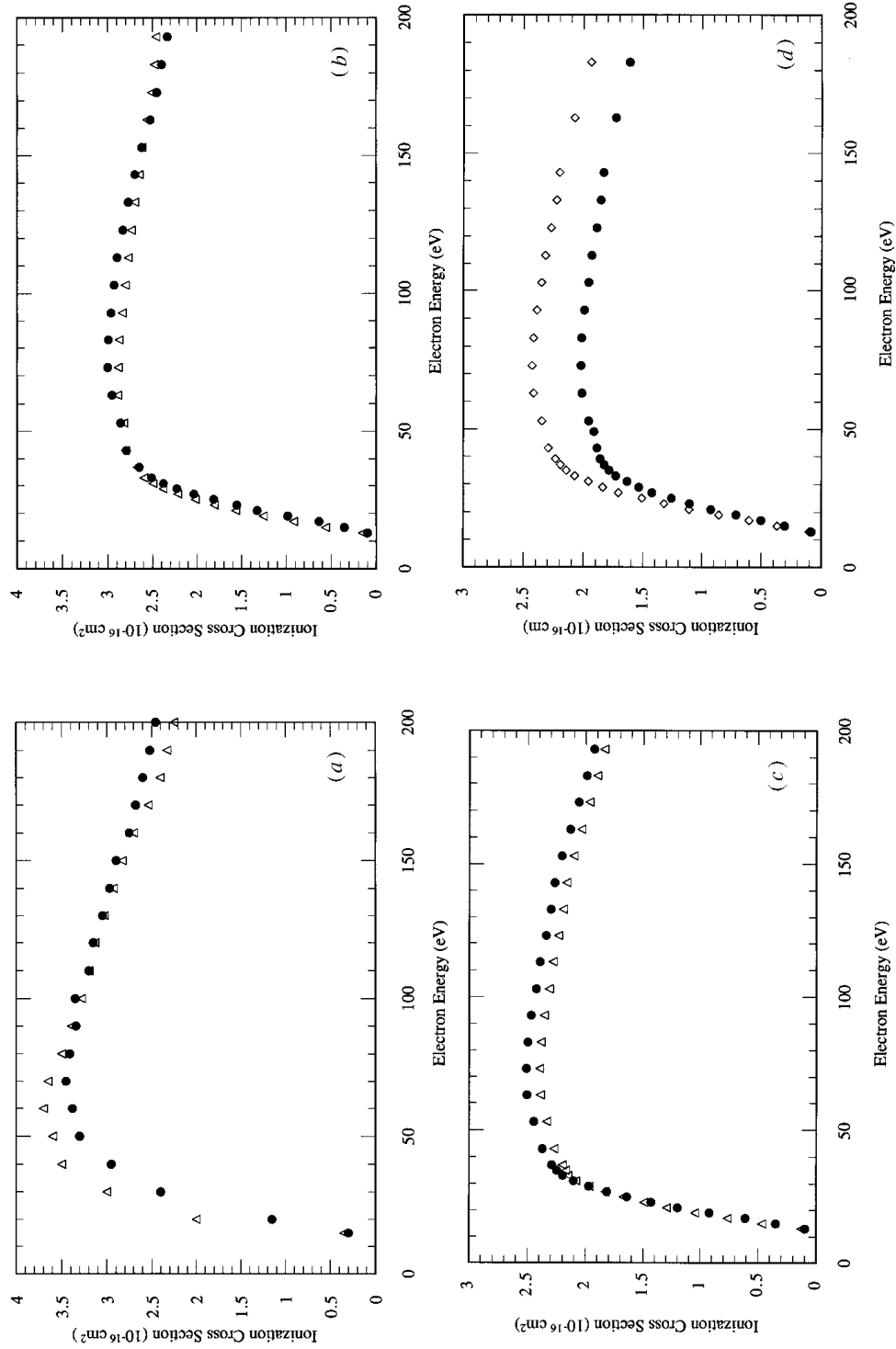
Figure 6. Experimental (●) and calculated (◇) total (single) ionization cross sections as a function of electron energy, (*a*) CD$_4$, (*b*) CD$_3$, (*c*) CD$_2$ and (*d*) CD.

