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ABATEMENT OF PERFLUOROCOMPOUNDS
AND CHLOROFLUOROCARBONS
USING SURFACE WAVE PLASMA TECHNOLOGY

A Dissertation

by

MICHELLE E. GUNN FRANTZEN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2005

Major Subject: Chemistry

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Approved by:

Chair of Committee, John W. Bevan
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Dwight Conway
Dan Robertson
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ABSTRACT

Abatement of Perfluorocompounds and Chlorofluorocarbons Using

Surface Wave Plasma Technology. (December 2005)

Michelle E. Gunn Frantzen, B.S., Texas Lutheran University

Chair of Advisory Committee: Dr. John W. Bevan

Application of surface wave plasma technology for effective abatement of environmentally harmful gases such as perfluorocompounds and chlorofluorocarbons is investigated. Perfluorocompounds (PFCs) are gases that contribute to forced global warming and have been favored for wafer etch and chamber clean applications in the semiconductor industry. Chlorofluorocarbons (CFCs) are ozone depleting gases that were used as refrigerants for commercial and domestic condensers and air conditioners, but current reserves still pose threats to environmental sustainability. Increased average global temperatures and further destruction of the ozone layer have prompted proposal of international initiatives such as the Montreal Protocols and the Kyoto Agreement to curtail emissions of such fugitive gases into the environment. These have increased the need for effective abatement technologies to control such emissions and include surface wave plasma abatement, the subject of this dissertation. Surface wave plasmas are considered high frequency non-equilibrium traveling wave discharges in contrast to the more frequently used standing wave discharges. The use of surface wave plasmas have the advantages of a variety of discharge vessel shapes, reproducibility of application,

numerous operating conditions and large plasma volumes which ultimately produce low, molecular weight byproducts that are associated with high effective electron temperatures but low heavy particle temperatures. For these reasons, surface wave plasma abatement technology was developed for the destruction and removal of PFCs and CFCs.

Results include final destruction and removal efficiencies (DREs) for octafluorocyclobutane greater than 99.8%, dichlorodifluoromethane greater than 99.995% and trichlorofluoromethane greater than 99.999% using moderate applied microwave powers of less than 2000 watts with the production of low molecular weight byproducts, such as CO_2, CO, HF and HCl, that prevent environmentally harmful process emissions from entering the atmosphere. Characterizations of the initial and final products were accomplished by the use of Fourier transform infrared spectroscopy and quadrupole mass spectrometry to provide independent quantitative analyses of plasma processes. In addition to these analytical methods, Global_Kin a kinetic model, of plasma reactions were conducted and compared to all the experimental data determined in order to facilitate understanding of the chemistry involved in the surface wave plasma abatement applications studied. Basic plasma reaction mechanisms were determined for the abatement of octafluorocyclobutane and dichlorodifluoromethane.

DEDICATION

To my best friend, JoHenry

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First and foremost, I would like to thank my mom who taught me that anything is possible and Perky for being my dad. Thanks to my grandparents, Mommom and PaPa, for understanding my dreams for life and always being there. Many thanks to Grandma and Grandpa, the Perkins Family, the entire Frantzen family, and my numerous friends for all their love, support, faith and understanding.

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CHAPTER I

INTRODUCTION

During the last century or so, concern over impacts on human health from fugitive anthropogenic chemicals have been increasingly recognized such as the increased incidence of cancer, and detrimental effects on the environment (1). Releases of global warming gases into the atmosphere such as perfluorocompounds, ozone depleting gases such as chlorofluorocarbons, and chemicals that enhance overall pollution and smog are all factors that can impact everyday living. Increases in human populations can be possibly contribute to increases in environmental problems since human populations grew by a factor of 4 between 1860 and 1961 while pollution associated with energy consumption increased 90 times over they same period (2). Pre-industrial revolution concentrations of carbon dioxide, CO_2, were approximately 278 parts per million (ppm) whereas methane, CH_4, was 0.7 ppm. However in 1992, these concentrations were 356 ppm and 1.71 ppm respectively. The increase of CO_2 can largely be attributed to the burning of fossil fuels which account for about three quarters of the anthropogenic emissions (3). The total of these growths in global warming gases can contribute to the rise of global surface temperatures which have been demonstrated to have increased 0.6 ± 0.2 °C over the 20th century (2). Such increases can be attributed to the uses of anthropogenic gases being released into the atmosphere but there are also variations from naturally occurring sources such as increases in methane and carbon

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This dissertation follows the style of *Environmental Science and Technology.*

dioxide previously mentioned.

The Earth's climate system is in constant change but attempts to remain in balance through natural and external changes. Natural changes that help keep the climate in balance can include the greenhouse effect, wind patterns like El Niño, and orbital variations (2). The natural greenhouse effect, which warms the surface of the Earth, involves trace gases with atmospheric concentrations of 0.000031% for nitrous oxide, water vapor 0.1-1%, ozone 0.000005%, and carbon dioxide 0.0355%. Such gases as water vapor and carbon dioxide allow shorter wave radiation, 0.1 – 2 µm, to reach the surface of the Earth while absorbing and re-emitting long wave radiation, 5-25 µm, thus helping to maintain the surface of the Earth an average 15 °C. Figure 1 which is adapted from (4) illustrates the absorption of radiation throughout the atmosphere. Forced global warming caused by increases of greenhouses gas, growth in the ozone hole and land-use changes such as deforestation are classified as external forcing that can change the climate of the Earth.

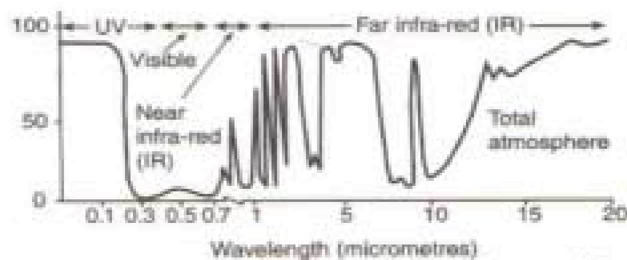


Figure 1: Atmospheric windows (4)

Global warming and ozone depletion are two environmental concerns that have prompted international treaties, such as the Kyoto Agreement and the Montreal Protocol along with the United States Clean Air Act. Therefore, investigations into viable destruction and removal of these environmentally harmful gases must be conducted to help meet the regulations of emissions imposed by these treaties.

Perfluorocompounds and Forced Global Warming

Perfluorocompounds, PFCs, are gases that are considered thermally stable, chemically inert and non-toxic under ambient conditions. PFCs have many uses including fire suppression agents, process cleaning solvents, heat transfer fluids or coolants, atmospheric tracers and semiconductor manufacturing (5). PFCs and hydrofluorocompounds (HFCs) such as c-C_4F_8, octafluorocyclobutane, CF_4, tetrafluoromethane, C_2F_6, hexafluoroethane, CHF_3, fluoroform, NF_3, nitrogen trifluoride, and SF_6, sulfur hexafluoride, are currently widely used for semiconductor manufacturing in dry etch and plasma enhanced chemical vapor deposition (PECVD) chamber cleaning operations. Tetrafluoromethane and hexafluoroethane are two of the main PFCs used in semiconductor manufacture for 200 mm wafer technology. Octafluorocyclobutane is being employed in some 300 mm semiconductor technologies with the probablity of increased future use of tetrafluoromethane in these latter operations. Perfluorocompounds and their uses within the semiconductor industry will be discussed in a later chapter.

There are a number of constituents in the atmosphere that absorb in different regions of the electromagnetic spectrum such as oxygen, ozone, carbon dioxide and water vapor. A large transparent region in the atmosphere, 8 to 14 μm is referred to as the atmospheric window with respect to infrared radiation. (4). Anthroprogenically generated perfluorocompounds are considered greenhouse gases because they are particularly effective at absorbing radiation, especially in this atmospheric window over the range from 1000-1360 cm^{-1}. This latter radiation is emitted from the Earth's surface and absorbed by such perfluorocompounds, which then reemits this infrared radiation towards Earth, which can result in forced global temperature increases. The control and regulation of such anthropogenic greenhouse gas emissions, and the decrease of subsequent forced global warming which would result, has thus been an area of active environmental interest as is evident from the recent Kyoto global climate change agreement (6). Whereas CO_2 remains the most important contributor to anthropogenic forcing of climate change, PFCs were included as one of the six component gases in the Kyoto agreement. The concentration of fluorine in the lower atmosphere was negligible in the 1930's. Today, its abundance can be measured throughout the polluted troposphere. Each of these primary sources, $CBrF_2Cl$, bromochlorodifluoromethane which has 1,000 metric tons released in 2002, C_2F_6 and C_2F_5Cl, pentafluoroethyl chloride, etc., are of anthropogenic origin (7).

A natural source of tetrafluoromethane was discovered from ice cores emissions and was determined to be 40 parts per thousand (ppt) as measured in 1750 and the corresponding natural abundance of sulfur hexafluoride was found to be 0.01 ppt.

However, the concentration of these gases has rapidly increased during the past two decades. CF_4 showed an increase of approximately 1.3% per year being 80 ppt in 1998, with the only sink for PFCs being photolysis in the mesosphere (3). Emissions of CHF_3 are increasing at rates of approximately 5% annually as well (8). Table 1 (3) illustrates that these gases are strong infrared radiation absorbers relative to CO_2 and have long atmospheric lifetimes making them significant greenhouse gases and potential contributors to global warming. The global warming potential, which is defined by the expression

$$GWP(x) = \frac{\int_0^{TH} a_x \bullet [x(t)]dt}{\int_C^{TH} a_r \bullet [r(t)]dt}$$

can be described as the cumulative radiative forcing of one gas over a certain time frame relative to carbon dioxide with TH as the time horizon, a_x radiative efficiency of the substance in question, a_r being the reference gas, x is the substance in question and r being the reference gas.

Table 1: Global Warming Potentials of PFCs

Gas	Global Warming Potential (100 year time horizon)	Atmospheric Lifetime (years)
CO_2	1	200
CH_4	23	12
CF_4	5700	50000
C_3F_8	8600	2600
CHF_3	12000	260
c-C_4F_8	10000	3200
C_2F_6	11900	10000
NF_3	10800	740
SF_6	22200	3200

At the present time, long-lived PFCs, HFCs and SF_6 greenhouse gases stemming from the semiconductor industry emissions contribute relatively little to global warming. In 1998 such PFCs, HFCs and SF_6 accounted for 2% of forced greenhouse gas emissions, but their projected growth, ~17%, (7) could contribute far more significantly due to the predictions of almost exponential increase in chip production and the consequential warming trends during the rest of the current century and beyond. In 1990, the total amount of global warming gas emissions, from the semiconductor industry was calculated at 5 $MMTCO_2$ (million metric tons CO_2) and is projected to be 124 $MMTCO_2$ in 2010 (9). It is now recognized that U.S. legislative initiatives on global warming semiconductor emissions are likely to occur in the immediate future around 2010, following the MOU of agreement between the EPA and semiconductor industry.

Chlorofluorocarbons and Ozone Depletion

Chlorofluorocarbons, CFCs, were once favored for industrial applications because these gases were considered chemically inert, non-toxic, non-flammable, chemically stable and could be used for a wide range of industrial and other applications. CFCs, CCl_3F (CFC 11) and CCl_2F_2 (CFC 12), were widely used in industry for air conditioners, domestic refrigerators and similar applications since their development in the 1920s (10). They have also been used by the electronics industry for cleaning electronic components as well as blowing agents for urethane and polyurethane foams (11). The development of CFCs as refrigerants was due in part to early refrigeration

chemicals that were toxic, flammable or both. CCl_2F_2, dichlorodifluoromethane, was first introduced as a refrigerant in the 1931 (12). Before 1990, CFC 12 had a rate of growth approximately 11,000 tons per year, which peaked in total emissions in 1987. Subsequently there was a 70% reduction by the year 2000 (13). Annual emissions of CFC 11 peaked at approximately 375,000 metric tons in 1988, with a 75% reduction in its use being accomplished by 1999 (14).

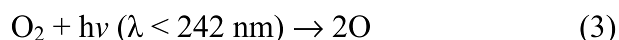
In 1974, annual production of CFCs was approximately 2 billion pounds. This consisted of CFC 11, CFC 12 and HCFC 22 0.681, 0.820, 0.246 billion pounds each respectively because they were considered inexpensive solutions to refrigeration problems, and they were also considered safe for commercial and private use. CFCs are inert and non-reactive in the troposphere as well as insoluble in water so their removal from the atmosphere by rain is not a possible sink, but they have been found to be highly reactive in the stratosphere. F.S. Rowland and M. Molina studied possible atmospheric sinks for chlorine containing gases and found that photolytic dissociation of chlorine occurs at altitudes of 20-40 km producing atomic and free radical chorine molecules as shown below (15).

$$CF_2Cl_2 + h\nu\ (\lambda < 200\ \text{nm}) \rightarrow CF_2Cl + Cl \qquad (1)$$

$$CFCl_3 + h\nu\ (\lambda < 265\ \text{nm}) \rightarrow CFCl_2 + Cl \qquad (2)$$

They suggested that probably all of the chlorine atoms are released from CFC 11 and 12 through these reactions. Rowland and Molina were awarded the Nobel Prize in Chemistry in 1995 for their investigations into chlorofluorocarbons and ozone depletion.

Free radical chlorine released from stratospheric dissociation of CFC 12 and 11 reacts with ozone, and it is estimated that one chlorine molecule can destroy up to 10^5 ozone molecules (16). Ozone is a naturally occurring atmospheric gas with an abundance of 1 ppm and resides in both the stratosphere and troposphere. In the lower stratosphere peak concentrations of ozone about 10^{12} cm^{-3} occur between 20 and 25 km altitude. Stratospheric ozone absorbs ultraviolet radiation given off by the sun in the range of 200 and 310 nm. The absorption of radiation at wavelengths from 250 - 320 nm, UV-B rays, is essential to human health because photons in this range can break chemical bonds in DNA and can cause skin cancer, cataracts, impair immune systems, decreased plankton in the ocean and can have negative affects on agriculture (17). Tropospheric ozone is a component of smog, an air pollutant and has been associated with adverse health affects (18). Ozone at altitudes from 8 to 14.5 kilometers can be formed from volatile organic compounds (VOCs), nitrogen oxides (NO_x), and carbon monoxide, which stem from industrial and automobile combustion. The majority of ozone, approximately 90%, resides in the stratosphere and is formed by the following reactions referred to as the Chapman cycle (1):



$$O_2 + h\nu\ (\lambda < 242\ nm) \rightarrow 2O \qquad (3)$$

$$O + O_2 \xrightarrow{M} O_3 \qquad (4)$$

$$O + O_3 \rightarrow 2O_2 \qquad (5)$$

$$O_3 + h\nu \rightarrow O + O_2 \qquad (6)$$

Atomic chlorine reacts with ozone in a fraction of a second causing destruction of ozone through the following reaction:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (7)$$

The ClO radical can then react with atomic oxygen to once again release a chlorine molecule.

$$ClO + O \rightarrow Cl + O_2 \qquad (8)$$

These two reactions will continue to occur in the stratosphere releasing atomic chlorine until being terminated due to the lack of ozone and an oxygen atom. The ClO_x radical is very efficient at destroying ozone in the stratosphere (19). This is due to the net effect of reactions 7 and 8, which converts ozone back to molecular oxygen that allows the reactions to be effective at destroying ozone.

The depletion of ozone is most evident over Antarctica. Following its discovery in 1985, the Antarctic ozone hole has shown trends that are largely seasonal with a decrease in September and a maximum loss in October. This seasonal loss is caused by very cold temperatures, below 190 K in midwinter which make the Antarctic stratosphere more prone to enhanced ClO_x and NO_x (20). In 1975, the total ozone was measured at 310 DU (Dobson units – used to express the amount of total column ozone with 100 DU equaling one layer of ozone 1millimeter thick) and dramatically decreased to 170 DU in 1987 with the record low of 91 DU in October 1993. The ozone hole in the year 2000 was approximately 28 x 10^6 km^2 large with most of the depletion occurring below 20 km. In 2002 the corresponding value was 15 x 10^6 km^2 (17).

Over the past 70 years, 8.7 million metric tons of CFC 11 were produced along with 11.5 million metric tons of CFC 12. The overwhelming production of CFCs, the lack of tropsospheric sinks and the capability to destroy much needed ozone layer prompted international controls and the development of the Montreal Protocol on Substances that Deplete the Ozone Layer of 1987. This action was aimed to limit the emissions of certain chlorofluorocarbons and halocarbons. A freeze on the use of CFC 11, 12, 113, 114 and 115 began in 1989 with total phase out occurring in 1996 for industrialized nations and contained a 14 year grace period for developing countries. Relative global production rates for the year 2002 were reported as 6,795 metric tons for CFC 11 and 20,181 metric tons for CFC 12. Hydrochlorofluorocarbons (HCFCs) are a likely replacement for CFCs but still have the potential to deplete ozone, so reduction in their production began in 2004 (21).

Ozone depleting potentials (ODP) and their classifications, atmospheric lifetimes and global warming potentials are shown in Table 2 (3,16) for various chlorofluorocarbons and hydrochlorofluorocarbons. Halocarbons are classified by their ozone depleting potential. Class I, includes gases whose potential is higher than 0.2 and Class II contains gases with a potential less that 0.2. Ozone depletion potential can be defined as the depletion of ozone by continuous emission of one gas by weight relative to CFC 11.

Replacement chemicals for CFCs as well as HCFCs are needed. The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) began to test alternative

chemicals as replacements. However, finding suitable replacements is difficult due to the properties of CFCs that are considered desirable for refrigerant applications.

Table 2: Ozone Depletion Potentials of CFCs and HCFCs				
Gas	Ozone Depletion Potential	Atmospheric Lifetime (years)	Global Warming Potential (100 yr time horizon)	Class
CCl_3F (CFC 11)	1.0	45	4600	I
CCl_2F_2 (CFC 12)	1.0	100	10600	I
$C_2F_3Cl_3$ (CFC 113)	0.8	11.9	1700	I
C_2F_5Cl (CFC 115)	0.6	85	6000	I
$CHClF_2$ (HFCF 22)	0.055	1700	7200	II
$CHCl_2F$ (HCFC 21)	0.04	1.7	210	II

Alternatives compounds must be environmentally friendly with low ozone depletion potentials, low global warming potentials, short atmospheric lifetimes, stable, and inexpensive to manufacture (22). HCFCs are currently being employed at replacements for CFCs though they still have small but significant ozone deleting potentials. The two most widely used HCFCs are CHF_2Cl, chlorodifluoromethane (HCFC 22) and CF_3CHCl_2, dichlorotrifluoromethylmethane (HCFC 123). HCFC 22 is favored as a replacement for CFCs because of its reactivity with hydroxyl in the troposphere resulting in less gas diffusing to the stratosphere. Production of HCFC 22 grew steadily from 1970 and peaked in 1996 with 271,243 metric tons, though has since been on the decline. The replacement of HCFCs with HFCs (hydrofluorocarbons) is a possible solution since these gases contain no chlorine. Possible replacements include CH_2FCF_3, tetrafluoroethane (HFC-134a) for air conditioners in cars, and $CF_3CH_2CHF_2$,

pentafluoropropane (HFC-245a) for foams. Other possible replacements include HFEs (fluorinated ethers) such as pentafluorodimethyl ether, CF_3OCHF_2 and 2,2,2-trifluoroethyl methyl ether, $CF_3CH_2OCH_3$, which can be employed for cleaning electronics and carrier fluids for lubricants.

Overview of Plasmas

Plasmas are often referred to as the fourth state of matter and are collections of charged particles in a gas that freely move in different directions (23). When a sufficient amount of energy is applied either in the radiofrequency or microwave wavelengths, molecules in a gas can decompose into radicals, molecular ions, atoms, or molecules in excited or non-excited states, electrons and photons (24). Within the ionized gas occur fundamental elastic and inelastic collisions that can induce the decomposition of the original gas. Elastic collisions or collisions of the first kind, are ones that have a transfer of kinetic energy, and inelastic collisions are ones in which there is a change in internal atomic or molecular energy. Inelastic collisions play a vital role in the production of intermediates because these collisions can create new particles in the plasma (25). Various types of reactions can occur in the gas phase of plasmas including electron impact, charge transfer and reactions with ions or molecules. Surface reactions can include etching, deposition and recombination. Various types of gas phase interactions with electrons include elastic scattering, ionization, excitation, fragmentation and

dissociative ionization. Charge exchange and oligomerization, formation of polymers, are two types of gas phase interactions with ions and molecules (26).

Generating and sustaining plasmas are most commonly achieved by applying an electric field to a neutral gas. This can be accomplished by various types of sources or discharges (27). Plasmas have been used for numerous types of industrial processes. Plasma aided manufacturing is key in the semiconductor industry for etching integrated circuits and other electrical devices. PFCs are often added to an etch chamber where a voltage is applied to breakdown the gas into radicals, ions and charged particles which then etch the silicon wafer. Also, plasmas can be used for printing of polymer films, hardening of tools and metals, welding, as well as lightening and displays (28).

Plasmas are now being employed to effectively abate environmentally harmful gases such as perfluorocompounds and chlorofluorocarbons (29-33). There are two general types of plasmas for industrial purposes: thermal and cold, non-equilibrium plasmas (34). Thermal plasmas are produced at high pressures and high temperatures by a variety of sources of electrical discharges, radio frequency or microwave generation. Possible uses of thermal plasma technology include pyrolysis of liquid hazardous waste, treatment of solid materials or slurries and reclamation of waste products from manufacturing processes (35,36). Plasma torches and plasma spray are two types of thermal plasmas (34). Thermal plasmas have high energy densities which lead to high process and quench rates but this high rate leads to strong gradients and the ion temperature, T_i, and the electron temperature, T_e, are in equilibrium with each other, T_e=T_i=T (23,37). Majority of thermal process employ electricity as the energy source,

but electricity is one of the most expensive forms of energy which makes thermal process not always favorable for applications (38,39). Uses of thermal abatement for destruction of environmentally harmful compounds will be explored in a later chapter (40,41).

Non-thermal or cold plasmas are plasmas in which the electron temperature is much greater than that of the ion temperature. Types of these plasmas include corona discharge, electron beams, dielectric barrier or silent discharges, high frequency, hollow cathodes, gliding arcs, radiofrequency (13.56 MHz) and microwave (2.54 GHz) and surface wave plasma (42). Abatement technologies involving non-thermal plasmas will be discussed in detail later chapters (29,43-45).

In the next chapter, surface wave plasmas will be explored along with the introduction of the surface wave plasma abatement device. Chapters III and IV illustrate the application of a surface wave plasma abatement technology to perfluorocompounds and chlorofluorocarbons. Chapter V discusses a kinetic based plasma model as it is applied to surface wave plasma technology. The final chapter includes a conclusion of the work in this dissertation along with possible further studies or commercialization of the abatement device.

CHAPTER II

SURFACE WAVE PLASMA ABATEMENT: AN OVERVIEW

Surface Wave Plasmas

High frequency (HF) discharges refer to both radiofrequency (≈1-300 MHz) and microwave (300MHz – 110 GHz) generated plasmas. Within HF discharges, is a classification of traveling wave discharge plasma which were investigated starting in the 1970s (46). Surface wave plasma (SWP) is a type of traveling wave discharge and can be produced within a cylindrical, dielectric discharge tube by an electrodless wave launcher and the electromagnetic wave propagates between the surface of this dielectric and the transmitted gas sustaining plasma (46,47). The plasma needs excitation at only one position along the plasma column, which allows a surfaguide for example to cover a smaller portion. Surface wave plasmas are considered low-pressure (1 mTorr – 1 Torr) high density discharges that can be produced with frequencies from 200 KHz to 10 GHz (23,47). These plasmas are often referred to as non-thermal or cold plasmas because the electron temperature T_e (5,000 K-100,000 K) is much greater than the overall temperature of the actual plasma (48) relative to thermal plasmas with equal ion and electron temperatures.

There are many advantages of surface wave plasmas, such as the ability to sustain discharges in large plasma volumes, large range of operating conditions and production of simple, low molecular weight byproducts in the abatement process.

