

# Chapter 1

## Introduction

### 1.1 Technological Plasmas and The Role of the $\text{CF}_2$ Radical

Over the last decade, dry etching silicon wafers in plasma reactors (plasma etching) has become one of the most commonly used techniques for processing semiconductor devices. The superior process control and fewer side products that plasma etching offers over older chemical etching techniques are critically important in today's competitive information technology market. Total worldwide sales of semiconductors in 2007 reached US\$270 billion [1], and the Semiconductor Industry Association predicts sales to increase to US\$321 billion by the year 2010 [2].

The performance of the plasma reactors depends heavily on the quality of the available corresponding models describing their chemistry [3]. The performance of these chemical models in turn depends on the extent and accuracy of their database. Amongst the most critical data inputs for the plasma models are the absolute electron collision rates and cross sections [3, 4] for the species comprising the plasma. The variety of species that are typically present in a technological plasma include not only the stable feedstock gas molecules, but also highly reactive species such as neutral radicals, metastables and ions formed in the electrical discharge. To successfully model technological plasmas one

therefore needs a rather extensive database of elastic, excitation, dissociation and ionisation cross sections for every species in the plasma. Further, since technological plasmas routinely operate at temperatures in excess of 600°C [5], the population of the vibrationally excited modes in the plasma etchants will be significant compared to the ground state. Therefore, the database also needs to include all the aforementioned cross sections for the vibrationally excited modes of the plasma etchants, as well as for the ground state species.

With such a large amount of data required, the current database is far from complete [6]. This lack of electron collision data means that optimisation and operation of plasma reactors is still largely based on empirical methods [3, 4, 6]. With plasma etching now underlying one of the world's most profitable industries, continuing to use empirical methods that are time-consuming and unreliable [3, 6] has become uneconomical. If the progress of this industry is not to be hampered by such a lack of fundamental data, more studies of electron collisions with technologically relevant species are required.

Electron collision cross sections are determined either by experimental measurements, or by theoretical calculations. The current experimental methods are extensively described in several review articles [5, 7] and therefore that detail is not repeated here. Typically though, experiments are classed as either (i) crossed beam experiments, which investigate single collisions between electrons and free molecules, or (ii) swarm experiments, which study the drift and diffusion of electrons through a molecular ensemble under an applied electric and/or magnetic field.

Theoretical models are also used to study electron-molecule collisions. However, as the full solution to the Schrödinger equation for the electron-molecule scattering problem in principle requires simultaneously solving an infinite set of coupled differential equations, various approximations need to be employed by theoreticians to make the problem more manageable. These various approximations have led to a variety of different theoretical models describing the scattering, with the

validity of these approximations determined by comparing theoretical results to experimental data. With the advent of parallel computing techniques, coupled with extensive efforts by the theoretical community, a number of sophisticated methods are now available to study electron-molecule collisions. Presently, the three most accurate methods for dealing with the electron-molecule scattering problem are the R-matrix method [8,9], the Schwinger Multichannel Method [10] and the complex Kohn approach [11]. A review of these and other theoretical methods is found elsewhere [11].

A range of electron interaction cross sections, both theoretical and experimental, for a variety of plasma feedstock gases is now available in the literature. These feedstock gases are typically comprised of fluorocarbon molecules such as  $\text{CF}_3\text{I}$ ,  $\text{C}_2\text{F}_4$ ,  $\text{c-C}_4\text{F}_8$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CF}_4$  and  $\text{C}_4\text{F}_6$  [3,4]. The current state of knowledge for electron scattering with fluorocarbon molecules is summarised in several review articles [4,6,12], with the general view being that while the database is not complete, the availability of absolute cross sections for stable fluorocarbon molecules (at least in their vibrational ground states) can be considered to be relatively satisfactory.

As well as the data for the primary feedstock species, absolute collision cross sections for secondary fluorocarbon radicals such as  $\text{CF}_x$  ( $x=1-3$ ), are required to accurately model the chemistry of plasma reactors [3,4,6,12]. Present in densities some 10,000 times greater than either ions or metastables [6], fluorocarbon radicals play a major role in the etch performance of technological plasmas [13,14]. A knowledge of their electron collision cross sections is thus critically important for modelling technological plasmas. However, while absolute electron interaction cross sections for the feedstock gases are generally available, the same cannot be said for the  $\text{CF}_x$  radicals. The reason for this lack of data is the fact that laboratory studies of  $\text{CF}_x$  radicals are highly problematic. For example, preparing a study sample of radical species is difficult on account of their high chemical reactivities. While theoretical calculations have been used to determine  $\text{CF}_x$  radical cross sections, some of which are reviewed in Section

1.3, these results are largely untested against experimental measurements and therefore a question as to their reliability could be asked.

