

## Dissociative Ionisation and Neutral Dissociation: CF<sub>4</sub>, a Case Study\*

*R. A. Bonham and M. R. Bruce*

Argonne National Laboratory, Argonne, IL 60439, U.S.A.  
Permanent address: Department of Chemistry, Indiana University,  
Bloomington, IN 47405, U.S.A.

### *Abstract*

New results for the total neutral dissociation cross section and an estimate of the gross cross section for the production of neutral fluorine by electron impact on CF<sub>4</sub> have been obtained by combining previously reported results for the total dissociation cross section and the counting cross section for the total dissociative ionisation. This advancement was made possible by recently reported results for multication formation obtained from coincidence experiments. The estimate of the neutral fluorine production cross section is of the same order of magnitude as the total dissociation cross section itself, a similarity which may explain why CF<sub>4</sub> is such an effective etching gas. The available cross section data for electron impact energies between 5 and 200 eV are reviewed.

### 1. Introduction

The molecule CF<sub>4</sub> is a commonly used etching gas whose cross sections are needed for modeling in low temperature plasmas. Until recently, few cross section measurements were available. The situation has now improved, but many crucial cross sections have yet to be measured. It therefore seems worth while to review what is currently known for this typical etching gas.

No reliable evidence has been found for the existence of stable CF<sub>4</sub><sup>+</sup> formed by electron impact (Stephan *et al.* 1985; Poll and Meichsner 1987; Ma *et al.* 1991). In addition, no fluorescence produced by electron impact upon CF<sub>4</sub> has been observed at impact energies below about 22 eV, and none of the emitted radiation above 22 eV has been attributable to the parent molecule (Wang *et al.* 1989; Roque *et al.* 1991). All the evidence to date indicates that all excitations of the molecule above 5 eV lead to dissociation. This finding suggests that for electron impact energies above 5 eV, the total inelastic cross section and the total dissociation cross section are synonymous. The total dissociation cross section was measured by Winters and Inokuti (1982) for impact energies above 12 eV, and the total gross dissociative ionisation cross section has been reported by two groups (Stephan *et al.* 1985; Ma *et al.* 1991). It would appear that the total neutral dissociation cross section could be obtained from the difference between these results. However, the total dissociation cross section is a counting cross section (for a definition of gross and counting cross sections see Inokuti 1971,

\* Paper presented at the Joint Symposium on Electron and Ion Swarms and Low Energy Electron Scattering, held at Bond University, Queensland, 18–20 July 1991.

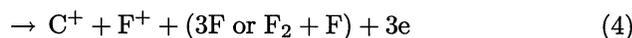
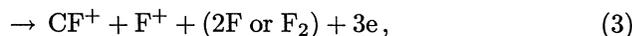
p. 330) that requires a knowledge of the total counting dissociative ionisation cross section, which has only recently become available with the measurement of double-ion production cross sections (Bruce *et al.* 1991). We report here the first results of such a comparison and review other available cross section data in the energy range 5–700 eV.

Table 1. Absolute cross sections for CF<sub>4</sub> in units of 10<sup>-16</sup> cm<sup>2</sup>

Cross section type	Electron impact energy	
	80 eV	150 eV
$\sigma_{\text{total}}$ (single ionisation)	4.18	4.14
$\sigma_{\text{total}}$ (double ionisation)	0.19	0.37
$\sigma_{\text{total}}$ counting	4.37	4.51
$\sigma_{\text{total}}$ gross	4.56	4.88
$\sigma_{\text{total}}$ dissociation	5.35	5.51
$\sigma_{\text{neutral}}$ dissociation	0.98	1.00
$\sigma_{\text{max F}}$	9.7	9.9
$\sigma_{\text{min F}}$	3.5	3.5
$\sigma_{\text{F}^+ + \text{CF}_3^+}$	0.028	0.043
$\sigma_{\text{F}^+ + \text{CF}_2^+}$	0.034	0.054
$\sigma_{\text{F}^+ + \text{CF}^+}$	0.048	0.13
$\sigma_{\text{F}^+ + \text{C}^+}$	0.009	0.051
$\sigma_{\text{CF}_3^{2+}}$	0.023	0.033
$\sigma_{\text{CF}_3^{2+}}$	0.046	0.066