Plasma volume, or *active zone*, is very large compared to the diameter of the dielectric tube. Figure 2, which is adapted from Moisan and Zakrzewski's review paper (49), illustrates that the plasma wave is launched at z = 0 and travels along the z axis as well as the axial distribution of the average electron density cross section. The plasma column or active zone ceases when z = l because the power has dropped below the level to sustain a plasma with n_D being the electron density at this point.

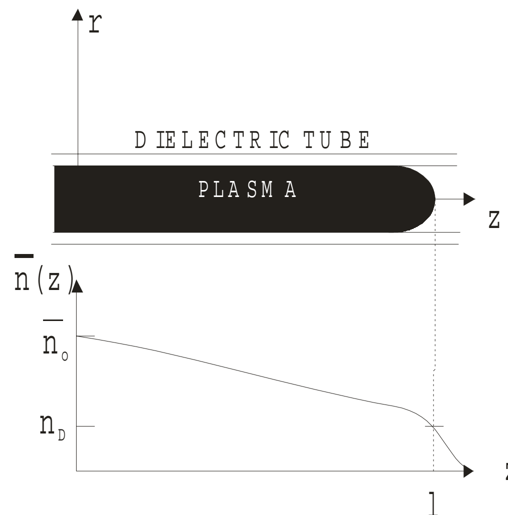


Figure 2: Illustration of the plasma column and the cross section of electron density as the plasma travels in the z direction and ceases when z = l

In considering the power balance of the surface wave discharge, one can study each of the sections, wave attenuation coefficient, power per unit length, power loss and power balance, separately because there is no net exchange of power along the sections. The power entering the plasma which is diverted from the main power flux, P(z), of the

traveling wave along the dielectric envelope over the distance, z, z + dz, is expressed by the wave attenuation coefficient in the following equation:

$$\alpha(z) \equiv -\frac{1}{2}\frac{1}{P(z)}\frac{dP(z)}{dz} \tag{9}$$

The power per unit length, A(z), from the main power flux over distance z and z + dz can be expressed as:

$$A(z) \equiv -\frac{dP(z)}{dz} = 2\alpha(z)P(z) \tag{10}$$

In the plasma, the power loss, expressed as Joule heating under steady state conditions and is expressed as:

$$2\alpha(n)P(z)\Delta z = 2\pi\int_0^a \sigma(n)E^2(r)rdr\Delta z \tag{11}$$

with the electron density expressed as n, a is the tube inner radius, σ(n) is the plasma conductivity and $E(r)$ denotes the average total electric field strength of the wave. The attenuation characteristic of the wave, $\alpha(\bar{n})$, depends only on the cross section of the average electron density which varies with z. The majority of power absorbed by the plasma, when the frequency is higher than a few MHz, is intercepted by electrons. The following expression describes the power per unit length lost by electrons through collisions with the power per unit lost per electron is indicated by θ.

$$L(\bar{n})\Delta z \equiv \pi a^2 \bar{n}\theta\Delta z \tag{12}$$

The power balance relationship under steady state conditions is expressed by

$$2\alpha(\bar{n})P(z) = \pi a^2 \bar{n}\theta \tag{13}$$

which equates to $A(\bar{n}) = L(\bar{n})$. The power to maintain the ion-electron pair in the plasma is θ, under steady state conditions.

The production of SWP can take place in a variety of vessel shapes and sustain larger plasma volumes since the plasma length increases with the amount of energy (47). Monomode operations, azimuthally symmetric mode, allow for great stability and reproducibility of the SWP. These modes are characterized by exp(j*m*φ) which affects the field intensity, with *m* being an integer, $j = \sqrt{-1}$, and φ is the azimuthal angle. The most commonly used mode is the lowest order *m* = 0 and which the field is independent of the azimuthal angle. Various types of surface wave launchers in the *m* = 0 mode, which include Ro-box, surfatron, waveguide-surfatron and a surfaguide launcher are modular and integrated design launchers. Modular design launchers have separate components that conducted field shaping and impedance matching whereas integrated launchers single design performs all actions. Launchers that employ a coaxial cable have limited power of about 400 W at a frequency of 2.45 GHz with waveguide structures able to operate at 5000 W at a frequency of 8GHz.

Illustrations of the surfatron, waveguide-surfatron and the surfaguide launcher have been adapted from Moisan and Zakrzewski (49) and are shown in Figure 3. Field shaping, which is achieved in the circular gap, and impendence matching integrated wave launcher, surfatron, are shown in Figure 3a. Components of the surfatron include a circular gap, coaxial structure, a coupler's plane and a short circuit. The working frequencies characteristic for the surfatron include relatively lower limits with maximum of 2.45 GHz and a power of 500 W with less than 30% reflected power. Figure 3b, the

waveguide-surfatron, which contains waveguide and coaxial line elements, was first proposed in 1982 by Chaker. The waveguide-surfatron has the tuning capabilities of the surfatron and the high power handling of the waveguide. Components include microwave generator, movable short circuit, air insulated coaxial line and a circular launching gap. The surfaguide, pictured in Figure 3c, is the simplest launcher described containing a field applicator and an adjustable short-circuit on one end of the waveguide with the applied power supply at the other end of the structure.

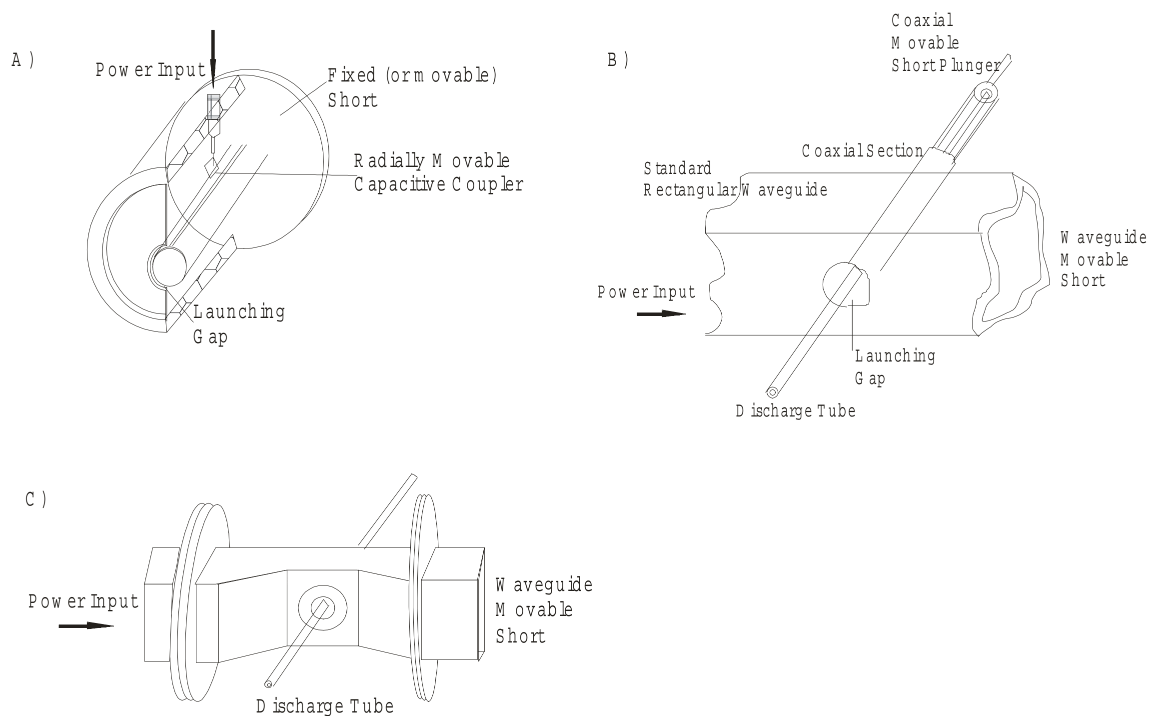


Figure 3: Three types of m = 0 surface-wave launchers: A) surfatron B) surfaguide field applicator C) waveguide-surfatron

To obtain a wave launching aperture, a circular gap is achieved by putting holes in both of the wide walls of the waveguide. Surfaguide operating frequencies ranges are from 915 MHz to 10 GHz with less than 10% of reflected power. Obtaining a surface wave plasma discharge is accomplished when part of the plasma vessel goes into the launching structure. Discharge tubes made of quartz, ceramic or glass, give the dielectric envelope for the plasma and help minimize the energy loss. For these reasons and the relative inertness of ceramic, surface wave plasma abatement technology has been used to effectively treat current semiconductor process emissions, which will be discussed in the next chapter.

Investigations of surface waves and their applications to sustaining plasmas have a long history (47,49). Applications include materials processing, lasers, ion sources and elemental analysis (49). More recently, surface wave plasmas have been applied to environmental problems such as acetone conversion and detoxification of trichloroethylene (50,51). Point-of-use plasma abatement has been applied to numerous gases mainly from the semiconductor industry such as hexafluoroethane, C_2F_6, tetrafluoromethane, CF_4, and trifluoromethane, CHF_3 (29-31,52). Hartz and co workers (30) studied application of SWPs to hexafluoroethane using a combination of oxygen and methane as additive gases. The investigation yielded an overall destruction for C_2F_6 of 99.6% with only 1950 watts of applied microwave power. Using only oxygen as an additive gas allowed for the formation of tetrafluoromethane, however adding methane caused any excess fluorine to combine with hydrogen to form hydrogen fluoride, HF. Wofford and Jackson (29) continued the investigations of perfluorocompounds using

surface wave plasma abatement studying the destruction and removal efficiencies of CF_4 and CHF_3. This study produced DRE results of 99.999% for CHF_3 and 99.8% for CF_4 using hydrogen and oxygen as additive gases with no detectable reformation of any perfluorocompounds. Subsequently Rostaing at Air Liquide conducted studies using atmospheric surface wave plasma on CHF_3, CF_6, c-C_4F_8 and CH_2F_2, difluoromethane, with DREs of 99% with over 3000 watts of applied power (52).

Experimental Procedures

Perfluorocompounds and chlorofluorocarbons contribute to jeopardizing the well-being and longevity of humans as well as environmental sustainability of the Earth through increased global temperatures and increases in the ozone layer. These concerns have lead to the development of effective abatement technology to combat this problem because their atmospheric fugitive emission is still prominent as a consequence various industrial manufacturing. Therefore, both global warming and ozone depleting gases were studied using this surface wave plasma abatement technology. The simulated manufacturing recipes for wafer etch processes (I-III) and sample gas compositions (IV-V) for the CFC gases are as follows:

	Simulated Etch Recipe		Additive Gases
I.	$16\ c\text{-}C_4F_8 + 90\ CO + 12\ O_2 + 700\ Ar$	+	$xH_2O + 40\ N_2$
II.	$16\ c\text{-}C_4F_8 + 45\ CO + 6\ O_2 + 350\ Ar$	+	$xH_2O + 40\ N_2$

III. 16 c-C_4F_8 + 12 O_2 + 700 Ar + xH_2O + 40 N_2

	Gas Composition	Additive Gases
IV.	40 CCl_2F_2	100 Ar + xH_2O + 40 N_2
V.	40 CCl_3F	100 Ar + xH_2O + 40 N_2

The simulated manufacturing recipes or gas compositions describe the flow rates (in standard cubic centimeters per minute or sccms) of each process gas as well as the addition of water and nitrogen. 40 sccm of dry nitrogen is typically included in simulated semiconductor wafer etch manufacture recipe contained in the manufacturing process as a purge gas for the turbo molecular pumps, that evacuate the actual plasma etch chambers. Consequently, experiments were conducted with N_2 as part of the feedstock to study any formation of NO_x along with any quality control problems on the plasma systems performance. Also, studies with N_2 in the simulated manufacturing recipes showed an improved DRE of 0.6% relative to that without additive nitrogen (29). Argon is included in CFC gas mixtures to initiate and help sustain the plasma during experiments in a similar manner to its use in semiconductor manufacturing processes. Water is added to the plasma to favor more thermodynamically stable byproducts such as such as HF, hydrogen fluoride, and HCl, hydrogen chloride in all abatement processes for both semiconductor and refrigerant industries. Trials were conducted where both the initial reactant concentrations and final product distributions were determined when the applied microwave power was increased 500, 1000, 1500 and 1950 Watts (W).

The abatement system used in this research has been designed especially for installation into an actual semiconductor process system considering the retrofit spatial requirements and the standard vacuum system connections. A schematic representation of the system is shown in Figure 4. The laboratory prototype system is aligned atop an Edwards QDP80 dry vacuum pump typical to that used in commercial semiconductor facilities. This arrangement, which simulates the real industrial installation, was desirable partly because any particulates, such as SiF_4, TiF_4 that may have been produced by the plasma device will pass through the vacuum pump, and partly to ensure that the operation of the plasma abatement system is transparent to the ongoing operations of the process tool.

The high frequency surface wave discharge system shown in Figure 1 consists of the following components: 2 kW variable output Sairem power supply, microwave generator, GMP 20 KSM, of 2.45 GHz, circulator, a three-stub tuner, A13S/30GR, and a surfaguide surface wave launcher, WR-430, with a sliding short circuit. Simulated process streams were metered using MKS type 1179 mass flow controllers at variable flow rates (200-10,000 sccm) depending upon the etch recipe studied. All gases for each recipe were metered, mixed, and delivered to the plasma system by a gas dilution system. The additive water was metered by a MKS type 1640A-230 pressure based mass flow controller and delivered to the backstream inhibitor/mixing device where it was mixed into the simulated process gas.

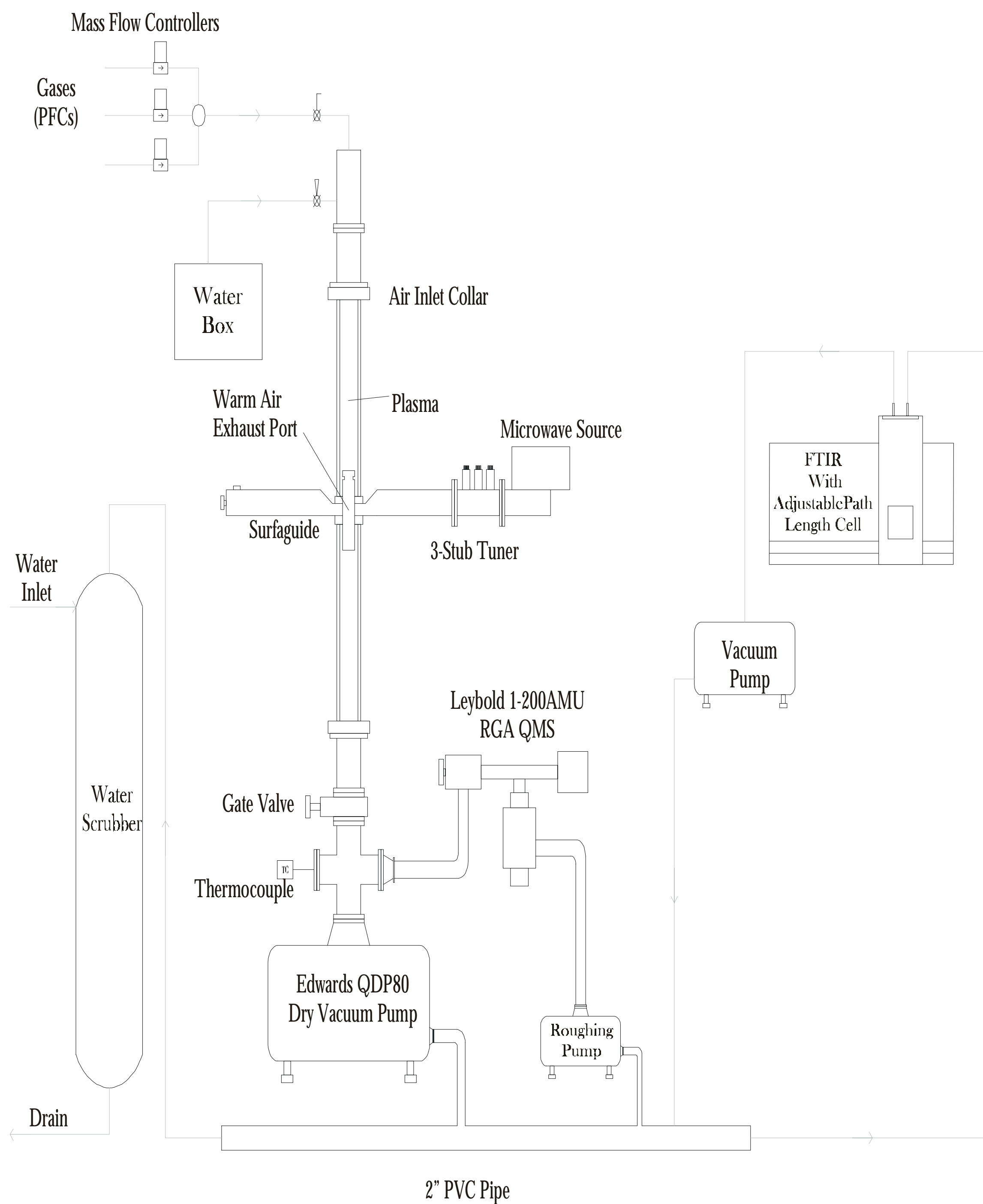


Figure 4: Schematic of plasma abatement system showing plasma reaction chamber, vacuum system and analytical instrumentation

The mixed gases were introduced into a 3-inch outer diameter (o.d.) and tubular ceramic reactor. This ceramic reaction vessel passed perpendicularly through the surfaguide surface wave launcher. After plasma ignition by a 2 kW short duration microwave pulse, the microwave power supply automatically returns to its preset power level of 500 W. The coarse microwave circuit tuning was accomplished by adjusting the sliding short circuit on the surfaguide launcher. Coarse tuning by the sliding short circuit allows for both enhancements of the destruction and removal efficiency percentage as well as plasma ignition. A three-stub tuner attached to the input of the surfaguide was then adjusted to optimize the forward power/reflected power conditions. The Sairem microwave plasma device incorporates a circulator to protect the magnetron from high back-reflected powers. The ceramic propagating tube resides inside a larger 3.5 inch o.d. brass tube. Compressed dry air from six individual inlets was passed at the rate of 24 cubic feet per minute between this brass containment vessel and the reactor tube for cooling purposes and exited one main exhaust. This brass containment system is a multiple-purpose device, which mechanically supports the surfaguide launcher and was introduced to prevent hotspots that would trigger Fab safety monitoring devices. It also serves to prevent toxic or hazardous gases from entering the operating environment in case of a catastrophic reaction tube failure. A Neslab refrigerated recirculating water chiller (CFT-75) was used to cool the microwave generator, circulator, and the surface wave launcher to restrict the temperature gradient at the center of the ceramic tube thus reducing mechanical stress on the latter. The vacuum integrity of the system was checked for leaks using the on-line Leybold Inficon Transpector 200 AMU Residual Gas

Analyzer mass spectrometer. Product gases exited the dry pump, where they were analyzed by FTIR and QMS, and then subsequently passed through water scrubber with 1.5 gallons per min washing water capacity to neutralize any fluorinated byproducts such as HF and COF_2, carbonyl fluoride.

Quantitative FTIR measurements were made using a Bio-Rad FTS 6000 spectrometer equipped with a potassium bromide (KBr) beamsplitter and liquid nitrogen cooled mercury cadmium telluride (MCT) infrared detector and were performed on the gases involving pre- and post-plasma application. One hundred scans were co-added for each spectral scan so that a final spectrum could be generated over the frequency range 4500-700 cm^{-1} at 1 cm^{-1} resolution. Other scan parameters included a scan speed of 20 kHz, sensitivity setting of 2, and an aperture setting of 0.25 in^{-1} at 2000 cm^{-1}. All gases were passed through a variable path length (2-10 meters) White cell which consists of three gold plated mirrors. The path length was set to 2 meters and the cell was heated to approximately 190 °F. All transfer lines were heated to this temperature of 190 °F to minimize condensation and avoid adsorption of analytes. The spectra were collected using Bio-Rad Win-IR Pro version 2.0 software with rapid-scan collection, which is used when the product gases have equilibrated. Identification of the reactants and final stable byproducts such as c-C_4F_8, CCl_3F, CCl_2F_2, CO, HF, HCl, COF_2, CO_2, carbon dioxide, and H_2O, water were accomplished on the basis of rotational constants and band origins frequencies as shown in Appendix B. A calibration matrix for each gas was then generated by measuring the absorbances of selected rovibrational features of different concentrations of each gas diluted in nitrogen. Certified calibration standard gases were

used when available to build the calibration matrix. The concentration of each calibration gas, with 1-10% ppm nitrogen balance, was chosen so that upon dilution to parts per million levels they could be used reproduce to interpret the concentration of the post-plasma chemical components. These curves are used to covert integrated peak area measurements measured using Bomem Grams software to parts per million for end product analysis of the plasma products.

Quantitative mass spectrometry was performed using a differentially pumped in-situ Leybold Inficon Transpector 200 AMU Residual Gas Analyzer. Spectra were collected by TranspectorWare application version 2.01. Instrumental characteristics included high electron energy, 70eV, and the capability of averaging 40 scans per experiment with each scan lasting approximately 10 seconds. The quadrupole mass spectrometer (QMS) is mounted on-line orthogonal to the vacuum foreline, which means that the samples were not diluted with the nitrogen purge gas as was the case with the FTIR samples. The QMS was backed by a Trivac D2A vacuum pump. This mass spectrometer consists essentially of an ion source, quadrupole mass filter, and a Faraday cup/electron multiplier detector. The Transpector 200 AMU Residual Gas Analyzer was equipped with an IPC28 pressure converter, which is an orifice system, designed to allow the mass spectrometer to sample the gas stream at one Torr. Typical ion source pressures in the mass spectrometer were 10^{-6} to 10^{-7} Torr. The mass spectrometer was used to provide alternative analytical capability including the opportunity to monitor IR inactive species such as Ar, N_2, and O_2. Most importantly, it provided a confirmation of the accuracy of measurement of reactants and product concentrations that could be

measured by both analytical techniques as well as giving possible insights into the reactions within the plasma.

Role of Experimental Design Changes

The surface wave plasma system is now a third generation design. Improvements must occur as the technology develops and must meet changing demands evolving in the semiconductor industry. First generation designs included an aluminum box, which enclosed a quartz tube as the dielectric and the sliding short circuit. Second generation system included an open design with a 5 foot long ceramic tube, twelve air inlets and outlets and employed molecular hydrogen and oxygen as additive gases. Using hydrogen and oxygen as additive abatement gases was an effective technique regarding abatement efficiencies (29-31) but would necessitate additional gas supplies in many semiconductor facilities which would increase the cost of ownership. Third generation design, as previously described, employs water vapor as additive gas which is an inexpensive solution for facilities that do not have on-line availability of such gases and also eliminates possible safety issues with using hydrogen and/or oxygen. A water box was designed to help contain and effectively deliver the additive water into the plasma chamber. Semiconductor pump rooms include water supply lines for distilled and filtered water than can be used for a water source for the water box. The water box is shown in Figure 5 and the dimensions were chosen 7 inches by 7 inches by 15 inches. Calculations show that 1 sccm of liquid water equates to 3207 sccm of water vapor. The

water box was constructed of stainless steel and is maintained under constant vacuum and also contains a viewing window. Two top flanges were included to help aid in replenishing the water supply and to attach a MKS type 1640A mass flow controller to meter the flow of additive water.

A water scrubber with a flow rate of 1.5 gallons per minute, which is 91 inches tall and is a 6-inch schedule 40 PVC pipe, was added downstream from the FTIR to help neutralize any fluorinated byproducts, which could possibly include HF, COF_2, and F_2. The length of the ceramic reactor tube was shortened from 5 feet in length to 26 inch with the diameter remaining the same. This was included to accommodate the space constraints in the actual semiconductor manufacture plant specified for operation at Motorola (now FreeScale). The decrease in length of the ceramic reactor tube was demonstrated to not affect the overall performance of the plasma abatement system. The number of cooling air inlets, which are used to help reduce the temperature of the ceramic reactor tube was decreased from twelve to six inlets with one main exhaust centered on the brass attachment. These changes of the surface wave plasma abatement device have been applied to investigate regarding PFCs and CFCs, which will be considered in the following chapters.