One radical of particular importance to plasma processing is  $\text{CF}_2$  as a large number of the fluorocarbon feedstock gases, including  $\text{CF}_3\text{I}$ ,  $\text{C}_2\text{F}_4$ , *c*- $\text{C}_4\text{F}_4$ ,  $\text{CF}_3\text{H}$  and  $\text{CF}_4$ , dissociate to form  $\text{CF}_2$  in plasma reactors. Once formed in the plasma reactors, the  $\text{CF}_2$  radical species is primarily responsible for etching the silicon wafer. Electron collisions with this particular radical are therefore particularly important for an understanding of the chemistry of technological plasmas.

## 1.2 Review of Literature for the $\text{CF}_2$ Radical

### 1.2.1 Spectroscopy of the $\text{CF}_2$ Radical

The  $\text{CF}_2$  molecule is triatomic possessing  $\text{C}_{2v}$  symmetry, with a fluorine atom bound to either side of a central carbon atom.  $\text{CF}_2$  contains three normal vibrational modes, with the ground electronic state energies of these modes now established, from infra-red absorption experiments, to within  $10 \mu\text{eV}$  (Table 1.1). Vibrational modes have also been experimentally assigned to the lowest lying excited singlet  $\tilde{A}(^1B_1)$  and triplet  $\tilde{a}(^3B_1)$  electronic states. The geometries and vibrational mode energies in the three lowest lying electronic configurations are summarised in Table 1.1. The equilibrium geometry for the ground state of the  $\text{CF}_2$  radical is also represented in Figure 1.2.1.

The permanent dipole moment and dipole polarisability of  $\text{CF}_2$  has been measured to be  $0.469 \text{ D}$  [25] and  $\sim 12.4 a_0^3$  [26], respectively. Since there are no experimental values for the dipole polarisability available in the literature, this value is taken as the average of those calculated by the Hartree-Fock, Density Functional and Möller-Plesset perturbation methods; each evaluated using a series of effective core potentials. Polarisation and the permanent dipole moment are expected to be important considerations in describing low- and intermediate-energy elec-

Table 1.1: Summary of the spectroscopy and geometries of  $\text{CF}_2$  radicals in various electronic configurations. The vibrational modes are assigned using the standard triatomic nomenclature [15]:  $\nu_1$  = symmetric stretch;  $\nu_2$  = bend;  $\nu_3$  = asymmetric stretch. The C-F bond distance is denoted by  $r$  ( $\text{\AA}$ ) and the F-C-F bond angle is denoted by  $\theta$  (in degrees).

Electronic state	$\Delta E$ (eV)	Ref.	$r$ ( $\text{\AA}$ )	$\theta$	Ref.	Vibration	Symmetry	$\Delta E$ (meV)	Ref.
$\tilde{X}(^1A_1)$	0.00		1.300	104.94°	[16]	$\nu_1$	$A_1$	151.9	[17, 18]
						$\nu_2$	$A_1$	82.6	[19]
						$\nu_3$	$B_2$	138.2	[17, 20]
$\tilde{a}(^3B_1)$	2.46	[21]	1.325	119.40°	[22]	$\nu_1$	$A_1$	126.5	[21]
						$\nu_2$	$A_1$	64.1	[21]
$\tilde{A}(^1B_1)$	4.62	[23, 24]	1.320	122.30°	[16]	$\nu_1$	$A_1$	125.5	[22, 23]
						$\nu_2$	$A_1$	61.6	[23]
						$\nu_3$	$B_2$	146.3	[22, 23]