## 2. Multi-ion Coincidence Studies

Bruce *et al.* (1991) have reported the results of positive ion–positive ion coincidence studies on CF<sub>4</sub>. Only the reactions



were observed. Very similar results have been reported by Codling *et al.* (1991) and Curtis and Eland (1985), who used a photodissociation coincidence technique. The lower limit of the cross sections that can be measured was about 10<sup>-21</sup> cm<sup>2</sup>. Coincidence intensities were measured at a number of different electron impact energies, and the results were placed on an absolute scale by matching them to a normal mass spectrum observed at the same time. Since no other processes were observed with appreciable intensity, these observations made it possible to correct the previously reported mass spectrum for CF<sub>4</sub> (Ma *et al.* 1991) for overcounting of the contributions from double-ion processes, in order to obtain a true counting cross section. The results for electron impact energies of 80 and 150 eV are given in Table 1.

Although the double ionisation contribution is only 5–10% of the single-ionisation contribution, the total neutral dissociation cross section estimated by using the gross cross section (Ma *et al.* 1991) is only half as large as the newly estimated

counting cross section. At the energies reported here, the majority of neutral fluorine production apparently comes from ionisation events. In fact, it is possible to construct upper and lower bounds for the gross fluorine production cross section (the gross cross section is weighted by the number of neutral fluorine atoms produced in a reaction; see Bruce *et al.* 1992 for specific equations). To do this we adopt the following rules: (i) For the lower bound we assume contributions only from sources about which we are absolutely certain, and we choose branching ratios so that F production is minimised. For example, we now know that the  $\text{CF}_3^+$  partial ionisation cross section corrected for the process producing  $\text{CF}_3^+ + \text{F}^+$  [reaction (1)] is equal to the F production cross section for this process, and we take, for example, the branching ratio for the reaction



to be one. (ii) For the upper bound we assume that all fluorine is released as neutral atoms and that all branching ratios are taken with the most favourable value to maximise F production. For example, we assume that the process



has a branching ratio of one. The results for these bounds are given in Table 1. Note that the average of the two bounds is very close to the total dissociation cross section at each of the two electron impact energies. This means that each excitation of  $\text{CF}_4$  at these two energies results in the production of a neutral F atom. Unfortunately, because of our lack of knowledge of neutral dissociation reactions like (5) and (6), we do not yet know how efficient electron impact dissociation is for F production at the lower energies that are of greatest interest to plasma processing.

At the bottom of Table 1, the absolute values of the cross sections for all double-charge-production processes with observable cross section values are given. A correlation seems apparent between the maximum double cation cross section ( $\text{CF}^{++} + \text{F}^{++}$ ) and the maximum multicharged ion cross section ( $\text{CF}_2^{2+}$ ), which should be the precursor of the former. It should be noted that the estimates of the multicharged ion cross sections given by Ma *et al.* (1991) are larger by a

**Table 2. Comparison of total, total elastic and total dissociation cross sections**

All cross sections are expressed in units of  $10^{-16} \text{ cm}^2$

$E$ (eV)	$\sigma_{\text{tot}}$ (Zecca <i>et al.</i> 1991)	$\sigma_{\text{total}}$ (Sakae <i>et al.</i> 1989)	$\sigma_{\text{tot dis}}$	$\sigma_{\text{tot dis}}$ (Winters-Inokuti 1982)
75	19.9	14.7	5.2	5.20 <sup>A</sup>
100	18.5	12.2	6.3	5.55
150	16.3	10.8	5.5	5.51
200	14.5	8.56	5.9	5.32
300	11.9	6.46	5.4	4.72
500	8.77	4.68	4.09	3.78
700	6.94	3.90	3.04	3.1 <sup>B</sup>

<sup>A</sup> Value obtained at 72 eV.