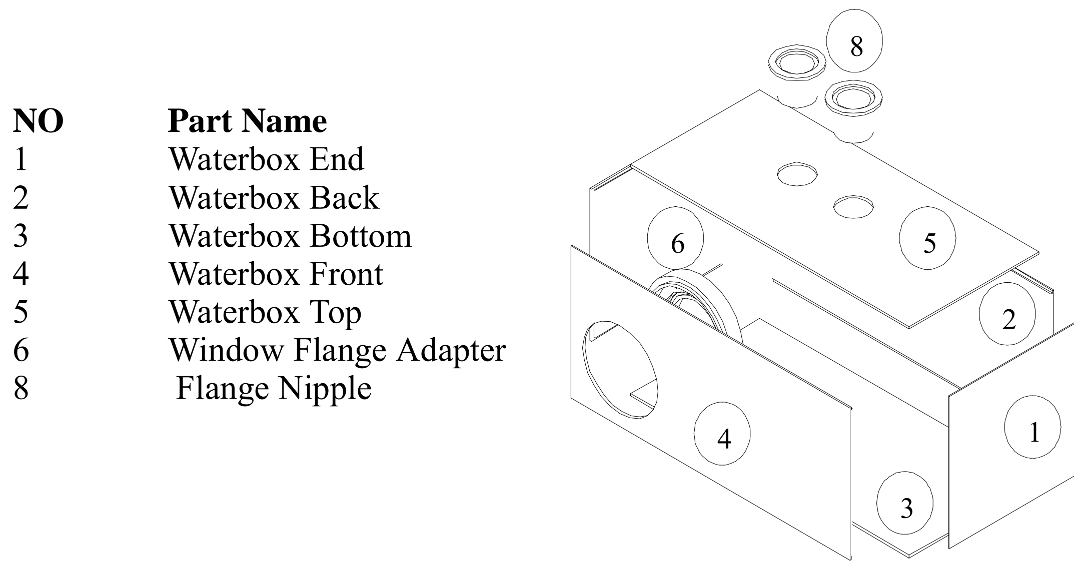


Figure 5: Water box for plasma abatement experiments

CHAPTER III

OCTAFLUOROCYCLOBUTANE FEEDSTOCK ABATEMENT

Review of Semiconductor Process Applications

PFCs are chemicals that are particularly significant for applications in the fabrication of semiconductor wafers as well as chemical vapor deposition (CVD) chamber clean processes (5). In these manufacturing processes, PFCs and hydrofluorocarbons, HFCs, are gases that provide sources of atomic fluorine for subsequent use in plasma processing for etching of silicon substrates used in integrated circuit manufacture (53). PFCs and HFCs are considered to have properties that appeal to the semiconductor industry for use in the etching of silicon, silicon dioxide and silicon nitride films including low impact on personal safety, low toxicity, and the ability to maintain a necessary ratio of carbon to fluorine to etch substrates (54). Over the last 25 years, the semiconductor industry has had a growth rate of about 15% per year over this time frame whereas the overall United States economy has only grown approximately 3% per annum. Consequently, there has been a higher emission of PFCs relative to global warming emissions from other anthropogenic sources (55).

The majority of the PFC and HFC emissions stem from the chemical vapor deposition (CVD) chamber clean operations, which account for approximately 60-75%. The remainder of the fugitive PFC and HFC emissions that are produced from the etch process are either from reformation of PFCs during plasma processing or incomplete utilization of the etch gas (56). Early reports suggested that typically 20-40% of the feed

gases are consumed in the actual via-etch processes for 200 mm recipes and the excess gases are subjected initially to an attempted thermal incineration prior to atmospheric release. Monitoring has demonstrated the increasing presence of PFCs and HCFCs in the atmosphere (41). Furthermore, the semiconductor industry is involved in a Memorandum of Understandings (MOUs) with the Environmental Protection Agency (EPA) to voluntarily reduce such forced global warming gas emissions (9). The World Semiconductor Council (WSC) in 1999 implemented a goal of reducing emissions stemming from semiconductor manufacturing plants by 10% for 2010 based on the emission level in 1995 as a standard. To meet this goal this would mean that the overall emissions must be reduced by 90% for etch processes and 95% for CVD chamber processes of the 1995 levels. To reach this goal of emission levels would require that suitable reduction strategies must be developed and employed (57).

The semiconductor industry has primarily applied four different strategies to reduce PFC process emissions into the atmosphere: i) optimization of the current technology, ii) alternative chemistry, iii) recycle/recovery, and iv) abatement (58). The semiconductor industry has been able to meet the chamber clean requirements in the MOU through optimization. However, this is not so for etch processes where 300 mm technologies will further increase use and emissions of HFCs and PFCs and particularly of CF_4, which has a lifetime in the atmosphere of greater than 50,000 years. Higher flow rates of PFCs are necessary for implementation of the newest 300 mm technologies and the size of the wafer increases by a factor of 2.25 which could lead to a further 225% increase in emissions (59). Optimization of wafer etch (56) has shown to reduce PFC

emissions by 90% for 200 mm manufacturing processes, but this percent reduction falls short of the semiconductor MOU with the EPA. Previous studies (41) have demonstrated that there are no current compounds that can be effectively used in place of PFCs for use in the etch process because no one gas has the correct etch rate, resist selectivity and sidewall polymer formation. Use of alternative chemicals such as iodo-hydrofluorocarbons and unsaturated PFCs have been attempted due to their shorter atmospheric lifetime and lower GWP, but their use has been restricted either by being too expensive or not meeting manufacturing quality control standards. Two gases that have been recently been studied as drop in replacements for C_2F_6 in chamber clean: C_3F_8 and *c*-C_4F_8 (55,60). Perfluoropropane and *c*-C_4F_8 are PFCs with C_3F_8 dissociating at a higher rate, which allows for better utilization of the gas. Furthermore, there is a reduction of GWP by a factor of 1.4 from C_2F_6 as well as the advantage of significantly shorter atmospheric lifetimes. Recycle/recovery is the capture of the unused gases and their reuse after purification (5). Recycle/recovery strategies consist of membrane separation and cold box approaches. Membrane separation entails pretreatment of the process exhaust gases, PFCs and wafer byproducts, which are then passed through membranes that are non-porous rubber polymers. After this pretreatment, the target gases are fed into a multi-stage membrane separation unit and are diffused through via pressure gradients. The gases are then passed through a N_2 rich steam vent for further scrubbing (5). The ability to cost effectively separate the PFCs from the gases (O_2, HF, SiF_4, CF_4, and N_2) in the exhaust stream are proving to be the hurdle for

recycle/recovery. Consequently, effective abatement strategies have become the front-runner in reducing semiconductor global warming emissions (9).

Abatement of perfluorocompounds is an ongoing approach using a variety of techniques including catalytic, thermal and plasma abatement. Catalytic abatement technology had been studied for CF_4 and C_2F_6 process streams with DREs of 99% and 95% for *c*-C_4F_8. A possible problem with this technology is poisoning of the catalyst by silicon from the etch chamber and decreasing effectiveness with time as well as not being cost effective for such applications (61). Alternative studies to this approach include the combined use of catalyst and plasma technology or combined plasma catalyst (CPC). An investigation into the destruction of CF_4 and C_2F_6 using CPC was conducted by Chang and Lee in Taiwan (62) with DREs of 66 and 83% respectively. CPC studied using dielectric barrier discharges were also investigated by Yu and Chang but only achieved 65.9% destruction for tetrafluoromethane and 94.5% DRE for C_2F_6 (63,64). A recently introduced abatement technique involves an inductively couple plasma with calcium oxide to trap fluorine. This technique results in greater than 70% of the fluorine molecules being trapped as CaF_2 (65). Thermal process technologies such as incinerators, pyrolsis systems and boilers have also been investigated. However, complications result due to the thermodynamic stability of chemical bonds in compounds generated in plasma products such as CF_4, C-F bond ~ 116 kcal per mol (66). Consequently, this technology does not effectively meet agreed reduction levels as required by the MOU. In addition, further disadvantages result from NO_X production, which is strictly regulated, and high capital and operating costs (67). BOC Edwards

developed a thermal processor unit for abatement. However, it was costly and produced NO_x emissions. A thermal reductive destruction technique using alkali halide has also been investigated by Lee and Choi (68). They proposed conversion of tetrafluoromethane to alkali metals with complete conversion, ~100%, using CsF at 600 °C. A thermal carbon arc plasma was also investigated but only 23% conversions of the PFC was accomplished (40).

Non-thermal plasma abatement includes radiofrequency (1-300 MHz) and microwave (300 MHz – 300 GHz) generated discharges. A radiofrequency generated micro plasma reactor was used to abate CF_4 and this study showed decomposition in N_2, approximately 94% is better than helium which ranges from 30-89.5% because they found that N_2 acts as a reactant in the abatement process (69). Abatement of CF_4 and C_2F_6 was also studied using microwave generated plasmas at atmospheric pressures (45,48,70-73). Radiou investigated several PFCs and achieved >98% DRE but obtained 3000 ppm, an unacceptable level of NO, which is regulated. Electrodeless microwave plasma torch studies were conducted by Hong et al. accomplished DREs of 98% for tetrafluoromethane in the presence additive gases oxygen and air with higher destruction rates of CF_4 using air due to a source of hydrogen (70). Studies on sulfur hexafluoride were conducted by Kabouzi, Moisan and co workers with DREs of greater than 95% at 6kW of applied microwave power at atmospheric pressure using O_2 as an additive gas to yield byproducts such as SO_2F_2 (45). Researchers at MIT, Vitale and Swain, studied the difference between radiofrequency power and microwave power to successfully abate perfluorocompounds (43). Using radiofrequency power, the reformation of PFCs were

prominent when just using oxygen as an additive gas but was overcome by using a source of hydrogen to favor thermodynamically stable byproducts whereas microwave power showed promising results with no formation of CF_4 (43). This work confirmed previous investigations (29,30) that the addition of hydrogen to form more stable byproducts such as HF can reduce the power needed for abatement. Microwave generated plasmas seem to have a better overall destruction rates for perfluorocompounds and hydrofluorocarbons than for radiofrequency plasmas because of the increased power and frequency.

An inductively coupled radiofrequency plasma reactor (44,74-77). Litmas blue, an ICP abatement system, has also been investigated at a semiconductor manufacturing site and accomplished DREs of 95% using additive gases of molecular oxygen or water vapor. Low flow rates of CHF_3 and CF_4, 40-60 sccm of CHF_3 and 4-6 sccm of CF_4, were used with approximately 250 sccm of water with the main byproducts being carbon monoxide and HF with no significant impacts on the commercial MERIE oxide etch tools (76). Researchers at University of Illinois also found that using molecular oxygen caused reformation of the initial PFCs but found that water vapor did not cause reformation of PFCs and yielded a DRE of 98% (74). Other abatement techniques for perfluorocompounds have involved combination glow discharge/ arc plasma. This approach achieved a maximum destruction rate of 95% using molecular hydrogen and oxygen with some formation of tetrafluoromethane (78). Process gases, additive gases, DRE and other information associated with a range of PFC abatement technologies are summarized in Table 3.

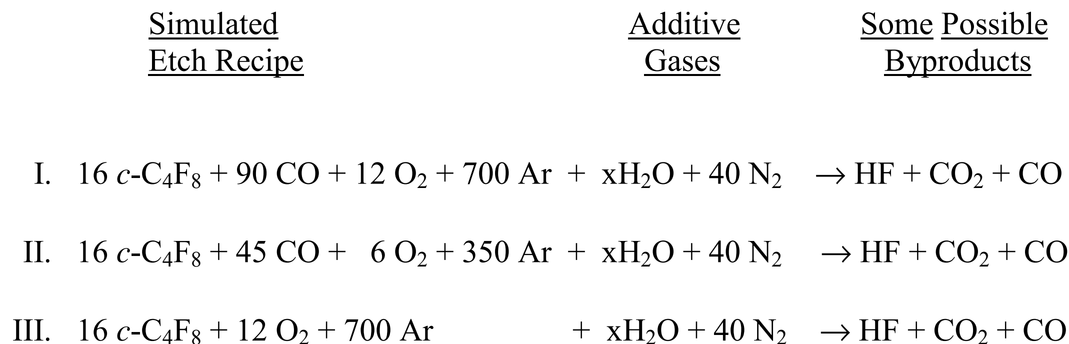
Table 3: Comparison of Some PFC Abatement Techniques

Technique	Gas	Additive Gas	DRE (%)	Negative aspects	Properties	Reference
Microwave	CF_4, CHF_3	H_2/O_2	>99%		Surface wave	(29,30)
Thermal	CF_4	Air, CH_4	96	NO_x		(67)
Radiofrequency	$C_2F_6 + O_2$	H_2, H_2O	83	CF_4	low temp	(43,79)
ICP	CF_4, CHF_3	O_2, H_2O	95	NO_2		(76)
Catalyst	C_4F_8		95	Poisoning of catalyst		(61)
Glow Discharge/Arc	CF_4	H_2/O_2, H_2O	95	CF_4		(78)
CPC	CF_4,C_2F_6	O_2	66,83			(62)
Microwave	CF_4, C_2F_6	H_2O, O_2	94	NO_x,CF_4	Atmospheric pressure	(48,71)

Plasma Abatement of Octafluorocyclobutane

As previously mentioned in chapter II, beta-studies using SWP plasma abatement on 200 mm recipes including CHF_3 and CF_4 have been conducted at Motorola (29,30). Additive gases separate from the initial manufacturing recipes for experiments included molecular hydrogen and oxygen with DREs greater than 99.8% with no notable negative impacts on the SWP system or the etch chamber. Therefore, this technology has the potential for further advancing 300 mm manufacturing recipes that are currently being introduced in manufacturing facilities. Actual manufacturing recipes for 300 mm technology were not used in this study because of propriety reasons but we have amended them to establish proof of principal applications of the surface wave plasma abatement technology. The main difference in the actual and simulated recipes is the starting flow rates of c-C_4F_8, which are approximately two times greater in the actual

recipes than the recipes below. Various simulated experimental recipes were studied using the previously discussed schematic shown in Figure 4, as follows:



	Simulated Etch Recipe	Additive Gases	Some Possible Byproducts
I.	$16\ c\text{-}C_4F_8 + 90\ CO + 12\ O_2 + 700\ Ar$	$+\ xH_2O + 40\ N_2$	$\rightarrow HF + CO_2 + CO$
II.	$16\ c\text{-}C_4F_8 + 45\ CO + 6\ O_2 + 350\ Ar$	$+\ xH_2O + 40\ N_2$	$\rightarrow HF + CO_2 + CO$
III.	$16\ c\text{-}C_4F_8 + 12\ O_2 + 700\ Ar$	$+\ xH_2O + 40\ N_2$	$\rightarrow HF + CO_2 + CO$

Each of these simulated manufacturing recipes, I-III, was studied extensively pre- and post-plasma. The simulated recipe was balanced to understand the quantity of water to be added to the reaction as well as the quantity of the predicated byproducts such as HF, CO and CO_2 prior to each plasma abatement experiment. The starting amount of additive water vapor for all of the above reactions is 64 sccm because the purpose is to drive fluorinated initial reactants to more thermodynamically favorable byproducts. Balanced pre-experimental byproducts for recipe I are 128 HF equivalents, 109 CO equivalents, and 45 CO_2 equivalents, recipe II are 128 HF equivalents, 76 CO equivalents, and 33 CO_2 equivalents while recipe III include 128 HF equivalents, 45 CO equivalents and 19 CO_2 equivalents as the byproducts. For each experiment, three independent spectra were co-added for pre-plasma components to obtain their FTIR spectra and between 25-30 scans for corresponding QMS for pre-plasma experiments. Each spectral recording was then repeated for the indicated applied powers at 500 W, 1000 W, 1500 W and 1950 W respectively.

Results and Discussion

Experiments were conducted to determine the destruction and removal efficiency of *c*-C_4F_8 in simulated semiconductor process feedstock and the optimization of additive water vapor at various applied microwave powers to generate the most desirable environmental products. The performance of the surface wave plasma (SWP) device can be characterized as destruction and removal efficiency. The percentage value that we use is that for the perfluorocompound that has been destroyed calculated using the relationship below (80)

$$\%DRE = \left(\frac{W_{in} - W_{out}}{W_{in}} \right) x\,100$$

where W_{in} and W_{out} describe the amount of perfluorocompound before and after the plasma application process considered in greater detail. Experiments were initially conducted without the additive water at different applied microwave powers in order to understand the byproducts that stem from wafer etch feedstock. The actual manufacturing etch chamber process uses applied radiofrequency power at 13 MHz so the products and the distributions may be slightly different than with microwave power due to power intensities and the presence of silicon tetrafluoride, SiF_4 generated in the commercial process. This silicon tetrafluoride is a byproduct from the reaction of the atomic fluorine and the wafer. The byproducts seen in the laboratory experiment include COF_2, *c*-C_4F_8, and NO_x. The reformation of PFCs, shown in Figure 6, can be attributed to the stability of the fluorinated molecule with no additive gas to drive the reaction

displaced from reformation and towards thermodynamically desired byproducts. The hydrogen content of the additive water was exploited to drive products to the formation of HF, an extremely stable diatomic molecule. This prevented the reformation of any PFCs since the H-F bond dissociation energy is 132 kcal per mol, which is stronger than the C-F bond. Modeling of the plasma verified the reformation of PFCs along with the absence of HF. Kinetic studies of recipe I without additive water were conducted to see the byproduct distribution versus using additive water. Stable PFCs such as C_2F_6 and CF_4 were apparent in the modeling studies along with various other fluorinated products (CF_3, CF_2, F, F_2, and C_2F_5), accounted for approximately 29300 ppm whereas with additive water under the same conditions the same PFCs accounted for 32.72 ppm. No HF could be detected in the plasma products without addition of water. In the presence of hydroxyl and oxygen radicals the carbon containing species are presumably oxidized to carbon monoxide and carbon dioxide through reactions such as $C + O_2 \rightarrow CO + O$ and $CO + OH \rightarrow CO_2 + H$. Therefore, the optimization of water vapor is vital to achieving an optimal DRE and optimized end product distribution. Detailed considerations of reactions in the plasma will be discussed in chapter 5, which considers the plasma mechanisms of the abatement process in greater detail. Initial experiments were conducted using a needle valve assembly to monitor the flow rate of water. However, using the needle valve approach caused instability and maintenance problems that adversely affected reproducibility of our measurements. Consequently, a MKS type 1640 pressure based MFC pressure based flow controller was substituted to monitor the flow rate of water giving more precision and reliable results.

Simulated manufacturing feedstock recipe I was extensively studied. The path-length setting on the White cell was set at 2 meters that corresponds to the lowest recipe I which includes 16 sccms c-C_4F_8, 90 sccms CO, 12 sccms O_2 and 700 sccms Ar are shown in Figure 7. The lower trace of the infrared spectra corresponds to recipe I with no additive water or applied power. The lower trace shows the ring deformation v_{21} at 980 cm^{-1}, CF_2 stretch v_{20} at 1219 cm^{-1}, ring deformation $v_{21} + v_3$ at 1317 cm^{-1}, and CF_2 stretch v_6 at 1336 cm^{-1}, which are the main infrared absorptions (81,82). The addition of the water vapor deterred the reformation of the PFC, by providing a pathway for more thermodynamically stable byproducts as well as decreasing the amount of COF_2 along with NO_x. The latter were not apparent in significant amounts as shown in the upper trace of Figure 7. At lower applied microwave powers such as 500 W, carbonyl fluoride was determined to be at 115 ppm corresponding to a DRE of 95.94%. Using the calibration curves, which are in Appendix A, along with the absorbance area of each byproduct, the DRE was calculated at 99.88 ± 0.02% using 1950 W of applied microwave power with a flow rate of 85 sccm of water vapor. Any harmful byproducts such as carbonyl fluoride, COF_2, and hydrogen fluoride, HF, were water scrubbed downstream and neutralized before the remaining gaseous byproducts were emitted into atmospheric release.

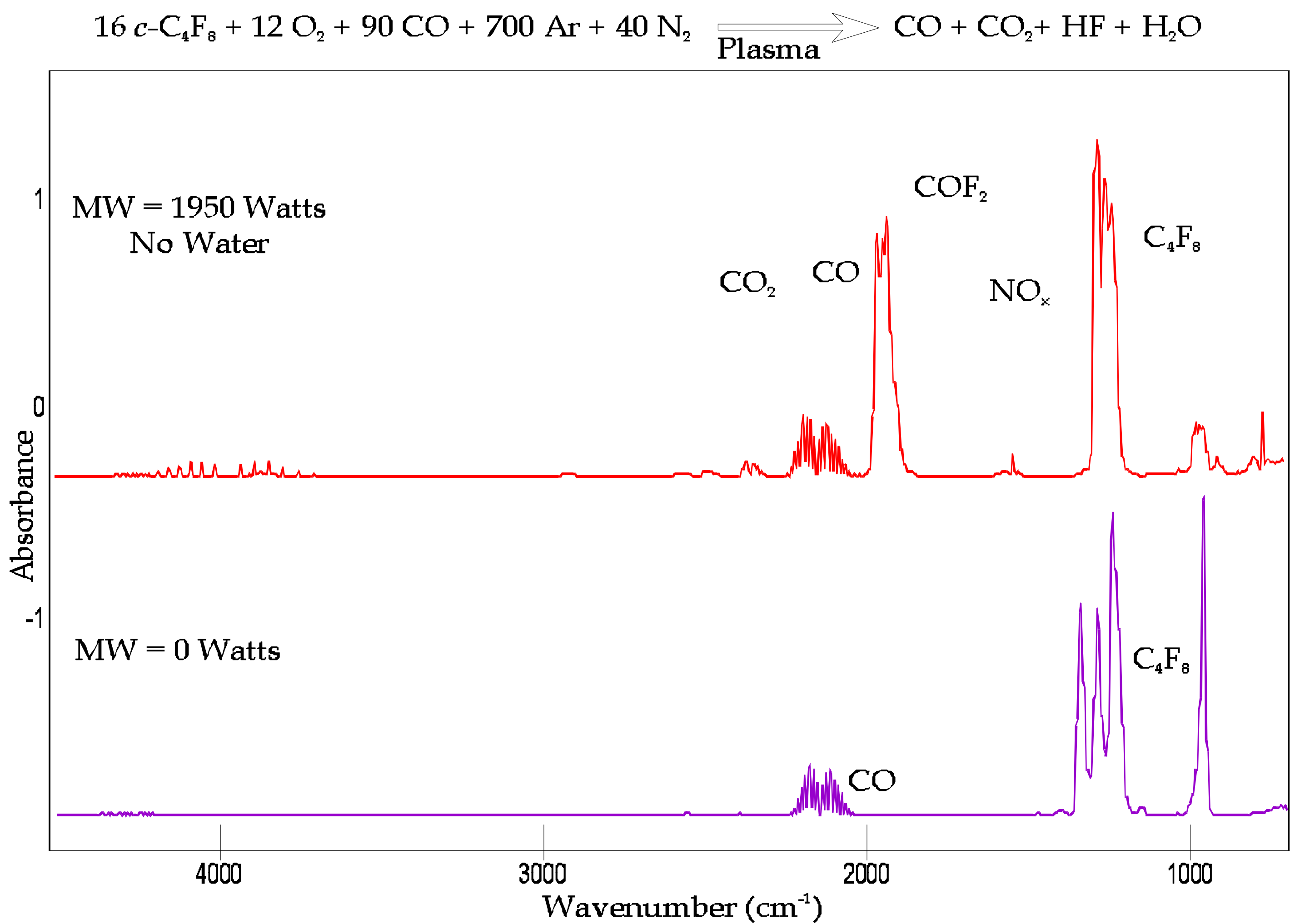


Figure 6: Ilustration of FTIR possible etch chamber byproducts due to the lack of additive water in the etch chamber