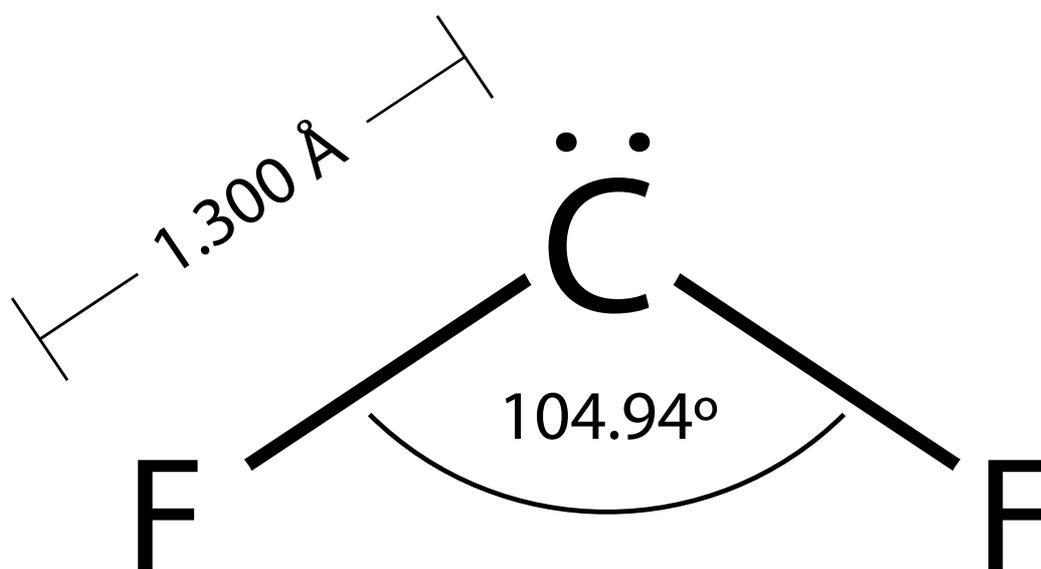


Figure 1.2.1: A schematic diagram of the equilibrium geometry of a ground state  $\text{CF}_2$  radical, showing the bond distances and bond angles. The location of the unbound electrons in the lowest electronic configuration is also highlighted.

tron collision processes with  $\text{CF}_2$  because the scattering event will be dominated by the long-range interactions between the incident electron and  $\text{CF}_2$ .

### 1.2.2 Electron Interactions with the $\text{CF}_2$ Radical

At this point in time absolute electron interaction cross section measurements for  $\text{CF}_2$  are scarce in the literature, in spite of the importance of these data to industry. Indeed the only absolute cross section measurements that have been reported for  $\text{CF}_2$  are partial ionisation cross section (PICS) measurements [27] and total ionisation cross section (TICS) measurements [28]. These data were obtained for incident electron energies from threshold to 200 eV, using a fast-neutral-beam technique.

Since experimental scattering studies on the  $\text{CF}_2$  radical are largely unavailable, the cross sections have been predominantly determined using theoretical models. The TICS of  $\text{CF}_2$  has been calculated, between threshold and 200 eV, using a modified binary-encounter-dipole model (si-BED) [28]. The TICS was also calculated between 20-2000 eV using a complex scaling potential-ionisation contribution (CSP-ic) method [29]. The si-BED cross sections are in excellent agreement with the experimental results [28] while the CSP-ic cross sections exceed those measurements by a factor of two. Of particular interest, the authors of the si-BED study noted that an accurate description of the long range dipole interactions between the incident electron and  $\text{CF}_2$  was critical in obtaining results which were consistent with those from the experiments. Those authors represented this long range interaction as a Born cross section, which they then screened to achieve consistent results with the measurements [28]. Noticeably the same calculation, but performed using an unscreened dipole-Bethe cross section, yielded very similar results to the TICS calculated with the CSP-ic method [28, 29]. On this basis, the highly electronegative C-F bond in  $\text{CF}_2$  was concluded [28] to reduce the dipole interactions during the collision. Note that the dipole polarisability employed in the CSP-ic calculation was calculated using commercial computational packages (DALTON and MOLCAS) [29] with

standard basis sets. Therefore, the more standard description of the polarisation of  $\text{CF}_2$  used in the CSP-ic calculation was probably the real reason for the discrepancy with the experiment and the si-BED calculation.