<sup>B</sup> Value obtained from a linear extrapolation from measured values at 500, 550 and 600 eV.

factor of 2–3 than those given by Stephan *et al.* (1985). Some of the difference has been attributed to the use of too low a value for the impact energy on the front surface of the detector (Ma *et al.* 1991); however, new results (Bruce and Bonham 1992*a*) are still nearly exactly a factor of 2 larger than those of Stephan *et al.* (1985). (This problem does not exist for  $\text{Ar}^{2+}/\text{Ar}^+$  ratio measurements; see Bruce and Bonham 1992*b*.) There are no clear causes for the remaining difference. A remote possibility, since the experiments differ dramatically in the length of time it takes to detect an ion after it has been formed, is that the doubly charged ions are metastable with a lifetime greater than  $10 \mu\text{s}$  (the typical time of flight). Why the lifetimes should result in exactly a factor of 2 difference (implying that the double ions have the same lifetime) is not understood.

### 3. Other Cross Section Data

The total (elastic plus inelastic) cross sections have been measured from 1 to 50 eV (Jones 1986; Szymkowski *et al.* 1989) and from 75 to 4000 eV by Zecca *et al.* (1991). Differential elastic-scattering cross sections are available over a sufficiently wide range of angles to allow estimation of the total elastic cross section (Sakae *et al.* 1989) at impact energies of 75, 100, 150, 200, 300, 500 and 700 eV. These data allow us to estimate the total dissociation cross section with the results shown in Table 2. The maximum deviation between the two estimates for the total dissociation cross section is 14%, and the average deviation is 7%. The values for the difference between the total and total elastic cross sections appear to be slightly higher on the average, but all deviations are well within the uncertainties in the three experiments involved. In fact, the new results constitute a very strong confirmation of the correctness of the Winters and Inokuti (1982) results and the assumption that the total inelastic and total dissociation cross sections are essentially identical.

The electron impact energy loss spectrum has been investigated at impact energies of 400 eV (Harshbarger *et al.* 1972; Harshbarger and Lassette 1973), 500 eV (Harshbarger and Lassette 1973; King and McConkey 1978) and 8 keV (Zhang *et al.* 1989). These experiments were all carried out with the intent of obtaining optical oscillator strengths, and the observations were confined to angles less than  $5^\circ$ . In addition, Zhang *et al.* (1989) measured the dipole scattering contribution to ion production by carrying out (e, e+ion) coincidence studies. The mass spectrum recorded in this work is amazingly similar to that reported by Ma *et al.* (1991) at an energy of 80 eV, but the dipole contribution is less than half of the total ionisation cross section at this energy. The first two changes in slope observed from 12 eV to higher energy in the total dissociation cross section of Winters and Inokuti (1982) correspond to the onset of the first two features in the energy loss spectrum, which occur at 12.5 and 14 eV. Although the magnitudes of the two processes cannot be compared directly, the total dissociation and total dissociative ionisation curves must be larger than the dipole contribution. At 22 eV, the dipole contribution is equal to the total dissociative ionisation cross section and accounts for 50% of the total dissociation cross section. By 30 eV, the dipole contribution accounts for only 39% of the dissociative ionisation and 17% of the total dissociation cross section. The dipole mechanism yields an even smaller contribution to the total cross sections at higher energies. These observations appear difficult to explain because one normally expects the dipole

contribution to be larger at higher electron impact energies. On the other hand, the energies considered here are so low that failure of the first Born approximation might be severe. Even if the Born approximation were valid, we have no idea of the contribution to ionisation from dipole forbidden processes that are allowed in the first Born approximation.