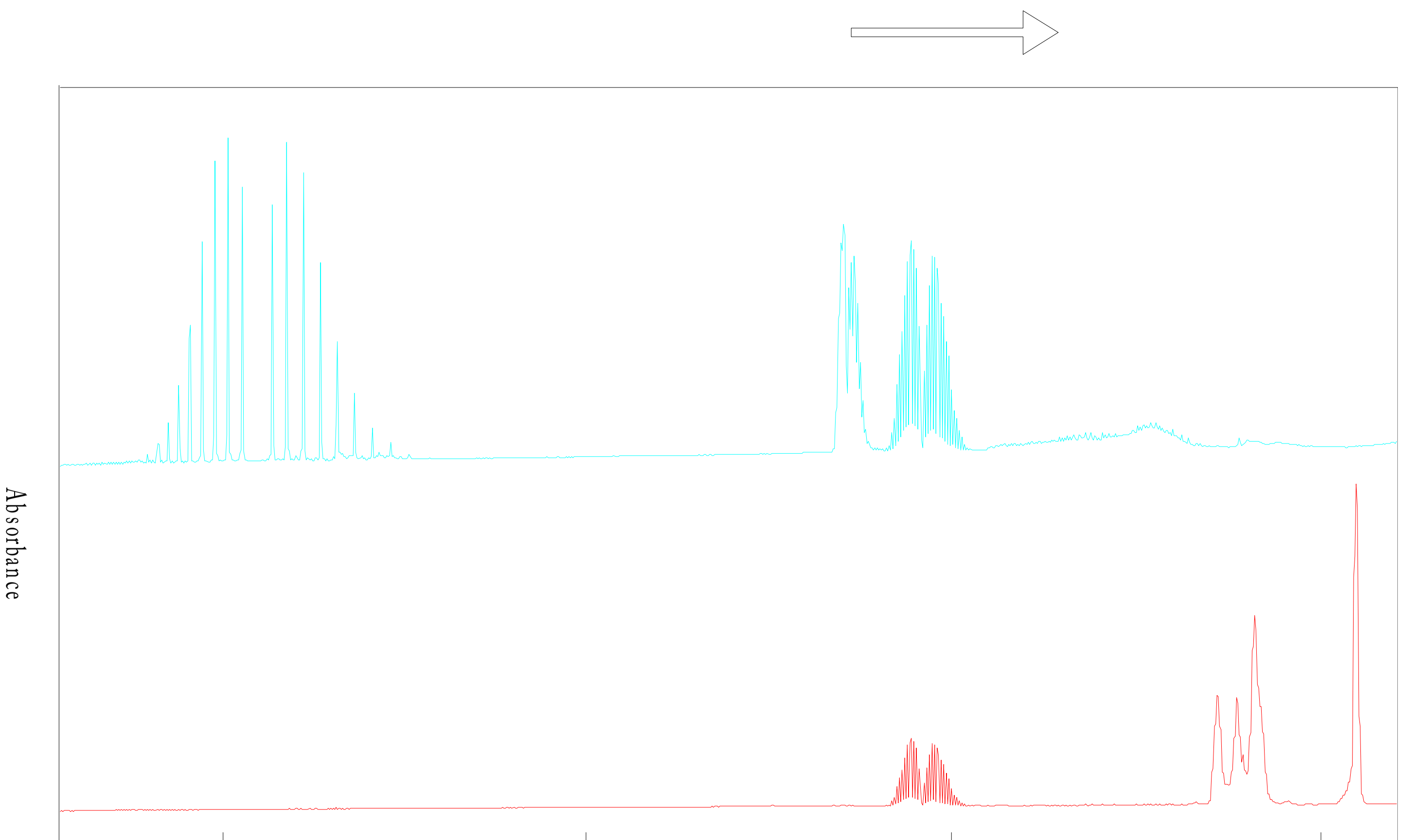


Figure 7: FTIR spectra of plasma abatement of recipe I which includes 16 c-C_4F_8, 90 CO, 12 O_2, 700 Ar and 85 H_2O at 0 watts and 1950 watts applied microwave power

Recipe II was studied to determine any differences in product distribution for abatement of c-C_4F_8 with specific changes in the flow rates of other feedstock components in the etch gases. Plasma abatement studies and spectral analysis were conducted on recipes II and III in the same manner as recipe I. Figure 8 demonstrates spectral recording from the plasma abatement experiments on simulated manufacturing recipe II in which the recipe contained the same amount of fluorine as recipe I but only half the CO:O_2 and Ar flow rates i.e. 45 sccm CO, 6 sccm O_2, and 350 sccm Ar. The pre-plasma infrared spectrum is shown in the lower trace of Figure 8, which contained no applied microwave power or any additive gases such as water, and the upper trace is the post-plasma abatement infrared spectrum. No significant changes were noticed spectrally regarding the final stable byproducts from recipe I to recipe II, which was not unexpected. Using the calibration curves in Appendix B along with the absorbance area of each byproduct, the DRE was calculated at 99.92 ± 0.03% using 1950 W of applied microwave power with a flow rate of 85 sccm of additive water. Again, any harmful byproducts such as carbonyl fluoride, COF_2, and hydrogen fluoride, HF, were subsequently water scrubbed and neutralized before atmospheric release.

Recipe III was also studied to see the effects, if any, of not having CO in the initial reactants. The initial ppm concentration of each reactant in Recipe III was determined to be approximately 40% greater than the previous recipes because the nitrogen dilution was lower than for the previous two recipes. Figure 9 illustrates the water vapor optimization experiments conducted on *c*-C_4F_8 with no initial/pre-plasma carbon monoxide.

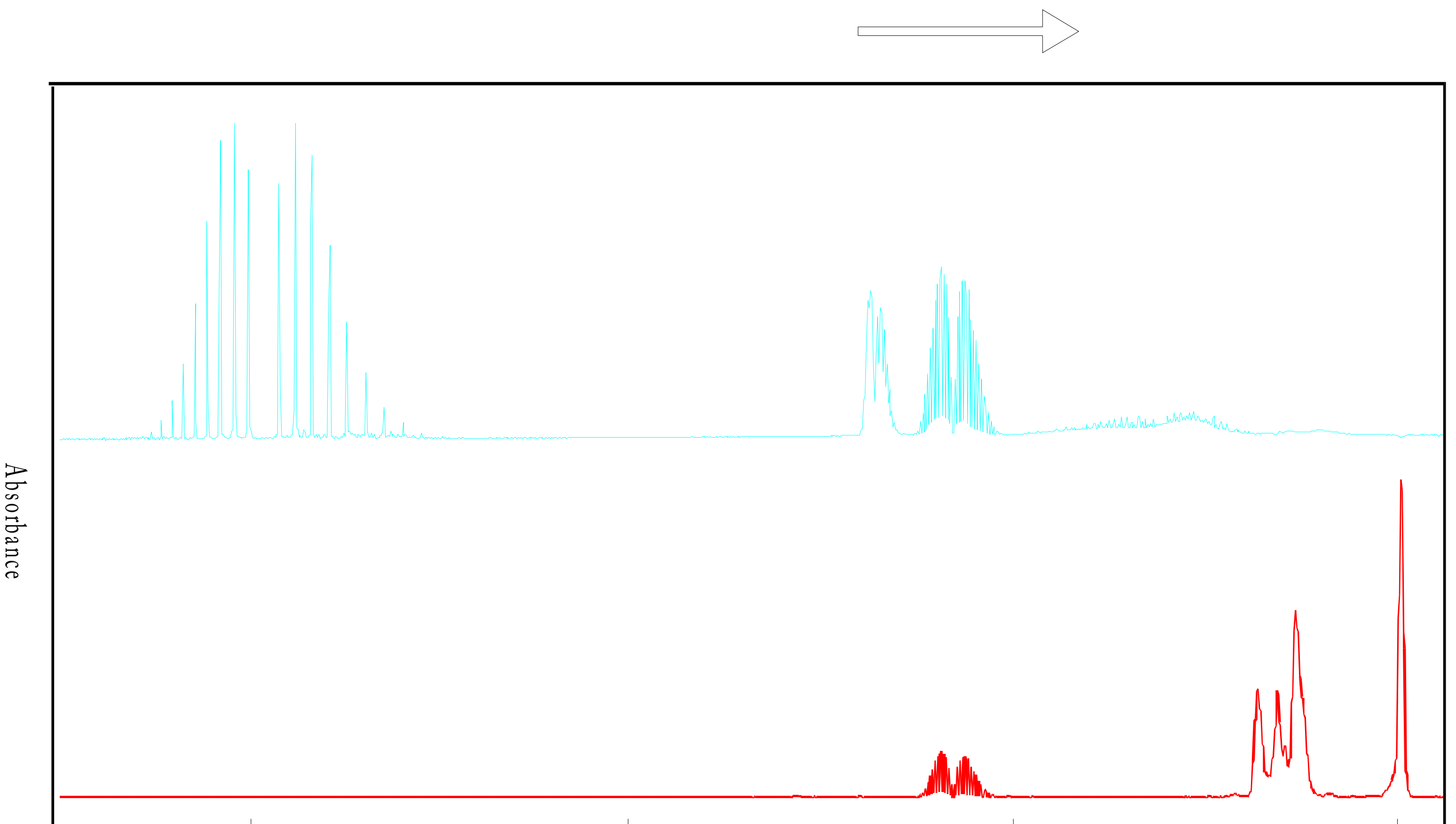


Figure 8: FTIR spectra for plasma abatement of recipe II which includes 16 c-C_4F_8, 45 CO, 6 O_2, 350 Ar and 85 H_2O at 0 watts and 1950 watts applied microwave power

This recipe was investigated to see the effects on the final product distribution, if any, due to the initial reactant concentration of. Pre-plasma infrared spectrum of recipe III does not contain any additive gases or applied power and is illustrated in the lower trace of Figure 9. The difference in the recorded spectrum from the previous two, Figures 6 and 7 is the absence of pre-plasma CO in the region of 2000-2250 cm^{-1}, which is identified with the stretching vibrational mode centered at 2143 cm^{-1}. Again, spectrally there are no obvious post-plasma changes regarding byproducts from the previous two simulated manufacturing recipes as shown in the upper trace of Figure 7. The absorbance of HF has increased with the respect to the previous recipes since the inlet concentration in ppm of C_4F_8 was greater. The calibration curves were again applied and the experiment yielded a DRE of 99.93 ± 0.02% using 1950 W of applied microwave power and a flow rate of 85 sccm of additive water. Any harmful byproducts such as carbonyl fluoride, COF_2, and hydrogen fluoride, HF, were water scrubbed and neutralized before atmospheric release.

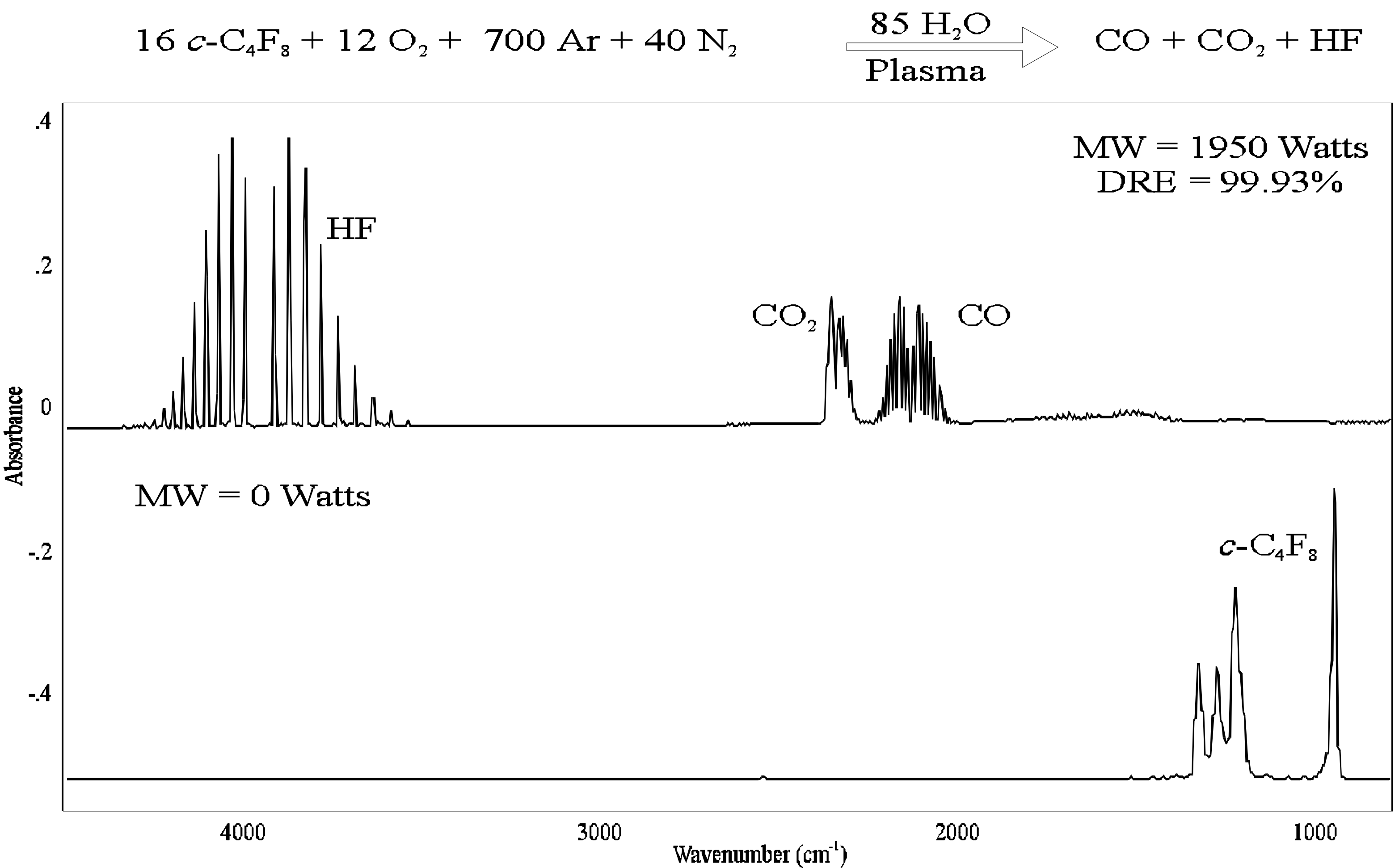
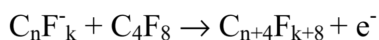


Figure 9: FTIR spectra of surface wave plasma experiments of recipe III with out component carbon monoxide at 0 and 1950 watts applied microwave power

Balancing the recipe equations with the premise that initial fluorine with be driven to thermodynamically very stable HF, gave a starting point for optimizing the concentrations of water vapor required to optimize experiments. Recipe I contained 128 fluorine equivalents, so it is optimal to drive all radical fluorine to HF in post-plasma experiments and that should be achieved with approximately 64 sccm of gaseous water. However, in practice it was found that 64 sccm of water yielded a lower DRE, approximately 97.8%, than that found using a higher flow rate of water. It also produced additional COF_2, 146.7 ppm, as opposed to the situation when 85 sccm of water vapor was added. Two plausible explanations for these observations can be made 1) some of the side reactions that drive fluoride present to HF took place in a cooler region of the plasma or post-plasma or 2) *c*-C_4F_8 generates polymerization products in the plasma. Various investigations into polymer formation and the mechanism by which this is possible were studied (83-85). Takahashi and Tachibana investigated the formation of octafluorocyclobutane polymer in a radiofrequency generated plasma (86). Plasmas including CF_4 and C_2F_6 show little or no formation of polymers since these molecules are quite stable. However, in *c*-C_4F_8 plasmas, a possible polymer chain could result that can form is through processes such as:



$$C_nF^-_k + C_4F_8 \rightarrow C_{n+4}F_{k+8} + e^-$$

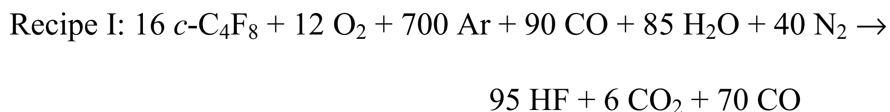
which can indicate associative electron detachment. PFCs are sometimes chosen for semiconductor wafer etch due to a certain degree of polymerization. Research suggests that a key to the generation of fluorinated polymers is the formation of CF_2. Dissociation of octafluorocyclobutane can yield CF_2 through a number of pathways

which will be explored later via mass spectrometry and thermodynamic modeling. This work indicates that it is possible for polymerization to be initiated which could give a reason for having to use more water vapor than would have been initially expected. Consequently, to deter formation of COF_2 and to achieve an optimal DRE for c-C_4F_8, 85 sccm of water vapor was applied for all experiments involving feedstock steams involving 16 sccm of octafluorocyclobutane.

Table 4 illustrates the destruction and removal efficiencies for *c*-C_4F_8 using the different simulated manufacturing recipes, microwave powers and contains reaction pressures along with air-cooled exhaust temperatures. All DREs were determined by collecting independent spectra and averaging experimentally recorded spectra together. Since the plasma is a non-equilibrium medium, three independent spectrum were taken for each recipe at each given power. For each independent spectrum, the initial and final byproduct transition profiles was integrated to obtain a total peak area. These peak areas were then averaged together for each experiment at each recorded applied microwave power. All peak calibrations were used to obtain concentrations of final stable byproducts.

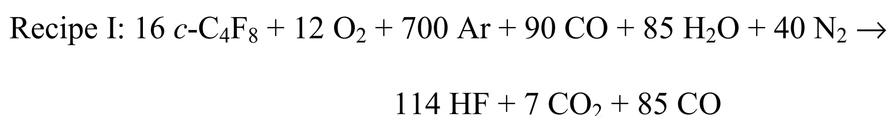
Determination of mass balance information for each recipe is essential for a quantitative evaluation of the different optimization experiments. Using the calibration curves, Appendix B, all byproduct measurements were converted to concentrations in ppm for use in mass balance equations. All recipes are balanced with respect to fluorine since there are complications associated with the accurate determination of water as in a detailed calculation in Appendix A. End product distributions of each recipe were

determined for each byproduct component for each recipe. Predicated on balanced equations for recipe I suggests that CO concentration should be slightly higher than HF. Experimental mass balance equation for recipe I below show:



$$\text{Recipe I: } 16\ c\text{-}C_4F_8 + 12\ O_2 + 700\ Ar + 90\ CO + 85\ H_2O + 40\ N_2 \rightarrow 95\ HF + 6\ CO_2 + 70\ CO$$

Applying a correction factor yields a mass balance equation of



$$\text{Recipe I: } 16\ c\text{-}C_4F_8 + 12\ O_2 + 700\ Ar + 90\ CO + 85\ H_2O + 40\ N_2 \rightarrow 114\ HF + 7\ CO_2 + 85\ CO$$

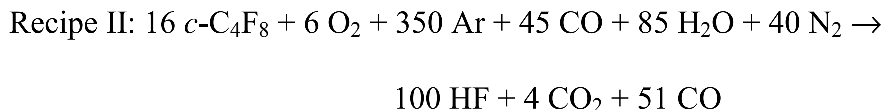
Table 4: Destruction and Removal Efficiencies of c-C_4F_8[a]

Recipe #	Power[a] (W)	Pressure[b] (mTorr)	Temperature[e] (˚C)	H_2O[e] (sccm)	FTIR DRE (%)
I	500	687	35.61	85	95.94
I	1000	706	50.78	85	98.99
I	1500	720	65.72	85	99.72
I	1950	731	78.38	85	99.88 ± 0.03
II	500	449	35.22	85	96.39
II	1000	465	50.33	85	99.35
II	1500	475	65.11	85	99.90
II	1950	486	77.78	85	99.92 ± 0.02
III	500	625	35.83	85	91.67
III	1000	646	51.22	85	99.23
III	1500	662	66.55	85	99.80
III	1950	671	78.22	85	99.93 ± 0.02

a DREs from FTIR and MS agree to within 1%
b Microwave power stability ± 0.1%
c Pressure measurements ± 0.5 mTorr
d Temperature measurements ± 0.05 °C
e Flow rate error ± 1% of full scale

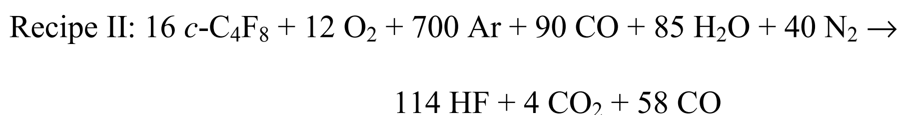
Recipe II contained half the amount of carbon monoxide and molecular oxygen relative to initial reactants used in recipe I. Decrease in the applied oxygen in the reactants could

change the byproduct distribution. The mass balance recipe for recipe II is illustrated below:



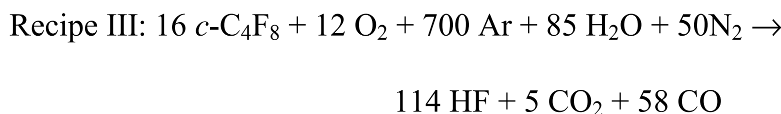
$$\text{Recipe II: } 16\ c\text{-}C_4F_8 + 6\ O_2 + 350\ Ar + 45\ CO + 85\ H_2O + 40\ N_2 \rightarrow 100\ HF + 4\ CO_2 + 51\ CO$$

Again, the correction factor was applied to this mass balance equation:



$$\text{Recipe II: } 16\ c\text{-}C_4F_8 + 12\ O_2 + 700\ Ar + 90\ CO + 85\ H_2O + 40\ N_2 \rightarrow 114\ HF + 4\ CO_2 + 58\ CO$$

The mass balance equation for recipe III using 85 sccm of applied water vapor is given as follows:



$$\text{Recipe III: } 16\ c\text{-}C_4F_8 + 12\ O_2 + 700\ Ar + 85\ H_2O + 50N_2 \rightarrow 114\ HF + 5\ CO_2 + 58\ CO$$

The various end product distributions for the recipes are illustrated in Table 5. The main differences between all three recipes are observed in the distributions between the product CO and CO_2 as well as HF. Initial fluorine equivalents and end product distributions are within 2% for all recipes involving 85 sccm of water vapor, which indicates great care in these experiments. This allows for reproducibility of experiments, which is key for ongoing investigations and for possible commercialization of this abatement technology.

Table 5: Plasma Product Distribution and Mass Recovery of c-C_4F_8[a]

Recipe	Power (W)	c-C_4F_8 (ppm)	H_2O (ppm)	COF_2 (ppm)	CO (ppm)	CO_2 (ppm)	HF (ppm)	Mass Recovery/ Corrected (%)
I[b]	1950	.430	37.5	5.79	768.2	61.11	1034	75/89
II[c]	1950	.381	33.7	5.76	479.4	36.70	946.8	77/89
III[d]	1950	.396	31.63	5.71	742.9	57.52	1461	89

a ppm errors ± 5% b initial ppm 422 of C4F8 c C4F8 ppm 419 d C4F8 ppm 590

Determination of the final experimental byproduct concentrations in recipes I-III indicated that carbon monoxide in the recipe had an effect on the final concentration of HF. To verify this observation, a known concentration of the plasma product HF was added to the plasma reactor at 1950 W with specific concentrations of carbon monoxide and oxygen. These additional experiments were conducted to determine the influence of the plasma on the presence of HF and if necessary to help determine a correction factor for the loss of HF as products such as F_2 for recipes I and II that could not be monitored using our analytical instrumentation. Recipe I initially included 2377 ppm of CO which led to the greatest lost of HF by 25.9% whereas recipe II which initially included 1181 ppm of CO had a corresponding loss of 22% HF. Since recipe III contained no initial CO it was assumed that no loss of HF could be attributed to this source. Therefore, the post-plasma experimental concentrations of HF were corrected by the appropriate amount as determined above to obtain a more accurate concentration. Concentrations of HF were observed to increase from 821 to 1034 for recipe I and 776 to 947 for recipe II

with an estimated error of 10%. Any atomic fluorine that is not recovered as HF can also be water scrubbed to reduce the environmental impact.