Table 4. Absolute cross sections for the formation of CD^+ and C^+ ions from CD by electron impact. The cross sections are given in units of 10^{-16} cm^2. Given are the partial cross sections measured in the present work. No other cross section values are available for comparison for this target.

Electron energy (eV)	Ionization cross section (in 10^{-16} cm^2)	
	CD^+/CD This work	CD_2^+/CD$_3$ This work
11.0	0.02	
12.0	0.04	
13.0	0.11	
14.0	0.23	
15.0	0.37	
16.0	0.46	< 0.01
17.0	0.53	0.02
18.0	0.62	0.03
19.0	0.72	0.04
20.0	0.85	0.06
22.0	1.00	0.11
24.0	1.15	0.16
26.0	1.22	0.20
28.0	1.30	0.24
30.0	1.38	0.28
35.0	1.45	0.33
40.0	1.48	0.37
45.0	1.50	0.39
50.0	1.53	0.41
60.0	1.57	0.43
70.0	1.58	0.45
80.0	1.57	0.45
90.0	1.55	0.45
100.0	1.54	0.43
120.0	1.48	0.42
140.0	1.42	0.41
160.0	1.35	0.40
180.0	1.28	0.38
200.0	1.20	0.35

the entire range of impact energies from threshold to 200 eV. In the case of CD (figure 6(*d*)), the calculated cross section exceeds the experimentally determined cross section by about 15%. A possible explanation is the fact that we did not include an estimate for the D^+/CD cross section (which was not measured) in the determination of the experimental cross section. Lastly, we note that both calculation and experiment agree on the ordering of the absolute total single ionization cross sections, i.e. the total single ionization cross section increases as one goes from CD to CD$_2$ to CD$_3$ to CD$_4$.

4. Conclusions

The fast-beam technique has been used in a series of measurements of the electron-impact ionization and dissociative ionization of the CD$_4$ molecule and the CD$_x$ ($x = 1$–3) free radicals for impact energies up to 200 eV. Very good agreement was found between the present results for CD$_4$ and the most recent data for CH$_4$ for impact energies above about

30 eV. Our measured CD$_4$ cross section data below 30 eV were affected by the presence of vibrationally excited CD$_4$ molecules in the incident target beam. The observed ionization thresholds in our experiments were shifted towards lower energies by almost 2 eV and we found enhanced ion signals up to about 25 eV. It is noteworthy that the measured maximum ionization cross sections were essentially unaffected by the presence of the vibrationally target molecules. This is an observation which agrees with other recent experimental and theoretical findings (Cacciatore *et al* 1982, Celiberto and Rescigno 1993, Capitelli and Celiberto 1995, Kühn *et al* 1995). Our results for the CD$_3$ and CD$_2$ free radicals were found to agree with earlier measurements of Baiocchi *et al* (1984) which were carried out under different experimental conditions. The present data for the CD free radical represent the first ionization cross secton measurements for this target. The two most noteworthy findings are the fact that the parent ionization cross section for all four targets CD$_x$ (x = 1–4) has essentially the same maximum value of 1.6–1.7 × 10^{-16} cm^2 at 70 eV and the fact that for all four targets, parent ionization is the dominant process and the most prominent dissociative ionization channel is the one in which one D atom is removed. The cross section for this dissociative channel becomes progressively weaker from CD$_3^+$/CD$_4$ which amounts to 80% of the parent CD$_4^+$ ionization cross section to C$^+$/CD which amounts to only 30% of the CD$^+$ parent ionization cross section. A comparison of the experimentally determined total (single) ionization cross sections with calculated cross sections based on a recently introduced modified additivity rule showed good agreement for all four targets.