A great deal of work has been reported on the measurement of electron impact excitation cross sections for the production of photon emission from  $\text{CF}_4$ . Van Sprang *et al.* (1978) investigated the spectral regions 2000–4000 Å and 6500–9000 Å and reported continuous emission from an unidentified fragment along with weak emission from CF in the former and atomic F in the latter. No emission from  $\text{CF}_2$  was observed. They reported observation of two excited states of  $\text{CF}_4^+$  with lifetimes of 9–16 and 180 ns. Aarts (1985) also observed strong continuum emission in the region 1500–4200 Å with electrons, protons,  $\text{He}^+$  and  $\text{Ne}^+$  as excitation projectiles. He concluded that only  $\text{CF}_4^+$  and  $\text{CF}_3^+$  can be emitters of the continuum radiation in the observed spectrum. Blanks *et al.* (1987) measured the absolute excitation cross sections between 6200 and 7800 Å for optical emission from F produced by electron impact dissociation of  $\text{CF}_4$ . Blanks and Becker (1987) reported studying the emitted radiation between 2000 and 6000 Å and concluded that the observed intense continuum emission was due to excited  $\text{CF}_3^+$  and not  $\text{CF}_4^+$  as previously suggested. Wang *et al.* (1989) studied the spectral region 500–1300 Å and reported emission from both atomic fluorine and carbon. Roque *et al.* (1991) reported a study of F emission from the spectral region 955–975 Å. In general, in all the work cited above on photon emission from  $\text{CF}_4$ , the absolute cross sections are relatively small, generally less than  $10^{-17} \text{ cm}^2$ . The one exception is the intense continuum radiation centred at 3000 Å, which has a maximum cross section approaching  $10^{-16} \text{ cm}^2$  and about whose origin ( $\text{CF}_4^+$  or  $\text{CF}_3^+$ ) some controversy still exists.

Table 3. Fluorescence thresholds and their current assignments

Electron impact fluorescence threshold (eV)	Maximum cross section	Assignment
22 <sup>A</sup>	<0.01	$e+\text{CF}_4 \rightarrow \text{CF}_4^+(\tilde{\text{C}}) \rightarrow (\text{CF}_3^+)^* \rightarrow h\nu$
30 <sup>A</sup>	0.65	$\rightarrow (\text{CF}_3^+)^* \text{ or } (\text{CF}_3^+)^* + (\text{F}^+)^* \rightarrow h\nu$
36 <sup>B</sup>	<0.03	$\rightarrow \text{F}^* + ? \rightarrow h\nu$
44 <sup>B</sup>	<0.03	$\rightarrow \text{F}^* + ? \rightarrow h\nu$
61 <sup>B</sup>	<0.03	$\rightarrow \text{F}^* + ? \rightarrow h\nu$
<200 <sup>B</sup>	<0.01	$\rightarrow \text{C}^* + ? \rightarrow h\nu$

<sup>A</sup> Blanks and Becker (1987).

<sup>B</sup> Wang *et al.* (1989). Note that all spectral transitions with appearance potentials within 1 V of the value given above have been grouped.

Table 3 gives the various thresholds for photon emission and their assignments. These results can be compared with the threshold values for ionisation (appearance potentials), zero translational kinetic energy thresholds, and the observed excess translational energy at threshold (Table 4). If we add the energy required to excite the lowest-lying excited state of F (12.7 eV) to the zero-kinetic-energy thresholds for all reactions producing atomic fluorine, we find that the possible values fall into groups at 27 eV (1 member), 35 eV (3 members), 43 eV (5 members), 50 eV (5 members) and 60 eV (2 members). The observed fluorescence thresholds fall

into groups at 35 and 42 eV, with a third group occurring somewhere between 48 and 60 eV. We conclude from these observations that the fluorine in the  $\text{CF}_3^+ + \text{F}$  reaction is most likely produced in its ground electronic state for impact energies up to 35 eV, because no threshold for F fluorescence around 27 eV has been observed. Certain other reactions in Table 4, labeled with an asterisk in the last column, have sufficient excess energy at threshold to produce one or more of the molecular fragments involved in an excited molecular state. Above 35 eV, both fragments in the reaction  $\text{CF}_3^+ + \text{F}$  may be produced in excited electronic states.

Some work has been reported on the translational kinetic energies of fragments produced by dissociation of  $\text{CF}_4$ . Brehm *et al.* (1974) measured the translational kinetic energy released in the formation of  $\text{CF}_3^+$  fragments produced by photodissociation with photon energies of 16.5–20.1 eV. The releases

**Table 4.** Appearance potentials, zero translational energy thresholds, and excess energy at threshold for the partial ionisation processes in  $\text{CF}_4$