Mass spectrometry was also performed to monitor IR inactive species as well as to provide an independent determination of the accuracy of measurement for both reactants and products for all recipes previously studied by FTIR. Recipes I and II contain the same pre-plasma reactants, *c*-C_4F_8, CO, N_2, Ar, and O_2. The molecular weight peak of *c*-C_4F_8 at $m/z = 200$ is not apparent in the spectrum without applied microwave power, either in Figure 10 for recipe I or Figure 10 for recipe II, indicating that the molecule can be easily dissociated by impact with 70 eV electrons in the spectrometer. Distinctive patterns of mass to charge ratio (m/z) were seen before plasma application for *c*-C_4F_8 (131$C_3F_5^+$:100 $C_2F_4^+$:69 CF_3^+), CO (28CO^+:12C^+), N_2 (28N_2^+:14N^+), Ar (40Ar^+:20Ar^{++}) and O_2 (32O_2^+:16O^+). Once the microwave power was applied the integrity of the spectral features arising from *c*-C_4F_8 decreased substantially and byproducts such as CO_2 (44CO_2^+:28CO^+:16O^+:12C^+) and HF (20HF^+:19F^+) arose along with CO as shown in Figure 10 and Figure 11. Such decreases in integrity correlate with DREs of 98.57% and 98.65% respectively at 1950 W corresponding to 85 sccm of additive H_2O. The difference in the DREs can be attributed to mechanisms or the non-equilibrium status of the SWP plasma. The absence of an observed peak at $m/z = 30$, NO^+, verifies that no nitrogen oxides were formed from the plasma abatement process.

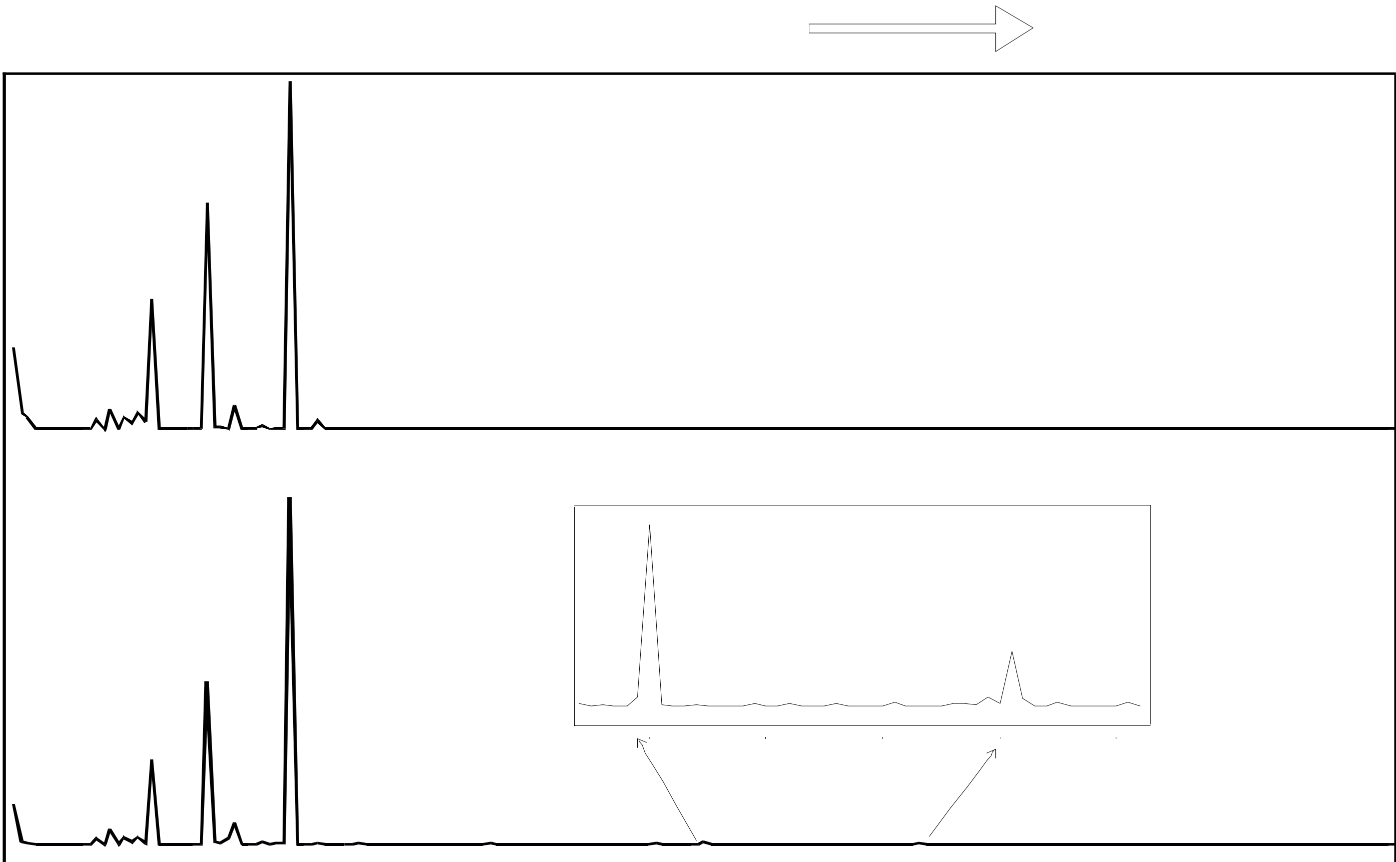


Figure 10: Mass spectra obtained during plasma abatement experiments of recipe I with and without applied microwave power

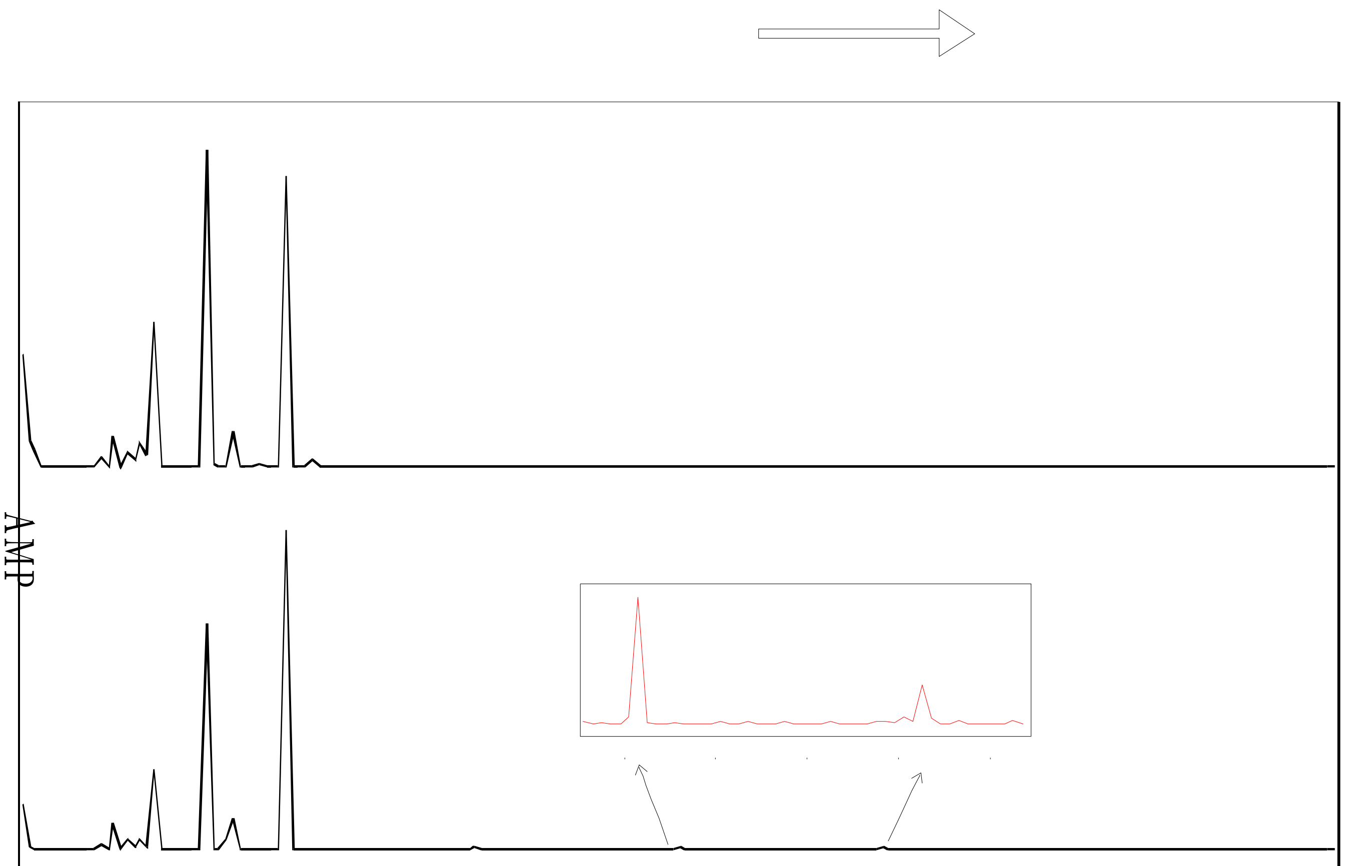


Figure 11: Mass spectra pre- and post- plasma abatement conducted using recipe II

Mass spectrometric studies were also continued on recipe III which contained *c*-C_4F_8, N_2, Ar, and O_2components in the feedstock. The absence of the molecular weight peak of *c*-C_4F_8 at *m/z* = 200 indicated that the molecule can be easily dissociated by electron impact from the MS source as shown in the lower trace of Figure 12. Distinctive patterns (*m/z*) for *c*-C_4F_8 (131$C_3F_5^+$:100 $C_2F_4^+$:69 CF_3^+), N_2 (28 N_2^+:14N^+), O_2 (32O_2^+:16O^+), and Ar (40Ar^+:20Ar^{++}) were seen before plasma application. Application of the microwave to the power surface wave applicator gave rise to spectral features of byproducts such as CO_2 (44CO_2^+:28CO^+:16O^+:12C^+), CO (28CO^+:12C^+), and HF (20HF^+:19F^+) as shown in the upper trace of Figure 10 giving a DRE of 98.57% at 1950 W. The absence of a peak at *m/z* = 30, NO^+, verifies that no nitrogen oxides were formed from the plasma abatement process.

Mass spectroscopy can also be useful in determining basic reactions that should occur in the plasma by studying the fragmentation patterns of the molecule being investigated. The two main fragments of *c*-C_4F_8 are the base peak $C_2F_4^+$, which occurs at *m/z* = 100, and $C_3F_5^+$, *m/z* = 131. These indicate a variety of intermediates that can form in the plasma through electron impact reaction such as CF_3, C_2F_2, and CF_2. C_2F_4 can dissociate into CF_2, CF and C + F. The formation of tetrafluoromethane is possible at lower applied microwave powers, but it not apparent at higher powers due to fluorine being converted to HF in reactions with hydrogen as shown in previous studies (29,31) as well as the possibility of products that can not be detected using our current analytical instrument. Possible intermediates could include OF, COF, CFH, $HOCF_2$, F_2, and CF (44,74), but these could not be detected using our current instrumentation. Modeling of

octafluorocyclobutane would be helpful to better understand the intermediates of the non-equilibrium surface wave plasma and the results of much investigation will be discussed in chapter V. Table 6 illustrates some basic plasma reactions that are likely to be significant during the plasma reaction along with their respective rate constants. Additional reactions are included in Appendix C.

Table 6: Plasma Reactions of *c*-C_4F_8			
Reaction	Rate Coefficient[b]	Reaction	Rate Coefficient[b]
$C_4F_8 + e \rightarrow C_2F_4 + C_2F_4 + e$	a	$H_2O + e \rightarrow H + OH$	a
$C_4F_8 + e \rightarrow CF_3 + C_3F_5 + e$	a	$H + F^- \rightarrow HF + e$	$1.6x10^{-9}$
$C_2F_4 + e \rightarrow CF_2 + CF_2 + e$	a	$C + O_2 \rightarrow CO + O$	$1.60x10^{-11}$
$C_3F_5 + e \rightarrow C_2F_4 + CF + e$	a	$CF + O \rightarrow CO + F$	$3.90x10^{-11}$
$CF_3 + e \rightarrow CF_2 + F$	a	$O + CF_2 \rightarrow COF + F$	$1.40x10^{-11}$
$CF_2 + e \rightarrow CF + F + e$	a	$N_2 + e \rightarrow N_2^* + e$	a
$Ar + e \rightarrow Ar^* + e$	a	$Ar^* + N^* \rightarrow N^+ + Ar + e$	$5.00x10^{-11}$
$Ar^* + e \rightarrow Ar^{**} + e$	$8.87x10^{-7}$	$N^+ + C_4F_8 \rightarrow C_4F_8^+ + N$	$1.75x10^{-9}$
$O_2 + e \rightarrow O_2^* + e$	a	$OH- + H \rightarrow H_2O + e$	$1.4\text{-}x10^{-9}$
$O + e \rightarrow O^* + e$	a	$H_2O + O^* \rightarrow OH + OH$	$2.50x10^{-10}$
$CO + e \rightarrow C + O + e$	a	$O^* + CF_4 \rightarrow O + CF_4$	$1.80x10^{-13}$
$F + CO \rightarrow COF$	$2.76x10^{-13}$	$COF + OH \rightarrow CO_2 + HF$	$1.0x10^{-11}$
$O^- + C_4F_8 \rightarrow O + C_4F_8^-$	$1.00x^{-10}$	$O^+ + C_4F_8 \rightarrow C_4F_7^+ + F + O$	
a computed using the electron energy distribution and electron impact cross section b units of $cm^3\ s^{-1}$			

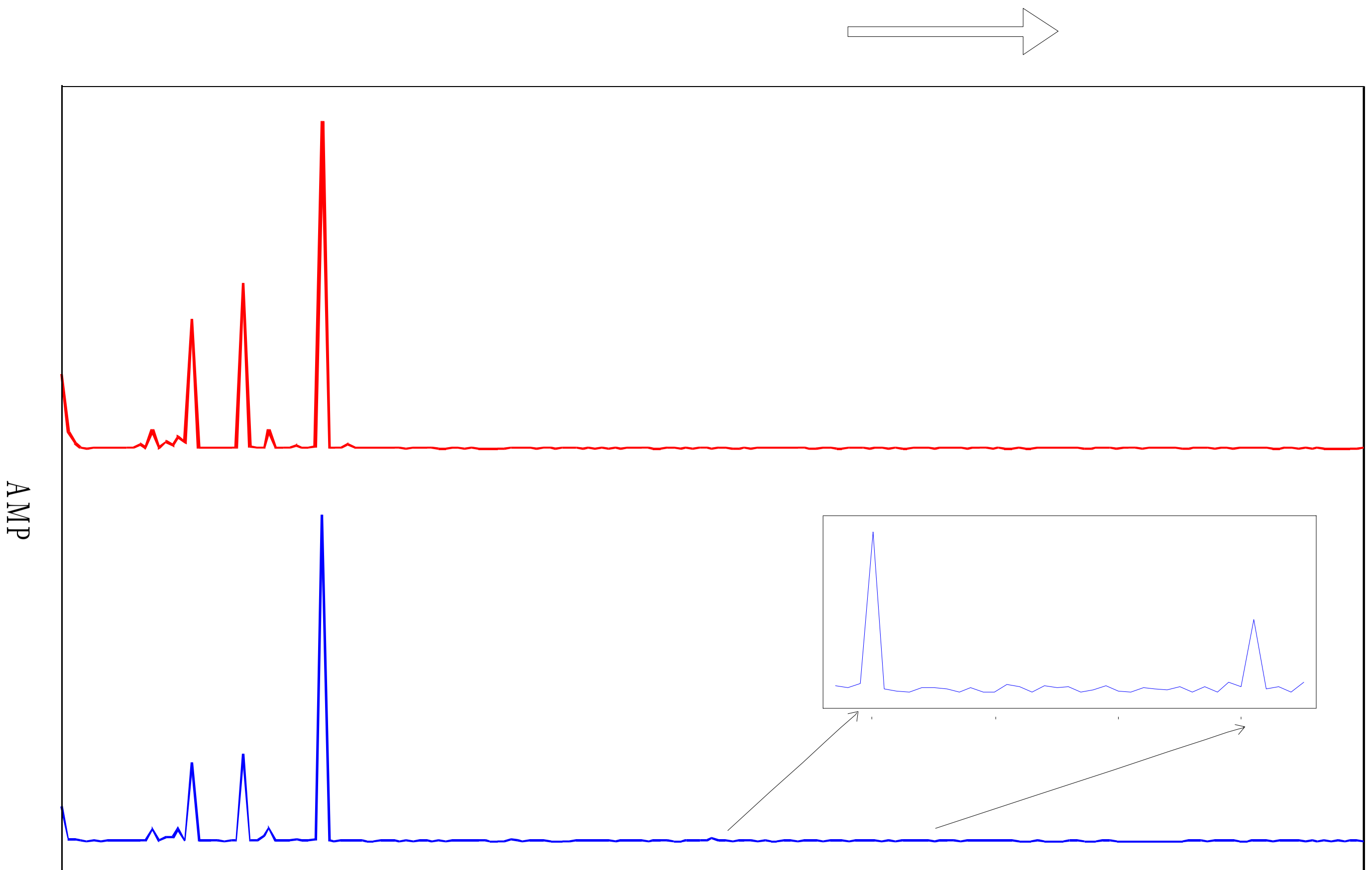


Figure 12: Mass spectra of plasma abatement of recipe III, 16 *c*-C_4F_8, 12 O_2, 700 Ar and 85 H_2O with and without applied power

CHAPTER IV

DICHLORODIFLUOROMETHANE

AND TRICHLOROFLUOROMETHANE ABATEMENT

Review of CFC Use Abatement in Refrigerant Industry

The Abortion of a Young Steam Engineer's Guide penned by Oliver Evans proposed the first believed refrigeration system in 1805, which involved a closed cycle of refrigeration to produce ice using a volatile liquid refrigerant. Jacob Perkins initially designed such a system and an experimental prototype was completed by Hague, Bramwell and Crampton. The first commercial vapor compression system employed ethyl and methyl ethers. Charles Telier of France began to experiment with ammonia as a refrigerant in 1862, and a patent for carbon dioxide in vapor compression systems was issued in 1850. Sulfur dioxide began use as a refrigerant in 1875 because it was low cost alternative and employed low operating pressures. Even though SO_2 is toxic, its noxious odor actually helped with safety (12). Frigidaire, General Motors and Du Pont began a search for less toxic alternatives after fatal accidents in the 1920's (87).

Dichlorofluoromethane, CCl_2F_2 or CFC 12, was first introduced as a refrigerant commercially in 1931 by Frigidaire for use in small ice cream cabinets. The Department of Agriculture was the first to use CFC 12 as an aerosol propellant in 1943. Trichlorofluoromethane, CCl_3F or CFC 11, was commercially introduced in 1932. It was first produced for commercial purposes by Kinetic Chemicals Company and began

use as a propellant in 1943 (12). The Alternative Fluorocarbons Environmental Acceptability Study (AFEAS) kept records of the production and sales of fluorocarbons. Production of CFC 11 was estimated at 8,311 metric tons in 2001. This is an approximate drop of 15% from the year of 2000. In the year 2000, the corresponding global average surface concentration of CFC 12 was 435 pmol mol^{-1} (13).

Stockpiles of CFCs were accumulated because of the ban on manufacturing resulting from the Montreal Protocol. Technology to destroy CFC stockpiles must be compliant with DREs greater than 99.99% and must not produce any perfluorocompounds or hydrofluorocarbons (88). Therefore, any abatement technology must meet these requirements to be employed for industrial applications in the U.S. Technologies available for abatement of chlorofluorocarbons range from catalytic to plasma-based. Destruction and removal of CFCs were investigated using a number of methods employing catalytic decomposition (89-99). The majority of these studies were conducted using CFC 12, CF_2Cl_2, because of the equal number of fluorine and chlorine molecules. Various types of catalysts have been employed such as WO_3/M_xO_y(M = Ti, Sn, Fe), vanadium oxides, γ-alumina, and $Zr(SO_4)_2$. Conversion rates of ~47% were achieved using γ-alumina and hydrocarbons. Research into catalytic decomposition abatement found that water was a driving force for conversion or decomposition of the CFCs. However a maximum of 5 mol% must not be exceeded because the excess water may start to adsorb in the active site of $Zr(SO_4)_2$. Any halogen acids such as HCl and HF have been washed with basic solutions for neutralization. Bypdroducts of catalytic abatement were CO_2 along with $CClF_3$. Application of thermal technologies for this

purpose include an incineration or destruction in a turbulent flame (88,100-102). Abatement of CFC 11, 12 and 113 has also been investigated and using this technology DREs >99.9% were demonstrated. Pederson and Källman found that the halogen to hydrogen ratio was critical to achieving optimal destruction when using water (101). An Australian PLASCON system has been employed using a thermal dc plasma torch however, using molecular oxygen and a 1:1 ratio of CFC to H_2O yields 7% byproducts such as CF_4 and $CClF_3$. A 1:2 ratio of CFC to water produced no CFCs or PFCs with a DRE of 99.99%. Non-thermal plasma studies for the destruction of chlorofluorocarbons include radiofrequency applications (32,33,103), microwave applications (104-107), atmospheric pressure discharge (108,109), dielectric barrier or silent discharges (110-112), and high-voltage glow plasmas (113). Researchers at National Cheng Kung University studied the abatement of dichlorodifluoromethane, CFC 12, using hydrogen in a cold plasma system (33). Approximately 94% of the Freon was decomposed, and up to 80% conversion occurred with the addition of excess hydrogen. Studies were then conducted for comparing additive gases such a oxygen and hydrogen to the process (103). In an oxygen rich plasma environment, formation of $CF_4 \sim 3$ % mole fraction and reformation of CCl_2F_2 were apparent. In the hydrogen rich environment, formation of HCl and HF waere seen to be produced which makes this plasma more favorable for the destruction of CFCs. Jian and coworkers also studied the decomposition of CFC 12 in a normal pressure plasma reactor via dielectric barrier discharge, but this process formed tetrafluoromethane (112). All of the non-thermal plasma based CFC abatements, fall short of the 99.99% DRE designated by the regulation requirements.

Other techniques that were used for abatement or conversion of CFCs include separation from air via membrane (114), decomposition of CFCs using a high-current pulse slipping surface discharge (115), destruction of halogenated methanes by non-electron capture process (116), plasmochemical methods (117), and reductive dehalogenation (118). Preliminary studies showed that anaerobic soils are capable of removing CFCs from ambient air (119) and the use of ultrasonic chemistry can possibly destroy CFCs (120). Comparisons of some of the previously discussed techniques are illustrated in Table 7.

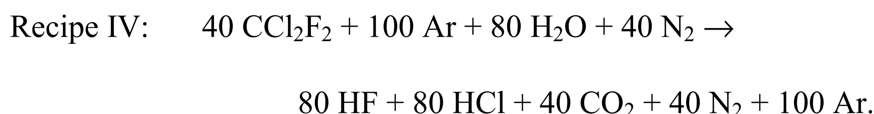
Wang, Lee and coworkers have studied reaction mechanisms of CFC 12 in an O_2/Ar and H_2/Ar plasma environment (103). This study showed that additive hydrogen is a driving force for the formation of HCl and HF and helps inhibit the reformation of CFC 12, CCl_4, and CFC 11. Dissociation mechanisms associated with CFC abatement by non-thermal plasmas has also been studied and the impact dissociation by high energy electrons seems to be responsible for the transformation/destruction of CFCs in the presence of nitrogen (109).