The CSP-ic method was also used to calculate grand total cross sections (GTCS) in the 50-2000 eV range [29]. The GTCS was determined by calculating the elastic and ionisation cross sections, which were then summed, with the TICS being assumed to be the dominant inelastic process at energies well above threshold. There are no other calculations in the literature to which these results can be compared, however, since the TICS calculated using the CSP-ic are included in this GTCS, it is fair to assume these results overestimate the true GTCS.

Low energy (<10 eV) elastic differential, integral and momentum transfer cross sections have been calculated using the R-Matrix method [30, 31]. This method was also used to determine integral inelastic cross sections for excitations between the ground and each of the 6 lowest lying electronically excited states. Elastic cross sections (differential, integral and momentum transfer) have also been calculated using the Iterative Schwinger Variational Method (ISVM), coupled with a distorted wave approximation [32] (2-400 eV) and by using the Schwinger Multi-channel method, coupled with a static exchange plus polarisation approximation (SEP) [13] (30-50 eV). The results from these latter calculations are generally in good agreement in terms of both their shape and magnitude; although there are some differences between them with regard to the resonance features predicted in the elastic channel. These differences shall be further discussed, in comparison with the present measurements, in Chapter 4.

### 1.3 Current Work

This thesis presents a study of elastic differential cross sections (DCS) for electron scattering from  $\text{CF}_2$  in the intermediate energy regime (25-50 eV). Elastic DCS for molecules are typically measured using crossed beam experiments, in which a

target molecular beam crosses an incident electron beam at  $90^\circ$ . Typically, in this configuration, the molecular beam is formed as an effusive flow of gas emerging from a single- or multi-capillary array [7]. However data for transient species, such as  $\text{CF}_2$ , have not yet been measured in an experiment employing an effusive gas beam. Conversely, molecular sources containing radicals have been realised in experiments in which supersonic gas beams were employed in conjunction with either flash photolysis or pyrolysis of the expanding gas jet. Supersonic beams have proven particularly useful for spectroscopic studies of radicals, where rotational and vibrational cooling of the targets in the supersonic expansion has allowed for very high resolution studies of their rovibrational structure [24,33–35].

While supersonic radical beams have been used quite extensively in spectroscopic experiments as yet such beams have never been employed in electron collision experiments attempting to measure interaction cross sections. Indeed, only a few electron collision experiments have ever been reported using supersonic beams of stable molecules [36–41]. These measurements were mostly relative; rather than absolute. Experiments that were, however, absolute were those by Allan [37], who measured absolute vibrational excitation cross sections for  $\text{O}_2$ , and Syage [39], who measured absolute ionisation cross sections for a series of molecules.

This lack of absolute data is no doubt due to the absence of a suitable normalisation technique, for crossed electron-supersonic beam experiments. An approximate normalisation technique was previously described [39] in which the scattering data for the target was normalised with respect to scattering data from a reference supersonic beam. This normalisation approach required that the density and profile of the two molecular beams were approximately the same. Therefore, to ensure that these criteria were met, a reference species of similar mass to the target was chosen [39]. Thus, this normalisation technique assumed that the mass of the relevant molecular species was the dominant factor in the dynamics of the supersonic expansion. However, theoretical studies [42–44] have demonstrated that the dynamics of a supersonic expansion actually depends

more on the internal (vibrational and rotational) structure of the expansion species than the mass.

So in summary, to measure the elastic DCS for electron scattering from  $\text{CF}_2$  radicals two major developments are needed. Firstly, a crossed beam-experiment featuring a supersonic gas source, coupled with a mechanism to dissociate the gas molecules, is required. The research detailed later in this thesis therefore describes the development of a new crossed beam apparatus that satisfies those requirements. In this experiment (Figure 1.3.1), a molecular beam containing  $\text{CF}_2$  radicals was formed by pyrolysis of a precursor ( $\text{C}_2\text{F}_4$ ) gas. The dissociated gas beam was cooled under a supersonic expansion and then collimated by a skimmer. This collimated molecular beam then crossed an electron beam, and the elastic angular distribution of the scattered electrons was measured. Finally, the molecular beam was mass analysed by a time-of-flight mass spectrometer to characterise the dissociation process.