Reaction products	Appearance potential	Zero translational energy threshold	Excess energy at threshold <sup>A</sup>
$\text{CF}_3^+ + \text{F}$	15.9	14.7	1.2
$\text{CF}_2^+ + \text{F}_2$	22	19.3	2.7*
$\text{CF}_2^+ + 2\text{F}$		20.9	1.1
$\text{CF}^+ + \text{F} + \text{F}_2$	27	22.1	4.9*
$\text{CF}^+ + 3\text{F}$		23.7	3.3
$\text{C}^+ + 2\text{F}_2$	34.5	28.2	5.8*
$\text{C}^+ + 2\text{F} + \text{F}_2$		29.8	4.7*
$\text{C}^+ + 4\text{F}$		31.4	3.1
$\text{F}^+ + \text{CF}_3$	34.5	27.9	6.6*
$\text{F}^+ + \text{CF}_2 + \text{F}$		27.0	7.5*
$\text{F}^+ + \text{CF} + \text{F}_2$		30.3	4.2*
$\text{F}^+ + \text{CF} + 2\text{F}$		31.9	2.6*
$\text{F}^+ + \text{C} + \text{F} + \text{F}_2$		36.0	-1.5
$\text{F}^+ + \text{C} + 3\text{F}$		37.6	-3.1
$\text{F}_2^+ + \text{CF}_2$	35	23.6	11.4*
$\text{F}_2^+ + \text{CF} + \text{F}$		28.6	6.4*
$\text{F}_2^+ + \text{C} + \text{F}_2$		32.6	2.4*
$\text{F}_2^+ + \text{C} + 2\text{F}$		34.2	0.8
$\text{CF}_3^{2+} + \text{F}$	41		
$\text{CF}_2^{2+} + \text{F}_2$	42		
$\text{CF}_2^{2+} + 2\text{F}$			
$\text{CF}^2 + \text{F} + \text{F}_2$	52		
$\text{CF}^2 + 3\text{F}$			
$\text{CF}_3^+ + \text{F}^+$	36	32.4	3.6
$\text{CF}_2^+ + \text{F}^+ + \text{F}$	40	38.1	1.9
$\text{CF}^+ + \text{F}^+ + \text{F}_2$	42	39.3	2.7*
$\text{CF}^+ + \text{F}^+ + 2\text{F}$		40.9	1.1
$\text{C}^+ + \text{F}^+ + \text{F} + \text{F}_2$	63	47.2	15.8*
$\text{C}^+ + \text{F}^+ + 3\text{F}$		48.8	14.2*

<sup>A</sup> Asterisks indicate that the reaction has sufficient excess energy at threshold to produce one or more molecular fragments in an excited molecular state.

ranged from 1 to 2 eV, with an average value around 1.3 eV. Ma *et al.* (1991) measured the kinetic energy distribution of  $\text{CF}_3^+$  fragments produced by 20 eV electron impact and found that the fragments had an average value around 1.5–1.7 eV. Sommerer and Kushner (1991) inferred from this latter observation, by applying energy and momentum conservation, that at least some of the neutral fluorine produced must be extremely translationally hot (4–9 eV kinetic energy) and that such hot fluorine atoms can be expected to have a deleterious effect in plasma etching applications.

It was recently proved possible to observe directly a certain metastable state of F ( $\text{F}(3s)^4\text{P}_{5/2}$ ) (van der Burgt and McConkey 1991). These workers reported thresholds for two-body-breakup reactions at 34.5, 37, 40 and 56.5 eV, while thresholds involving total fragmentation were observed at 33, 38 and 57 eV. The kinetic energy distributions of the metastable F atoms were also measured and found to vary with impact energy, with most probable values of about 2.5 eV at 42 eV impact energy to 4 eV at 300 eV impact energy. Absolute cross sections were not obtained in this study.

#### 4. Conclusions

With new cross section data becoming readily available, at least for electron impact energies above 20 eV, a coherent picture is beginning to emerge as to the main mechanisms for neutral fluorine production. However, at electron energies below 20 eV, there is still a critical need for more cross section data. Unfortunately, the lower energy cross sections may be more important to the understanding of plasma etching processes, since low temperature plasmas are used where most of the electrons have kinetic energies less than 20 eV.

#### Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Energy Research, Office of Health and Environmental Research, under Contract W-31-109-Eng-38, and by the National Science Foundation, under Grant NSF PHY-8913096.

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Manuscript received 23 October 1991, accepted 3 February 1992