Table 7:Comparisoin of Some CFC Abatement Techniques						
Technique	Gas	Additive Gas	DRE (%)	Negative aspects	Properties	Ref
Catalytic hydrolysis	CFC 12	H_2O	100 97.7	CFC 113	WO_3/SnO_2(475 °C) WO_3/TiO_2 (340 °C)	(98)
	CFC 12	H_2O	~100	CFC 11	$Zr(SO_4)_2$ (400 °C)	(90,92)
	CFC 12	H_2O/Air	100	$CClF_3$	$TiOSO_4$ (310 °C)	(99)
	CFC 12	H_2	~95	CH_4, CFC 12	Alumina supported palladium	(97)
Destructive Adsorption	CFC 12		98	CCl_4	FeO_x/MgO	(96)
Thermal	CFC 11,12		99.995	chlorobenzene	turbulent flame	(101)
Thermal Plasma	CFC 12	Steam O_2	99.99	$CClF_3$, CF_4	dc plasma torch	(88,102)
Microwave	CFC 11	Air	>99.99	Cl_2/F_2	MW torch discharge flame	(105)

Plasma Abatement of Chlorofluorocarbons

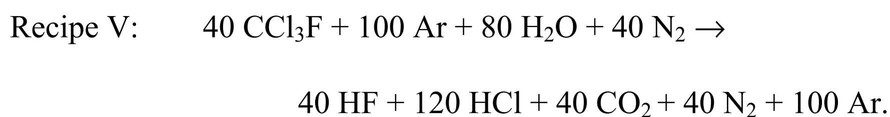
The reduction and ultimate phase-out of the manufacture and use of chlorofluorocarbons has led to industrial stockpiles of CFCs, which must ultimately be destroyed. Surface wave plasma technology is now being applied to the abatement of chlorofluorocarbons for the destruction of gaseous stockpiles. CFC 12 and CFC 11 abatement experiments have thus been conducted using the same surface wave plasma abatement technology as described for the abatement of PFCs in chapter II. The only modifications that were applied included changing the orifice on the mass flow controllers for each new gas and adjusting the sliding short circuit. Adjusting the sliding short circuit allows for coarse tuning of the applied microwave power to the surfaguide which helps enhance the DRE in our experiments. Additive gases were found to

facilitate abatement process and consequently were added to the experimental gas mixture/composition including argon, nitrogen and water. Argon was added to the gas mixture to help ignite and sustain the plasma throughout the abatement experiments. Nitrogen was added to help with purging of the transfer lines and to help enhance the DRE in the plasma abatement experiments. Water, as previously mentioned, is added to favor thermodynamically stable byproducts such as HF and HCl. The ideal amount of additive water vapor was predicted to be 80 sccm because there are 80 fluorine and 80 chlorine equivalents in CF_2Cl_2 so therefore post-plasma there should be a yield of 80 HF and 80 HCl, respectively. Therefore, the idealized stoichiometric equations are:



Recipe IV: $40\ CCl_2F_2 + 100\ Ar + 80\ H_2O + 40\ N_2 \rightarrow$

$$80\ HF + 80\ HCl + 40\ CO_2 + 40\ N_2 + 100\ Ar.$$



Recipe V: $40\ CCl_3F + 100\ Ar + 80\ H_2O + 40\ N_2 \rightarrow$

$$40\ HF + 120\ HCl + 40\ CO_2 + 40\ N_2 + 100\ Ar.$$

Results and Discussion

Experiments were conducted in the same manner as those for the perfluorocompounds to determine the destruction and removal efficiency of CCl_2F_2 and CCl_3F pre- and post-plasma abatement and the optimization of additive water vapor at various applied microwave powers. Abatement experiments were conducted using 500 W, 1000 W, 1500 W, and 1950 W of applied power together with 80 sccm of the additive water vapor.

The ideal byproducts of both initial gas compositions, according to recipes IV and V, should contain carbon dioxide (CO_2), hydrogen chloride (HCl) and hydrogen fluoride (HF). However, the FTIR spectra recorded reveal the presence of carbon monoxide which is not unexpected since the previous PFC surface wave plasma abatement experiments revealed carbon monoxide as a byproduct as reported and discussed in chapter IV. One plausible mechanism for the formation of CO is the appearance of carbonyl fluoride. Carbonyl fluoride, COF_2, is prominent at lower microwave powers for most of the plasma abatement experiments involving fluorine and a source of oxygen. This highly reactive fluoride can dissociate at higher applied microwave powers thus leading to the formation of the carbon monoxide. For example: $COF_2 + e \rightarrow COF + F$, $COF + e \rightarrow CO + F$. Other possible formations of carbon monoxide include dissociation of CO_2 through electron impact, and through the formation from intermediates, $CF + OH \rightarrow CO + HF$, $CHF + O \rightarrow CO + HF$, or $CF + O_2 \rightarrow CO + OF$ (74,121). The dissociation mechanism of carbonyl fluoride, as seen from our experimental data and the previously the previously given reactions, seem to be the most probable mechanism because the concentration of COF_2 decreases with applied power by 72 ppm and correlates with an increase of 191 ppm for CO is seen in the experimental data.

Figure 13 illustrates the abatement CCl_2F_2 using surface wave plasma technology with and without applied microwave power. The lower trace of the infrared spectra is CFC 12 with no additive water or applied power. This trace shows the v_1, CF_2 symmetric stretch at 1101 cm^{-1}, v_6, CF_2 anti-symmetric at 1159 cm^{-1} stretch, v_8, CCl_2 anti-symmetric

stretch at 992 and 882 cm^{-1}, as the main infrared absorptions (34) of CFC 12. The addition of the water vapor deterred the formation of a perfluorocompound or the reformation of a CFC and significantly decreased the amount of COF_2, which was not apparent in significant amounts as shown in the upper trace of Figure 11. The formation of a PFC or reformation of a CFC is not apparent because of the formation of byproducts of HF and HCl. The average DRE was calculated using calibration curves, Appendix B, along with the absorbance area of each byproduct. The determined was 99.995 ± .002% using 1950 W of applied microwave power with a flow rate of 80 sccm additive water. The experimental DRE is within the guidelines required for commercial technologies by OSHA and for successful abatement of CFCs as stated by the U. S. regulatory requirements.

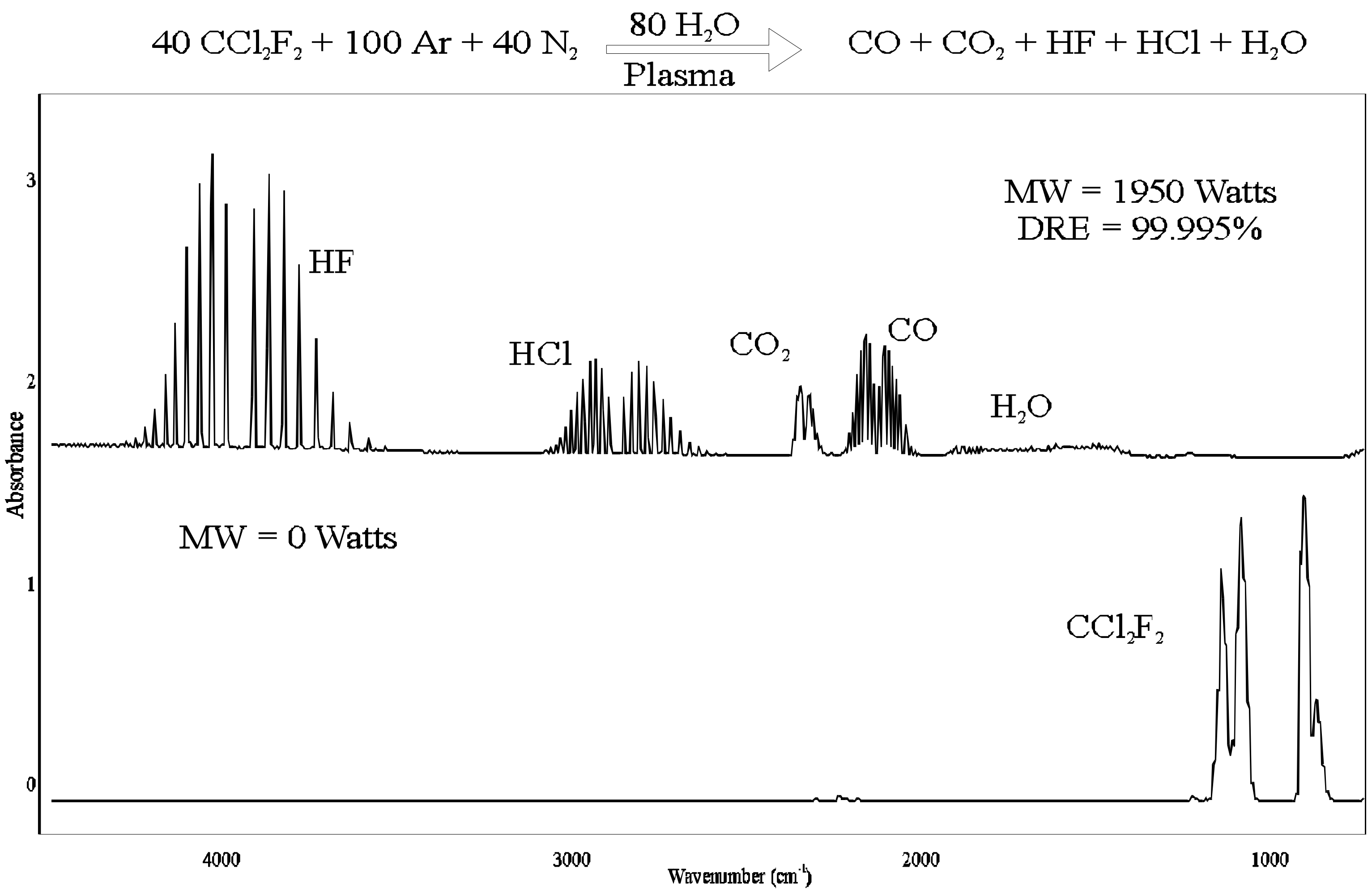


Figure 13: FTIR spectra illustrating plasma abatement experiments of CF_2Cl_2 using 0 watts and 1950 watts of applied power

Mass spectrometry was also performed to monitor IR inactive species as well as to give the opportunities for independent conformation of the previously analyzed FTIR experimental DRE. The isotopic distribution of ^{35}Cl and ^{37}Cl in CFC 12 is apparent in their recorded mass spectra in Figure 14. The molecular weight peak of CFC 12 at *m/z* = 120 is not apparent in the spectrum without applied microwave power which indicates that the molecule is easily dissociated by the applied 70 eV electron impact from the MS source. Spectral features (*m/z*) were seen before plasma application for CCl_2F_2 (103, 101, CCl_2F^+:87, 85 $CClF_2^+$: 68, 66 $CClF^+$:50 CF_2^+:31 CF^+), N_2 (28 N_2^+:14N^{++}) and Ar (40Ar^+:20Ar^{++}). Once the microwave power was applied, the spectral features arising from CCl_2F_2 decreased substantially and byproducts such as CO (28CO^+:12C^+), CO_2 (44CO_2^+:16O^+:28CO^+:12C^+), HCl (38, 36 HCl^+) and HF (20HF^+:19F^+) arose as shown in Figure 12 that a DRE of 99.65% at 1950 W. The absence of a peak at *m/z* = 30, NO^+, verifies that nitrogen oxides were formed with a concentration <XX ppm during the plasma abatement process. Findings from the QMS included independent confirmation of the DRE through the use of the different analytical instrumentations as well the natre of fragmentation products from CFC 12. These fragmenting patterns suggest to us that chlorine dissociates from the parent molecule easier than fluorine because CF_2Cl and CF are the prominent peaks in the pre-plasma MS.

Table 8 tabulates the destruction and removal efficiencies for both dichlorodifluoromethane and trichlorofluoromethane using additive water vapor to enhance these processes. Since the plasma is a cold, non-equilibrium medium, independent peak areas associated with specific products were generated from co-added

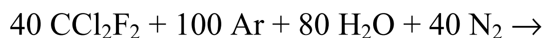
spectra for each experiment at each power. All DREs were determined from the previously recorded spectra in conjunction with appropriate calibration measurements.

Table 8: Destruction and Removal Efficiencies of CFCs[a]

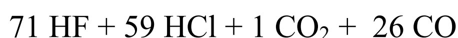
Gas	Power[b] (W)	Pressure[c] (mTorr)	Temperature[d] (˚C)	H_2O[e] (sccm)	AVG DRE (%)
CCl_2F_2	1950	286	77.5	80	99.995 ± .002
CCl_3F	1950	280	76.38	80	> 99.999

a DREs from FTIR and MS agree to within 0.3%
b Microwave power stability ± 0.1%
c Pressure measurements were ± 0.5 mTorr
d Temperature measurements were ± 0.1 °C
E Flow rate errors are ± 1% of full scale or 2 sccm

Results for experimental mass balance and end production distribution of the post plasma experiment for the gas composition involving dichlorodifluoromethane are shown in Table 9. Equation 16 illustrates the experimental chemical reaction at 1950 W applied power study of CCl_2F_2:



$$40\ CCl_2F_2 + 100\ Ar + 80\ H_2O + 40\ N_2 \rightarrow$$



$$71\ HF + 59\ HCl + 1\ CO_2 + 26\ CO$$

End product distributions indicate some post-plasma water and not complete recovery of HCl. One possibility for this extra water is due to lack of formation of HCl or dissociation of HCl.

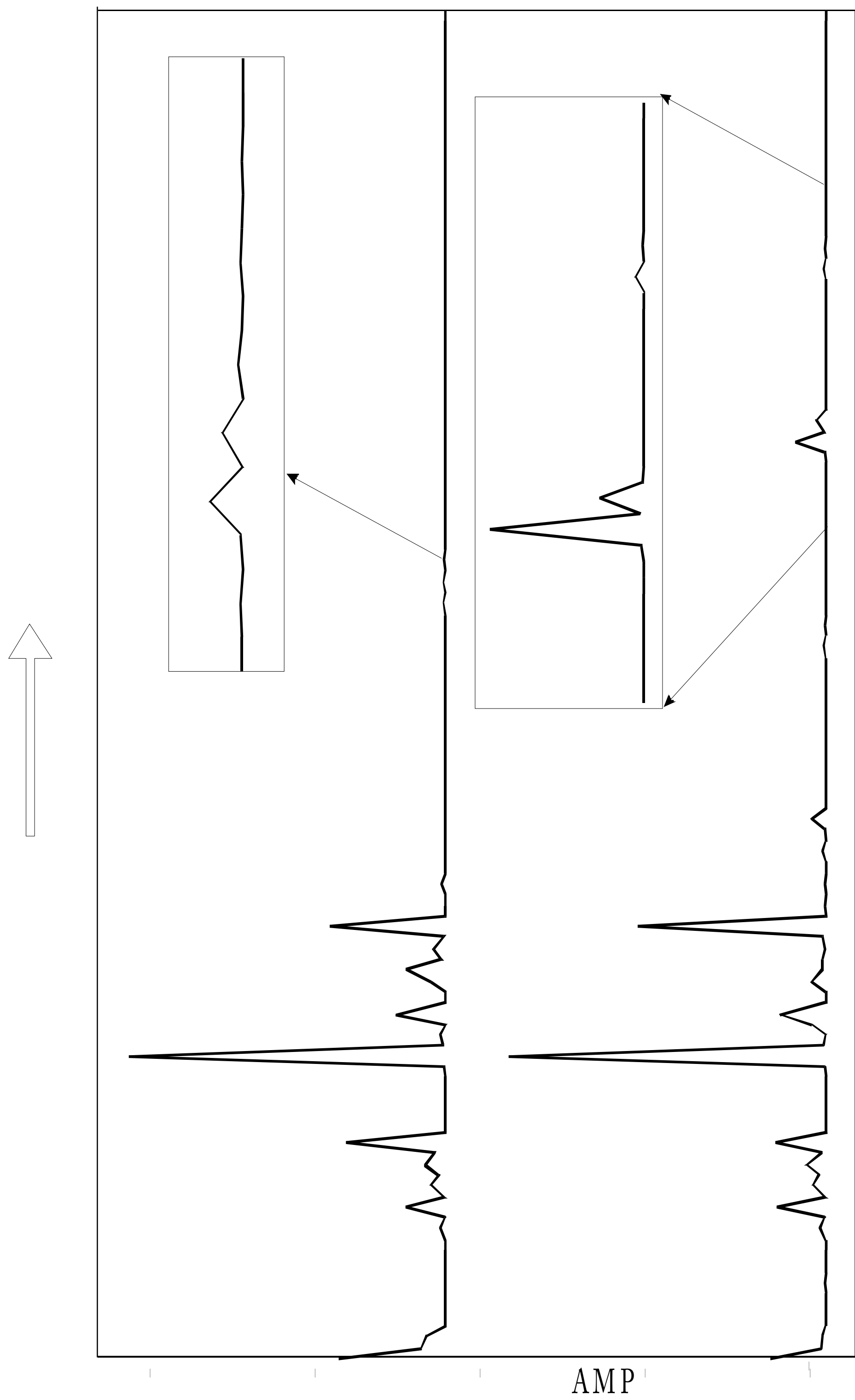


Figure 14: Mass spectra of pre- and post-plasma abatement illustrating destruction of CF_2Cl_2 at 0 watts and 1950 watts of applied power

The bond strength of C-F is 116 kcal per mol and dissociates at higher powers and H-Cl bond strength is 103 kcal per mol which could indicate dissociation of HCl. Less than half of the expected product chlorine, 41%, was actually recovered as HCl based on calibration data. The concentrations of HCl also decrease with increased power as shown in Table 9. Recovering the extra chlorine as molecular chlorine is not completely feasible, in the plasma, because the bond strength is only 57.8 kcal per mole but can possibly reform downstream from the plasma reactor. This trend was noticeable for both CFCs studied as is apparent in the previously recorded QMS results. Reaction mechanisms were studied for CF_2Cl_2 in O_2 and H_2 radiofrequency plasmas by Wang et al. and in their results only 46.5% of chlorine was recovered as HCl in the hydrogen based plasma (103) which helps verify the results of our experiments. Also, kinetic reactions were found in the literature that shows numerous reactions of HCl reactions with oxygenated products to form H_2, H, Cl_2 and Cl.

Table 9: Plasma Product Distribution and Mass Recovery for CCl_2F_2[a]

Power (W)	CCl_2F_2 (ppm)	H_2O (ppm)	COF_2 (ppm)	CO (ppm)	CO_2 (ppm)	HCl (ppm)	HF (ppm)	Mass Recovery (%)
1500	0.3397	220	6.2	873	46	2093	1905	89
1950	0.1132	206	6.1	885	41	2002	2417	89

a ppm errors are ± 5% b starting ppm of CCl_2F_2 1250 ppm

Loss of HCl is apparent in abatement of chlorofluorocarbons not only in the recorded product spectra but also upon inspection of the final concentrations of

byproducts. As previously described for the PFCs abatement, additional experiments can be conducted to determine the effect of applying plasma to calibrated flows of HCl as well as with varying concentrations of CO and O_2. The resulting HCl experiments were different from the previous HF experiments because majority of the HCl loss occurs upon plasma ignition. The addition of CO reduced the amount of HCl by only ~1-2%. The amount of CO post plasma yielded a correction factor about approximately 0.8 to increase the concentration of HCl from 1112 to 2002 ppm. No other chlorinated products were detected in the FTIR, such as $COCl_2$; however Cl was detected in the mass spec along with a minute amount of Cl_2. Any chlorinated byproducts are water scrubbed to reduce the impact on the environment. It was again assumed that no loss of estimated in the reported results.

Trichlorofluoromethane or CFC 11 experiments were conducted only to obtain destruction and removal efficiency and no mass balance studies were conducted due to the fact that CFC 11 is a liquid, which can damage the mass flow controllers and would cause additional complications in experimental design. Figure 15 illustrates the water vapor optimization experiments conducted on CCl_3F. The lower trace of the infrared spectra in CFC 11 is illustrated independent of additive water or applied power. The lower trace shows the CF stretch at 1085 cm^{-1} and the CCl_3 deformation at 847 cm^{-1} (122,123). The other vibrational modes of CFC 11 are below the range of transparency the windows in the White cell. The upper trace of the figure is post-plasma abatement at 1950 Watts of applied microwave power. The addition of water vapor at 80 sccm gives a DRE of 99.999%. The addition the water vapor deterred the formation of any PFCs

and significantly decreased the amount of COF_2, which were not apparent in significant amount as shown in the upper trace of Figure 15. Any harmful byproducts such as carbonyl fluoride, COF_2, hydrogen chloride, HCl, and hydrogen fluoride, HF, are easily water scrubbed and neutralized before atmospheric release.

Mass spectrometry was performed along with FTIR monitoring of IR inactive species in order to provide accurate measurement for both reactants and products. The molecular weight peak of CCl_3F at *m/z* 137.35 is not apparent in the spectrum without applied microwave power, Figure 16, which indicates that the molecule is again easily dissociated by electron impact at 70eV. Spectral features (*m/z*) were seen before plasma application for CCl_3F (105, 103, 101 CCl_2F^+:84, 82 CCl_2^+: 68, 66 $CClF^+$:49, 47 CCl^+:31 CF^+), N_2 (28 N_2^+:14N^{++}) and Ar (40Ar^+:20Ar^{++}). Once the microwave power was applied the spectral features arising from CCl_3F decreased substantially and byproducts such as CO (28CO^+:12C^+), CO_2 (44CO_2^+:16O^+:28CO^+:12C^+), HCl (38, 36 HCl^+) and HF (20HF^+:19F^+) arose as shown in Figure 16 giving a DRE of 99.667 % at 1950 W. Mass spectrometer data verified the FTIR DRE and gave no indication of unusual byproducts not seen with the FTIR technique.