Acknowledgments

References

Adamcyk B, Boerboom A J H, Schramm B L and Kistemaker J 1966 *J. Chem. Phys.* **44** 4640
Appell J and Kubach C 1971 *Chem. Phys. Lett.* **11** 486
Baiocchi F A, Wetzel R C and Freund R S 1984 *Phys. Rev. Lett.* **53** 771
Basner R, Schmidt M, Deutsch H, Tarnovsky V, Levin A and Becker K 1995 *J. Chem. Phys.* **103** 211
Cacciatore M, Capitelli M and Gorse C 1982 *Chem. Phys.* **66** 141
Capitelli M and Celiberto R 1995 *Atomic and Molecular Processes in Fusion Edge Plasmas* ed Janev R M (New York: Plenum)
Celiberto R and Rescigno T N 1993 *Phys. Rev.* A **47** 1939
Chase M W Jr, Davis K A, Downey J R, Frurip D J, McDonald R A and Syverud A N 1985 *J. Phys. Chem. Ref. Data* **14** 1
Chatham H, Hils D, Robertson R and Gallagher A 1984 *J. Chem. Phys.* **81** 1770
Deutsch H, Märk T D, Tarnovsky V, Becker K, Cornelissen C, Cespiva L and Bonacic-Koutecky V 1994 *Int. J. Mass Spectrom. Ion Proc.* **137** 77
Freund R S, Wetzel R C, Shul R J and Hayes T R 1990 *Phys. Rev.* **41** 3575
Furuya K, Kimura K, Sakai Y. Takayanagi T and Yonekure H 1994 *J. Chem. Phys.* **101** 2720 and references therein to earlier work
Hariharan P C and Pople J A 1974 *Mol. Phys.* **27** 209
Hayes T R, Shul R J, Biaocchi F A, Wetzel R C and Freund R S 1989b *J. Chem. Phys.* **89** 4035
Hayes T R, Wetzel R C, Biaocchi F A and Freund R S 1989a *J. Chem. Phys.* **88** 823
Kühn M, Kortyna A, Keil M, Schnellhaaß B and Bergmann K 1995 *Z. Phys.* **33** 109

Lias S G, Bartmess J E, Liebman J F, Holmes J L, Levine R D and Mallard W G 1988 *J. Phys. Chem. Ref. Data* **17** 1

Märk T D and Egger F 1977 *J. Chem. Phys.* **67** 2629

Märk T D, Egger F and Cheret M 1977 *J. Chem. Phys.* **67** 3795

Orient O J and Srivastava S K 1987 *J. Phys. B: At. Mol. Phys.* **20** 3923

Rapp D and Englander-Golden P 1965 *J. Chem. Phys.* **43** 1465

Robertson R, Hils D, Chatham H and Gallagher A 1983 *Appl. Phys. Lett.* **43** 544

Schramm B L, Moustafa H R, Schutten J and de Heer F J 1966 *Physica* **32** 734

Shul R J, Hayes T R, Wetzel R C, Biaocchi F A and Freund R S 1989 *J. Chem. Phys.* **89** 4042

Sugai H, Kojima H, Ishida A and Toyoda H 1990 *Appl. Phys. Lett.* **56** 2616

Tarnovsky V and Becker K 1992 *Z. Phys.* **22** 603

——1993 *J. Chem. Phys.* **98** 7868

Tarnovsky V, Kurunczi P, Rogozhnikov D and Becker K 1993 *Int. J. Mass Spectrom. Ion Proc.* **128** 181

Tarnovsky V, Levin A and Becker K 1994 *J. Chem. Phys.* **100** 5626

——1995 *J. Chem. Phys.* **102** 770

Tate J T and Smith P T 1932 *Phys. Rev.* **39** 270

Wagman D D, Evans W H, Parker V B, Schumm R H, Halow I, Bailey S M, Chuney K L and Nutall R L 1982 *J. Phys. Chem. Ref. Data* **11** 1

Wetzel R C, Biaocchi F A, Hayes T R and Freund R S 1987 *Phys. Rev.* A **35** 559