Secondly, to determine absolute DCSs, a normalisation technique that places the measured relative data onto an absolute scale is required. Thus, as well as the construction and development of the experiment, a major component of this research was the development of a new normalisation method for providing absolute elastic scattering data. This new normalisation technique is similar to that previously reported [39] in that the unknown scattering data is normalised with respect to a reference species. However, here a more thorough description of the dynamics for the skimmed supersonic expansions than that previously employed [39] is used to match the respective molecular beams' density and profile.

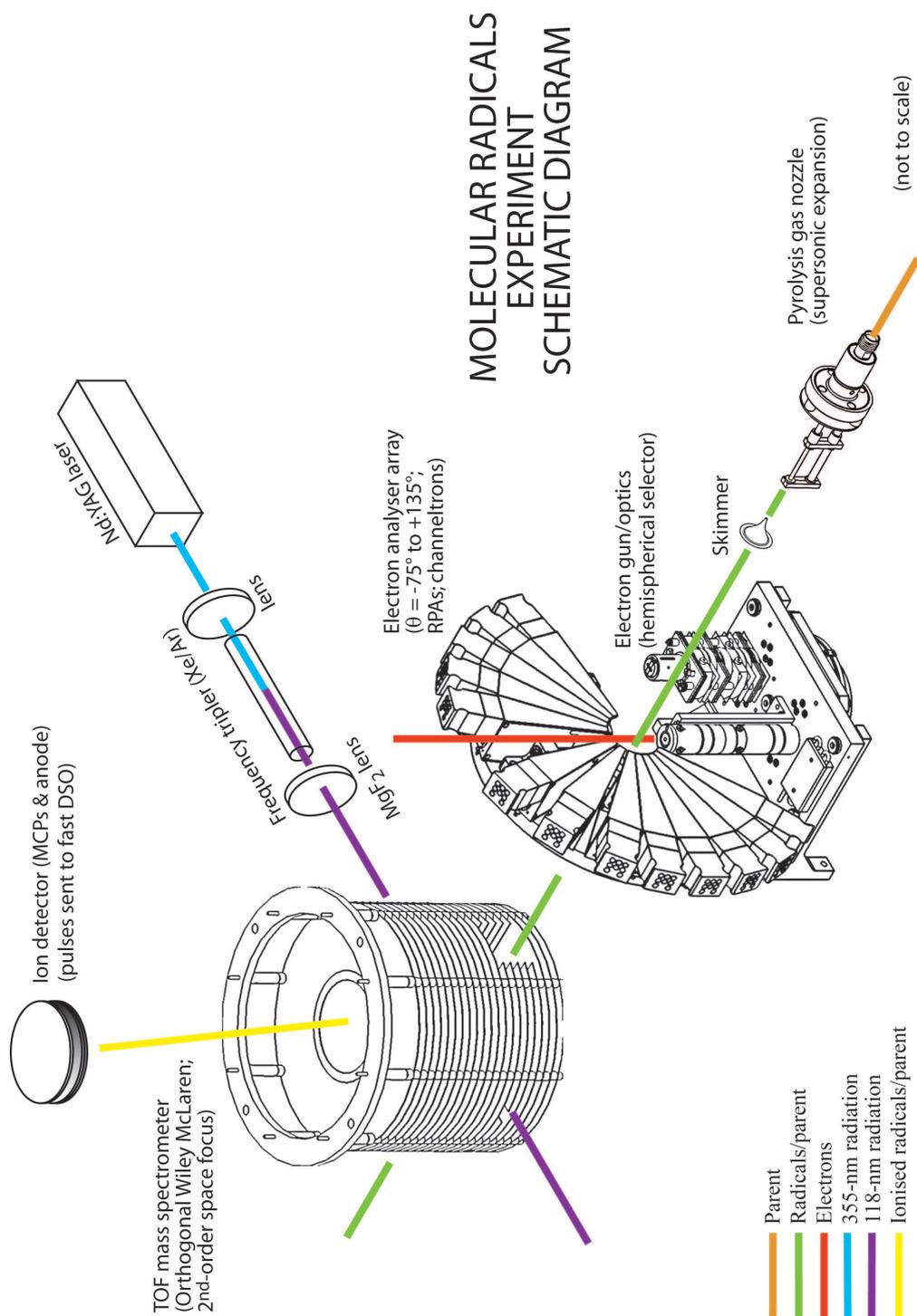


Figure 1.3.1: A schematic diagram of the present molecular radicals experiment.