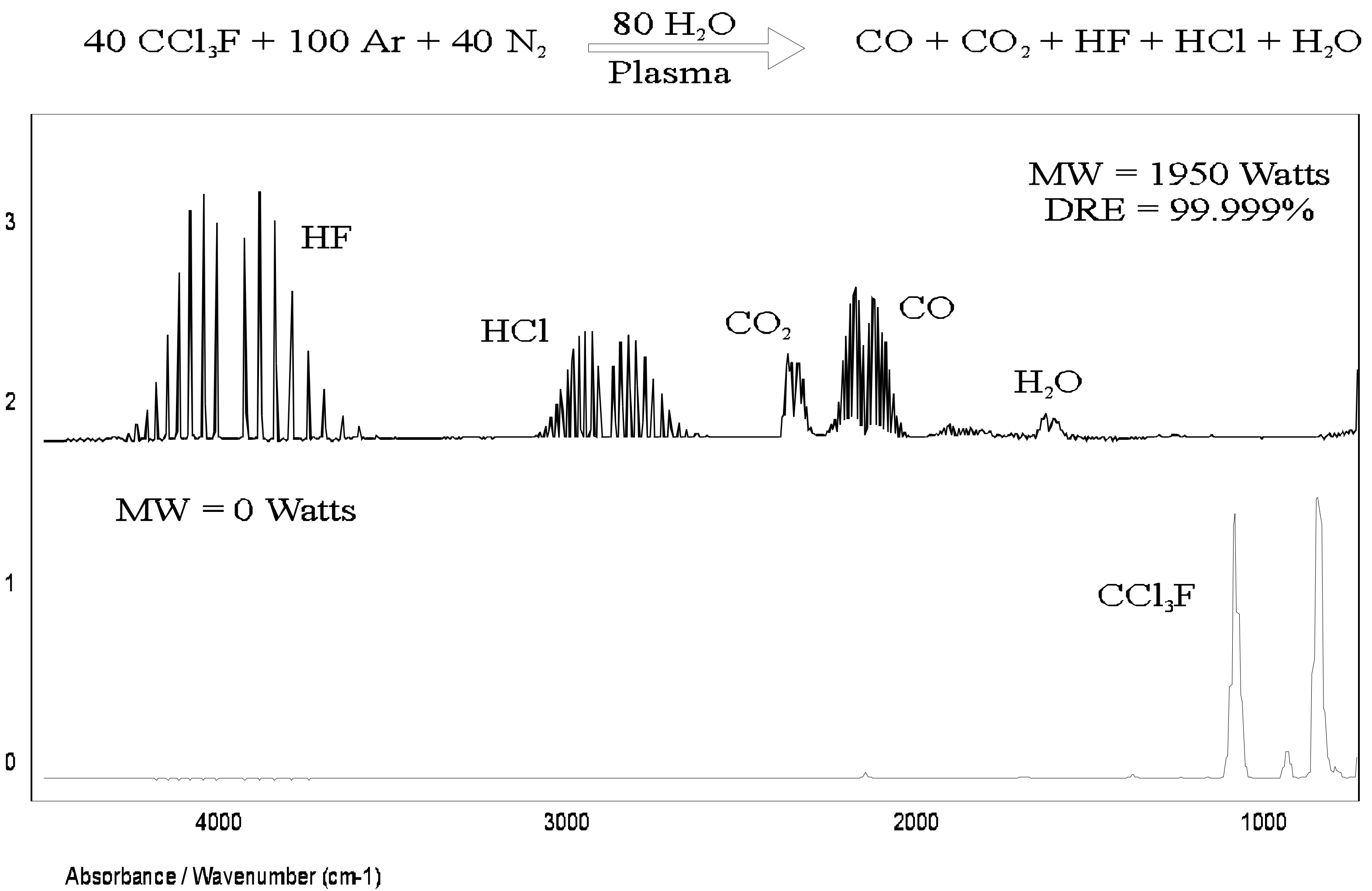


Figure 15: FTIR Spectra at 1cm^{-1} resolution showing plasma abatement of 40 sccm CCl_3F and 80 sccm H_2O at 0 watts and 1950 watts of applied power

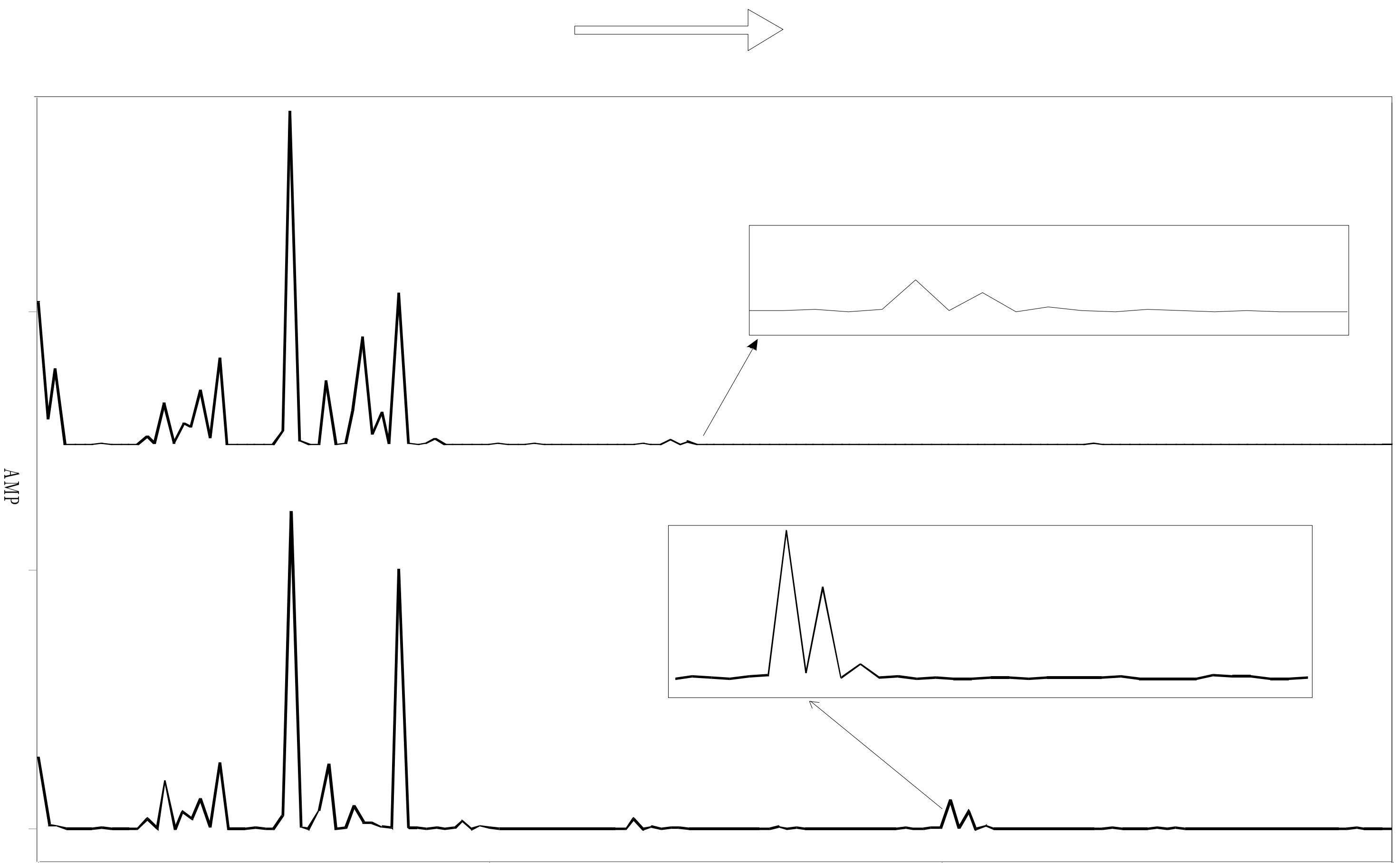


Figure 16: Mass spectra from plasma abatement experiments of CCl_3F at 0 watts and 1950 watts of applied power

The possibly of formation of a perfluorocompound is possible at lower applied microwave powers, but it not apparent at higher powers. Studying the fragmenting pattern of CFCs in the mass spectrometer can give insight into possible plasma reactions such as those shown in Table 10.

Table 10: Plasma Reactions of CFCs

Reaction	Rate Coefficient[b]	Reaction	Rate Coefficient[b]
$CCl_2F_2 + e \rightarrow CClF_2 + Cl + e$	$2.79x10^{-12}$	$H_2O + e \rightarrow H + OH$	a
$CClF_2 + e \rightarrow CF_2 + Cl + e$	$3.70x10^{-12}$	$H + F^- \rightarrow HF + e$	$1.6x10^{-9}$
$CF_2 + e \rightarrow CF + F + e$	a	$C + O_2 \rightarrow CO + O$	$1.60x10^{-11}$
$CCl_3F + e \rightarrow CCl_2F + Cl$	a	$CF + O \rightarrow CO + F$	$3.90x10^{-11}$
$CF_3 + e \rightarrow CF_2 + F$	a	$O + CF_2 \rightarrow COF + F$	$1.40x10^{-11}$
$CF_2 + e \rightarrow CF + F + e$	a	$HCl + H \rightarrow H_2 + Cl$	$4.49x10^{-13}$
$Ar + e \rightarrow Ar^* + e$	a	$Ar^* + N^* \rightarrow N^+ + Ar + e$	$5.00x10^{-11}$
$Ar^* + e \rightarrow Ar^{**} + e$	$8.87x10^{-7}$	$CN + HCl \rightarrow HCN + Cl$	$6.91x10^{-15}$
$O_2 + e \rightarrow O_2^* + e$	a	$OH^- + H \rightarrow H_2O + e$	$1.4x10^{-9}$
$O + e \rightarrow O^* + e$	a	$H_2O + O^* \rightarrow OH + OH$	$2.50x10^{-10}$
$CO + e \rightarrow C + O + e$	a	$OH + HCl \rightarrow H_2O + Cl$	$2.60x10^{-12}$
$F + CO \rightarrow COF$	$2.76x10^{-13}$	$COF + OH \rightarrow CO_2 + HF$	$1.0x10^{-11}$
$O(1D) + HCl \rightarrow OH + Cl$	$1.00x10^{-10}$	$HCl + e \rightarrow H + Cl$	$2.59x10^{-12}$

a computed using the electron energy distribution and electron impact cross section
b units of $cm^3\ s^{-1}$ rate constants taken from NIST

CHAPTER V

PLASMA MODELING

As previously described, research to successfully abate perfluorocompounds and chlorofluorocarbons using surface wave plasma technology is an important ongoing endeavor capable of making significant contributions to environmental sustainability. While intuitively, surface wave discharges abate gases through a combination of electron collision driven and thermal dissociation processes, the details of abatement mechanisms are far from being understood. Detailed plasma chemistry mechanisms are necessary to design and optimize abatement processes. A useful means of clarifying these mechanisms is to compare predicted and measured product distributions for the plasma investigations reported from plasma simulations of the surface wave discharge. Hindrances to this approach are that surface wave discharge models and plasma chemistries relevant to abatement are not developed. In addition, commonly encountered plasma diagnostics involving abatement processes usually do not resolve important dimensional information relevant to the plasma chemistry including sufficient spatial distributions of reactants, final products, and intermediates. Plasma modeling simulations, themselves, can be subdivided into the three-subcategories that include zero-, one- and two-dimensional programs that can be used to obtain virtual experimental results without experiments or can be compared with results such as ours that quantify only initial reactant and final product distributions. As our reactant and product analysis are chemically detailed but lack the necessary dimensional information

for a multi-dimensional treatment, zero-dimensional plasma chemistry models will be used in our analyses of abatement mechanisms.

The particular simulation we have used, Global_Kin simulation, is well described in literature related to plasma abatement. Global_Kin derives from two-dimensional models that have been used to simulate the abatement of PFCs via inductively coupled plasma through a set of axisymmetric equations (44) and using HPEM, Hybrid Plasma Equipment Model (74), as well as modeling an argon plasma (124). Investigations into abatement of PFCs using inductively coupled plasma have been reported throughout the literature as well as modeling of ICP abatement (44,124-126). Mechanisms of abatement of C_2F_6 and c-C_4F_8 were studied using two-dimensional models with various reaction pathways including ionization, dissociation, electronic and vibrational excitation and electron scattering. Modeling of C_2F_6 with O_2 as an additive gas, reported by Fiala, Kiehlbauch, et al, illustrated that the main dissociation of C_2F_6 was electron impact to produce two CF_3 radicals (44). This CF_3 radical can react with oxygen or fluorine atoms to produce molecules such as CF_4 or COF_2. It was found in this study that the major neutral species of ICP abatement were oxygen and fluorine atoms and main positive ions include O^+ and F^+. Formation of the PFC, tetrafluoromethane, was through a combination of CF_3 and F which were shown to occur at similar densities, approximately 10% of the initial C_2F_6 level, at 400 and 900 W of power. Modeling the destruction of C_2F_6 showed a maximum level of C_2F_6 destruction at 900 W with a maximum formation of CF_4 at 700 W of applied rf power. Modeling abatement of octafluorocyclobutane via ICP was studied to investigate the dissociation mechanism

and main plasma species (125) Rauf and Ventzek illustrated that dissociation pathway is electron impact to form C_2F_4 which further dissociates to produce CF_x radicals with CF_2 being the most abundant species. Large unstable radicals such as C_3F_5 and C_4F_7 were produced but then dissociated rather quickly to form more stable byproducts such as CF_2, C_2F_4, CF, and C_3F_6. The addition of argon in the plasma allowed the Ar/*c*-C_4F_8 discharge to become reasonably electronegative with the main negative species being F^-. Increases in coil power and gas pressure can increase the appearance of species such as CF_2 and CF. Further applications of modeling ICP to experimental data includes the byproducts of wafer etch processes and reactor wall byproducts and how these can influence the plasma chemistry.

One-dimensional modeling using CHEMKIN was performed on thermal plasma destruction of hazardous waste (39), microelectronics manufacturing (127) along with the study of atomic chlorine wall recombination (128). Zero-dimensional modeling was applied to dielectric barrier discharges of perchloroethylene (129), trichloroethylene (130), simulated diesel exhaust (131,132), removal of nitric oxide (133) and sulfur dioxide (134), etching of silicon dioxide via PFCs (135) and the modeling of breakdown in argon/xeon electric discharges (136). We thus will focus on modeling of surface wave plasma abatement of perfluorocompounds which was achieved using zero-dimensional Global_Kin for end product comparisons and reaction mechanisms.

Global_Kin Modeling Program

Global_Kin is a zero dimensional, plug flow or well stirred reactor, model used to understand the kinetic relationship between plasma chemistry in the gas phase along with surface reactions and effluent properties. The model is typically used for homogenous reactors that operate with moderate to high pressures with averaged volume quantities and no spatial variations considered, but has allowed for investigations of a chemical kinetic model of surface wave plasma. The simulation contains models for discharge circuitry, species kinetics, Boltzmann's model for the electron energy distribution and a plasma chemistry model, which is illustrated in Figure 17. Models for the chemistry and species transport are given by:

$$\frac{dN_i}{dt} = \sum_{j=1}^{R} a_{ji} k_j \prod_{l=1}^{S} (N_l)^{b_{lj}}$$

where $\frac{dN_i}{dt}$ is the rate of change in the species density N_i with respect to time, j spans reactions in the network, l spans the species in the system, k_j is the reaction coefficient of reaction j, R is the total number of reactions in the system, and S indicates the number of species in the participating reactions.

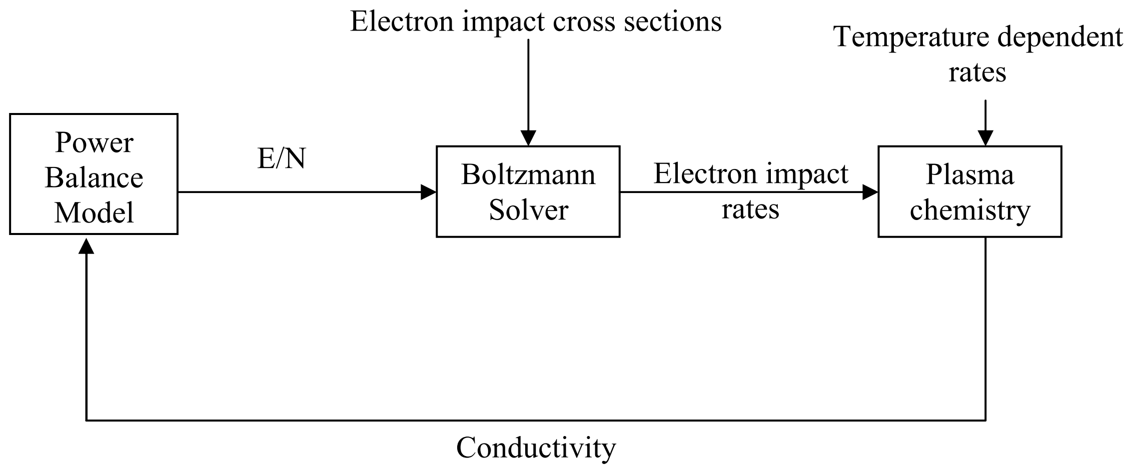


Figure 17: Schematic of zero-dimensional Global_Kin model

A second order derivative equation can be used to approximate in a spatially uniform volumetric model with Λ as the diffusion length and accounts for the diffusion to and from the walls and reaction sources which is as follows (137):

$$\frac{dN_i}{dt} = \frac{1}{\Lambda^2}\left(-\gamma_i D_i N_i + \sum_j D_j N_j \gamma_j f_{ji}\right) + S_i - \frac{N_i}{T_g}\frac{dT_g}{dt}$$

The last term in the equation accounts for the gas temperature, T_g, assuming a constant pressure.

The plasma chemistry module produces species densities as a function of time via rate coefficients, which were obtained from solutions to Boltzmann's equations as well as temperature dependent heavy particle reaction rates. Two separate equations are used for the temperature of the gas and the temperature of the electron. Temperature of the gas includes terms for gas heating from elastic and inelastic collisions with electrons, gas phase reaction sources and conduction to the walls:

$$\frac{d}{dt}\left(Nc_p T_g\right) = \sum_i \frac{3}{2} n_e \nu_{mi} \left(\frac{2m_e}{M_i}\right) k_B \left(T_e - T_g\right) +$$
$$\sum_j n_e k_j N_j \Delta\varepsilon_j - \sum_j \Delta H_j + \frac{\kappa}{\Lambda^2}\left(T_w - T_g\right) - \frac{d}{dt}\left(\frac{1}{2} M_w N v_x^2\right)$$

with N as the total gas density, c_p indicating the mixture averaged heat capacity. The final term of this equation describes the transfer of internal energy to kinetic energy as the gas expands. Electron temperature can be described as:

$$\frac{d}{dt}\left(\frac{3}{2} n_e k_B T_e\right) = P_d - \sum_i \frac{3}{2} n_e \nu_{mi} \left(\frac{2m_e}{M_i}\right) k_B \left(T_e - T_g\right) + \sum_l n_e k_l N_l \Delta\varepsilon_l$$

with P_d being power deposition and includes contributions from Joule heating and energy transferred in elastic and inelastic collisions with heavy species. A general form of the Boltzmann equation is given by (138)

$$\left(\frac{\partial}{\partial t} + v \bullet \nabla_r + \frac{eE}{m} \bullet \nabla_v\right) f(r, v, t) = \left(\frac{\partial f}{\partial t}\right)_{collisions}$$

where $f(r,v,t)$ is the distribution function for electrons with t being time and r indicating spatial location with a velocity v. The homogenous version of Boltzmann equation that is solved is described in (138). Once electron energy distribution f has been computed, reactions are determined using $k = \int_v f(v) \sigma v \, d^3 v$. The reaction set includes electron impact ionization $A + e \rightarrow A^+ + 2e$, dissociation $AB + e \rightarrow A + B + e$, attachment processes along with heavy species reactions that can describe neutral chemistry and charge exchange, ion-conversion and ion recombination processes. The power balance module provides the electric field/number density (E/N) and successively obtains the rate coefficients of electron impact reaction based on electron temperature.

Modeling Reactions and Input Parameters

The Global_Kin model accounts for the behavior of 75 species and 585 gas phase reactions with corresponding rate constants with all rate constants in an Arrenhius format. All reactions used in these plasma modeling experiments are included Appendix C (125). Included in the model are 43 neutral species and 32 charged species. Of the total reactions, one hundred forty electron impact reactions include excitation, ionization, dissociation and attachment.

For each set of experimental conditions that exists, a suitable set of theoretical conditions must be developed and optimized. Various parameters such as gas inlet velocity, pressure and temperature, power length and cross sectional area of the plasma reactor, diffusion length, and wall temperature must be calculated to satisfy the plasma experiment conditions which were done through trial and error. Power deposition is an important parameter in the modeling simulation because it mimics the experimental applied microwave power over the length of the plasma active zone. The active zone was approximated at 8 cm with powers of 0.85, 1.26, 1.51, and 1.68 which corresponds to 500, 1000, 1500 and 1950 W respectively. Boltzmann parameters are calculated over the length of the active zone at various points along the active plasma zone.

Octafluorocyclobutane Abatement Mechanisms

The plasma chemistry mechanism is the key to relating effluent measurements to chamber operating conditions. To better understand the primary species degradation

pathways, the full plasma chemistry scheme included in Appendix C, (125) was simulated in Global_Kin. The important pathways which were an outcome of the simulation study are presented in Figure 18.

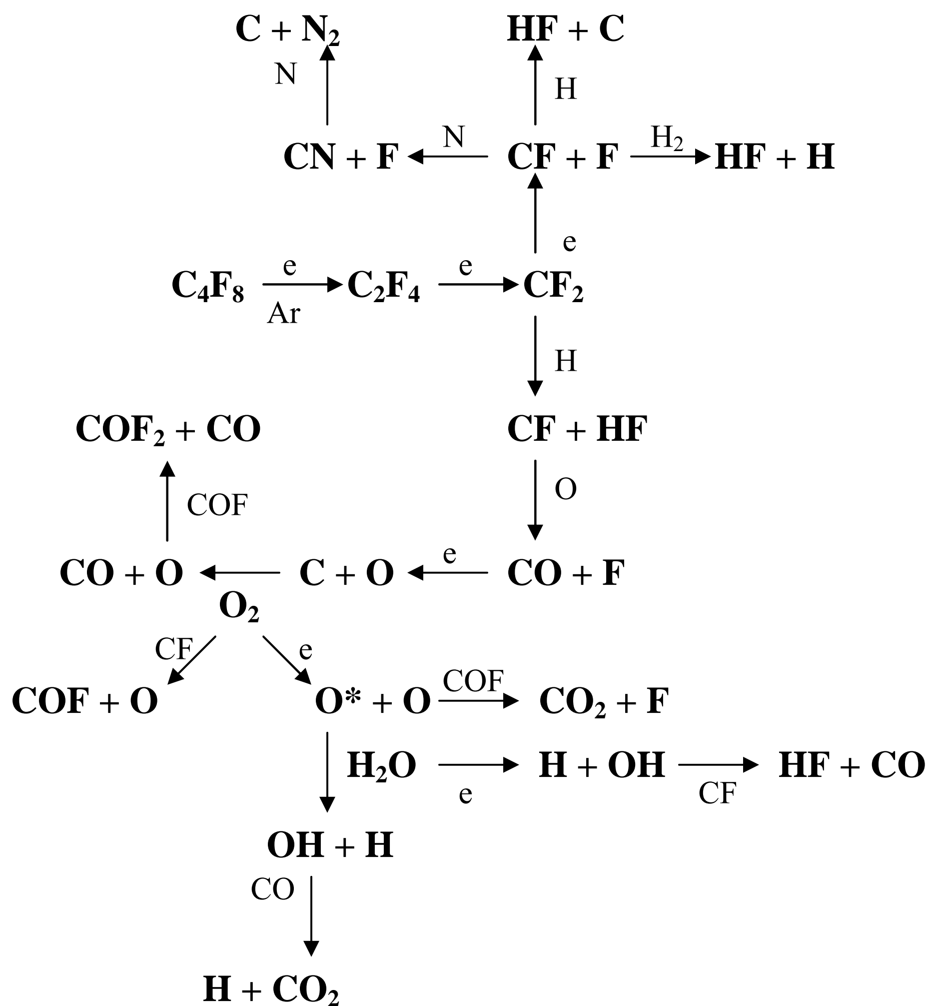


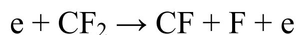
Figure 18: Dominant reaction mechanisms for surface wave plasma abatement of octafluorocyclobutane in our experiment

Electron impact dissociation is seen to be the dominant primary C_4F_8 degradation pathway. Dissociation reactions of c-C_4F_8 include products such as C_2F_4, C_4F_7, CF_3,

C_3F_5, C_3F_6, etc with the dominant consumption pathway being electron impact to yield C_2F_4 which then continues to dissociate C_xF_y and CF_y (125,139):

$$e + c\text{-}C_4F_8 \rightarrow C_2F_4 + C_2F_4 + e$$

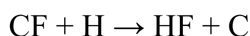
$$e + C_2F_4 \rightarrow CF_2 + CF_2 + e$$



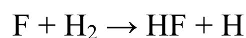
$$e + CF_2 \rightarrow CF + F + e$$

Using species densities calculated from the program, the dominant fragment of these reactions is C_2F_4 and CF_2 which has been indicated in the literature (139-141) but only accounts for 0.004 ppm of end product at the 1950 Watts for applied microwave power. There is no appearance of reformation of C_4F_8 or any stable perfluorocompound using additive water. Dominant dissociation reactions of O_2, CO and H_2O include electron impact. Molecular nitrogen and argon are excited by electron impact reactions.

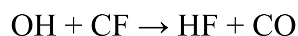
Upon dissociation or excitation of the initial gaseous species there are numerous reactions that can contribute to the final end product distribution. Each species, radical, fragment, or excited state element that was formed via electron impact reactions was analyzed for the dominant reaction. Formation of HF, an important byproduct, can be generated through the following reactions (74,142):



$$CF + H \rightarrow HF + C$$

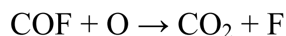


$$F + H_2 \rightarrow HF + H$$

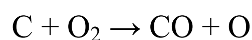


$$OH + CF \rightarrow HF + CO$$

Carbon monoxide and carbon dioxide are also formed from various reactions as indicated below (74,143):



$$COF + O \rightarrow CO_2 + F$$

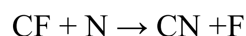


$$C + O_2 \rightarrow CO + O$$

$$CO + OH \rightarrow CO_2 + H$$

All the byproducts and species from these reactions can further react to form other byproducts which can create a cyclic pathway within the plasma.

Experimental data is quantified through FTIR and QMS and no unexpected byproducts are apparent. However, using Global_Kin yielded various fragments and stable species are not seen in the end product analysis by the analytical methodologies. Various species such as F_2 and CN are apparent in the model, but can be highly reactive so that they are not seen experimentally. The prominent reaction for the formation of CN is

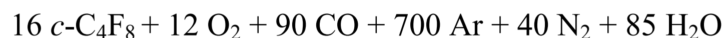


$$CF + N \rightarrow CN + F$$

but can react with N to form N_2 with CN only contributing to $< 0.2\%$ of the final end product modeling plasma distribution. Other comparisons will be discussed in a later section.

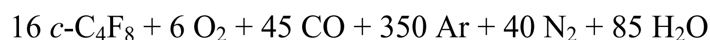
Modeled Results for Octafluorocyclobutane Reactions

Modeling studies were completed using Global_Kin on each of the simulated etch manufacturing recipes previously stated in chapter 3 for comparison to experimental end product distribution. Modeling study A consists of



$$16\ c\text{-}C_4F_8 + 12\ O_2 + 90\ CO + 700\ Ar + 40\ N_2 + 85\ H_2O$$

modeling study B consists of



$$16\ c\text{-}C_4F_8 + 6\ O_2 + 45\ CO + 350\ Ar + 40\ N_2 + 85\ H_2O$$

and lastly, modeling study C consisted of:

$$16\ c\text{-}C_4F_8 + 12\ O_2 + 700\ Ar + 40\ N_2 + 85\ H_2O$$

All case studies included parameters such as wall temperature settings of 573 K, inlet gas temperature of 300 K, with Boltzmann calculations starting at 0.5 centimeters ending at 8 centimeters at every 0.5 centimeters along the reactor. Parameters were adjusted, mainly at the highest applied microwave power, through trial and error until an optimized velocity setting was achieved to mimic experimental end product distributions. Too high of a velocity such as > 2000 cm per sec, yielded an extremely low ppm of C_4F_8, > 1 ppm, and too low of a velocity, such as 505 cm per sec, yielded a low DRE. Allowing the Boltzmann calculation to be computed more frequently along the length of the dielectric tube, would allow for the use of a lower velocity. However, changing the frequency of the Boltzmann calculation for the same velocity did not change the data output by more than ± 0.5 parts per million. All output data was converted to concentrations in ppm as was the experimental mass balance equations were converted as well for end product comparison.

Comparisons of end product distributions for modeling study A are shown in Figure 19. Experimental data is represented on the left of each end product and the corrected experimental data is illustrated as the solid block with modeling data on the right of the graph. No unexpected species contributed to the final output. Molecular oxygen yielded approximately 17000 ppm which accounts for 1.7% of the final output and was only ~ 50% consumed and hydrogen species accounted for 38500 ppm or

3.85% of the output and CN was approximately 0.02%. The major discrepancy concern CO_2 differences which will be expanded upon later in this chapter.

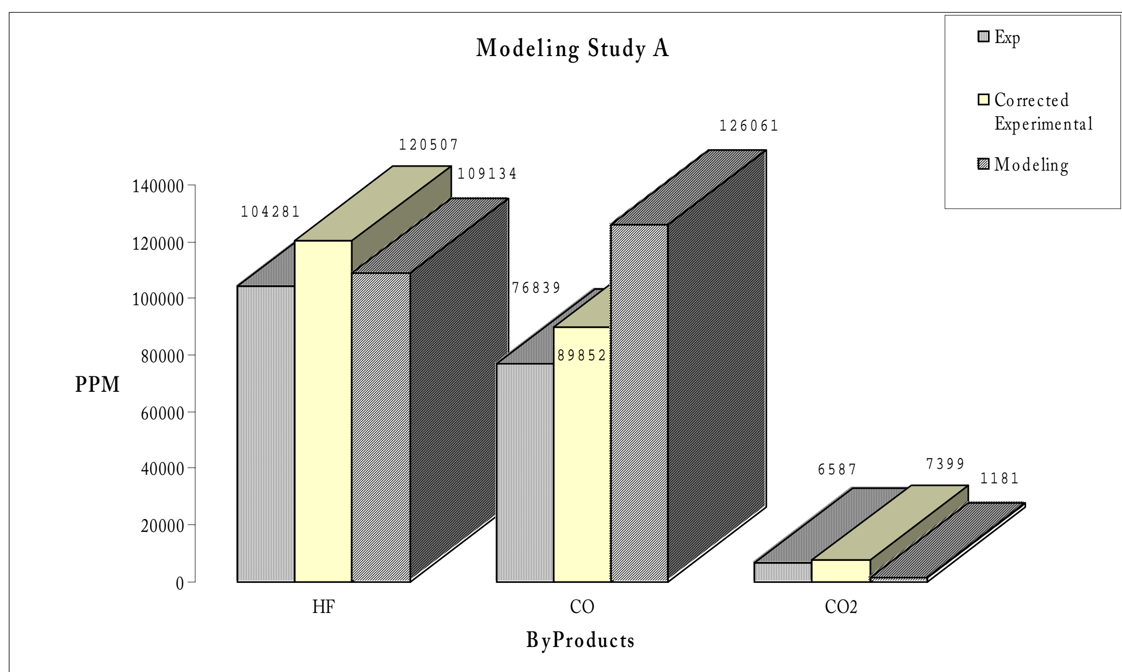


Figure 19: Comparison of experimental versus Global_Kin for major byproducts for 16 C_4F_8, 12 O_2, 90 CO, 700 Ar, 85 H_2O and 40 N_2

The graphical representation of end product distributions for modeling study B is illustrated in Figure 20. Again, the corrected experimental mass balance recipe was added to this comparison. This plasma simulation is within a factor of 9 from the experimental data. Molecular oxygen was 85% consumed; water was 95% consumed with greater than 99.5% destruction of C_4F_8. Cyanide accounted for approximately 0.7% of the final output.

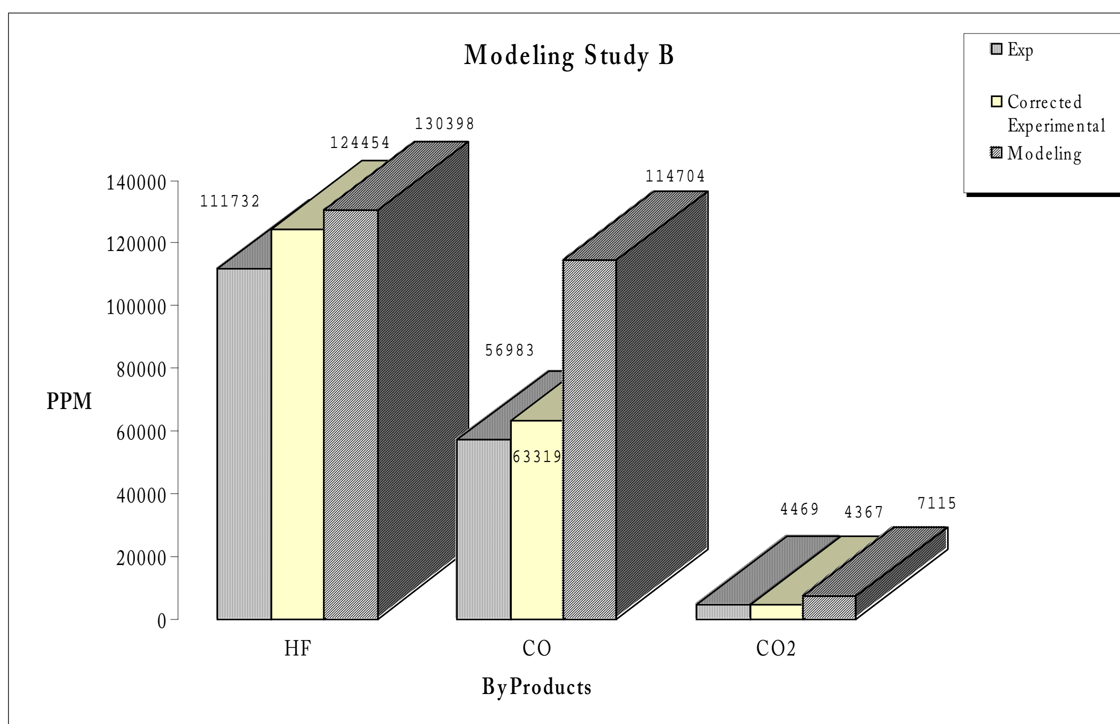


Figure 20: Comparison of experimental versus Global_Kin for major byproducts for 16 C_4F_8, 6 O_2, 45 CO, 350 Ar, 85 H_2O and 40 N_2

Figure 21 illustrates the end product comparisons of modeling study C, simulated manufacturing recipe without initial CO. This plasma simulation resembled the experimental rather closely again with the expectation of CO_2. Initial byproducts like molecular oxygen is over 78% consumed, water is ~ 97% consumed, and C_4F_8 is 99.8% destroyed. CN only accounted for less than 0.1% of the final output. No unexpected species or byproducts were observed in this case study.

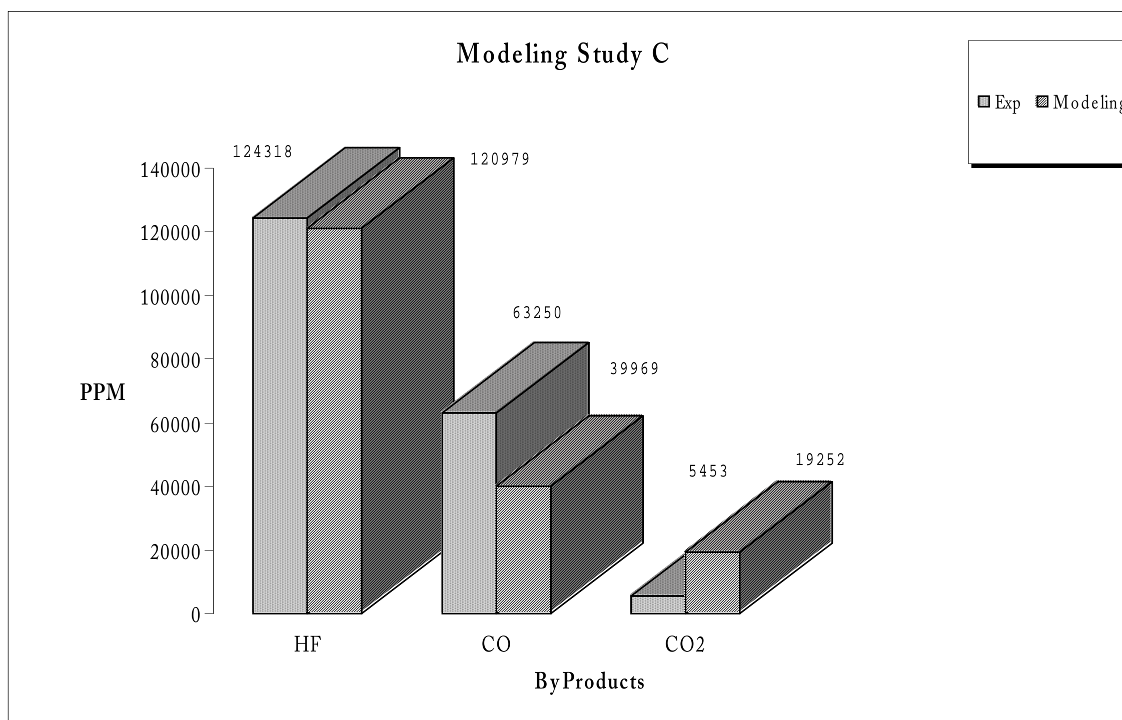


Figure 21: Comparison of experimental versus Global_Kin for major byproducts for 16 C_4F_8, 12 O_2, 700 Ar

Byproduct distribution for preliminary modeling studies varied with velocity and did not always agree with the experimental data differing by a factoring of 30 at one point. Initial studies were conducted using a reaction database that did not have any type of carbon dioxide dissociation, which yielded large differences between experimental and modeling data especially for modeling study B with a difference of 375%. To help remedy this, two dissociation reactions of CO_2 were added to the database. However, too many reactions with CO_2 as a reactant caused the difference in experimental and modeling data to grow with each reaction addition because there are uncertainties in the reactions for the excited states. The final percent differences between experimental and Global_Kin modeling data are shown in Figure 22. Plausible reasons for this

discrepancy are that Global_Kin is used to model plasmas that are at higher pressures, > 1 Torr, than surface wave plasma and also for plasmas that are closer to equilibrium and that are typically more uniform. Futhermore, we have used this zero-dimensional model whereas a more sophisticated modeling treatment would require a two-dimensional model to take into account electron density distributions in the and in propagating and radial dimensions. An experimental discrepancy could be the loss of oxygen through water because water has tendencies to adsorb onto transfer lines. Other explanations that could account for observed differences in experimental observations and the model can be that the reactions are not accounting for all the contributing excited states of C, O and CO_2.

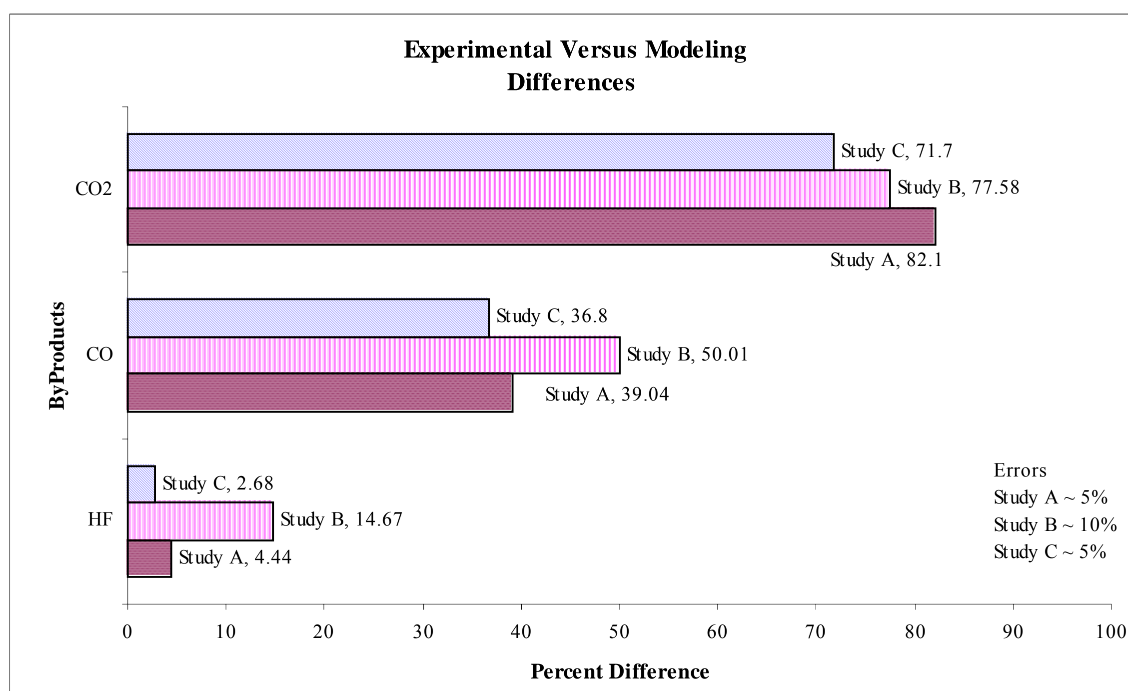


Figure 22: Percent difference of experimental and Global_Kin modeling data for each PFC modeling study

Differences between the output of Global_Kin and the experimental output may result from the possibility of downstream formation end products. Global_Kin calculates species density of the length of the dielectric reaction from 0 to 66 cm and experimental instrumentation is located downstream of the plasma reactor. Modeling reactor species such as C, H, N, and O are evident at 66 cm from which we can conclude that there is possible formation of stable species upon exit of the reactor and in the transfer lines. Plasma electron temperatures can average 5000 K in the reactor. However at a displacement of approximately two feet from the exit of the reactor, experimental temperatures were measured at 310 K. This significant temperature difference could lead to downstream reformation of species.

As mentioned throughout this work, additive water is important for effective plasma abatement given that it hinders the reformation of perfluorocompounds. Modeling simulations were conducted using recipe I without water to illustrate this circumstance as shown in Figure 23. Without water in the plasma simulation, no HF was formed at 1950 Watts of applied microwave power. Octafluorocyclobutane was not reformed in a significant amount, 0.165 ppm, but other perfluorocompounds such as CF_4 and C_2F_6 were formed. Approximately 15300 ppm of CF_4 was produced in post-plasma simulations along with 4300 ppm of C_2F_6. Perfluorocompound fragments such as CF_3, CF_2, C_2F_5 and F_2 account for 13700 ppm of final byproducts as well. Using water as an additive gas yielded approximately 28 ppm of PFCs in comparison with 33300 ppm without the presence of additive water. This plasma modeling simulation verifies all

experimental conclusions that water plays a vital role in formation of HF and hinders the reformation of PFCs.

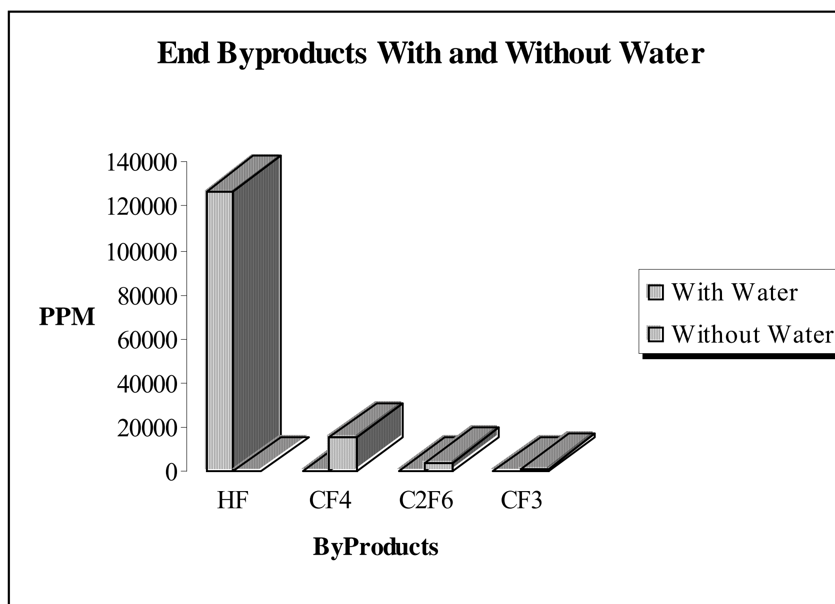


Figure 23: Comparison of end product concentrations with and without additive water

Chlorofluorocarbon Abatement Mechanism

Plasma modeling of chlorofluorocarbons provide a difference set of challenges for abatement modeling because the original Global_Kin database was designed for PFCs so additional appropriate reactions for dichlorodifluoromethane were gathered from alternative sources such as the NIST Kinetics Database and various other literature sources. The basic input parameters were the same for modeling of both PFCs and

CFCs. Appropiate reaction mechanism was developed similar to PFCs to understand the consumption pathways of CF_2Cl_2 with the use of additive water. This also lead to investigations of the formation pathways of the various byproducts, which is shown in Figure 24.

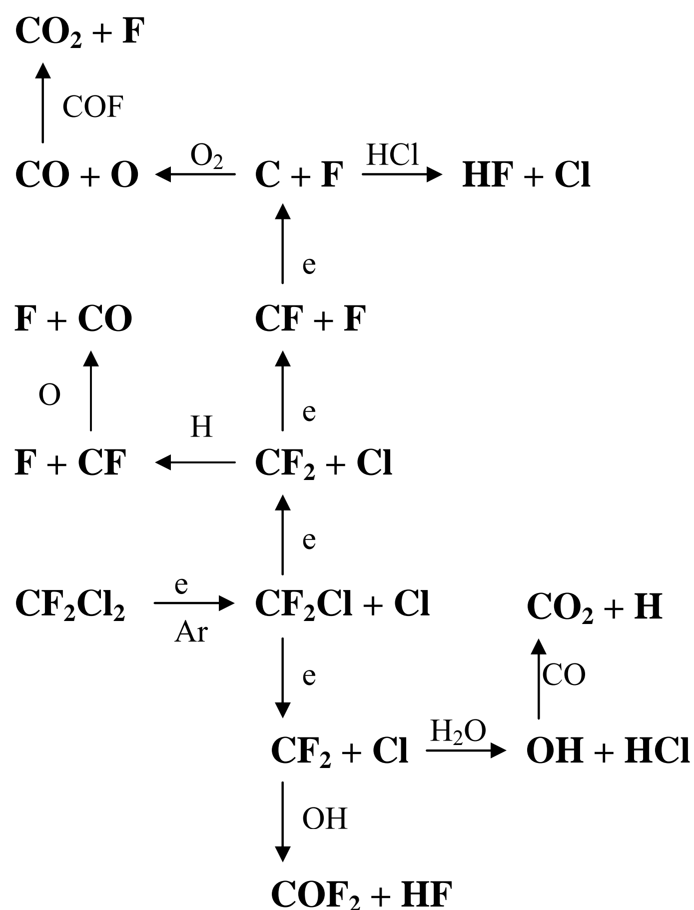
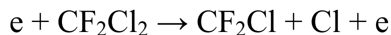


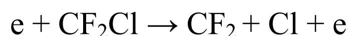
Figure 24: Reaction mechanisms for CFC 12 during surface wave plasma abatement experiments

Electron impact reactions appear to be the initial pathway for abatement of CF_2Cl_2 with a chlorine molecule leaving more often than a fluorine molecule to yield

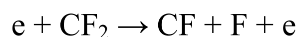
CF_2Cl. Further reaction includes electron impact to reduce the initial molecule to C, F, and C (103).



$$e + CF_2Cl_2 \rightarrow CF_2Cl + Cl + e$$



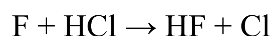
$$e + CF_2Cl \rightarrow CF_2 + Cl + e$$



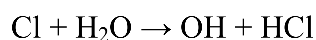
$$e + CF_2 \rightarrow CF + F + e$$

Dominant reaction pathway for dissociation of water includes electron impact. Molecular nitrogen and argon are excited by electron impact as well.

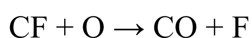
Various reactions contribute to the final byproduct distributions but certain reactions are much more dominate. Byproducts such as HF, HCl, CO and CO_2 can be formed through different reactions which include (103,144):



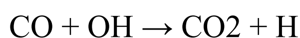
$$F + HCl \rightarrow HF + Cl$$



$$Cl + H_2O \rightarrow OH + HCl$$



$$CF + O \rightarrow CO + F$$



$$CO + OH \rightarrow CO2 + H$$

These reactions can continue throughout the plasma and keep reacting with various other byproducts to form a cyclic mechanism within the plasma. The overall mechanism is similar to the PFC mechanism regarding formation of byproducts.

Modeled Results for Chlorofluorocarbon Reactions

Modeling studies were only conducted on CFC 12 because it was studied more extensively experimentally and it is assumed that there will be considerable similarities

in the elementary mechanisms responsible for abatement of CFC 12 and CFC 11 with the exception of the dissociation of the initial molecule. In this case, all input modeling parameters were similar as in the PFC studies with the expectation of velocity, which was higher, and pressure, which was lower. Predictions of end product distributions breakdown of the of the data yielded no noticeable differences in the model calculations of CFC 12 and the results of the corresponding experimental data, as shown in Figure 25. With the exception for CO_2 with a difference of ~95% but this is again considering the effects of excited states in the modeling database. Chlorine accounted for ~3.6% of the final output and less than 0.1% of the output was $COCl_2$. No unexpected species were formed along with any formation of any major PFCs. The predicted differences in the distributions of HCl and HF were 15%, which is similar to the difference experimentally of 18%. Overall differences of modeling and experimental total concentrations of HF, HCl, CO and CO_2 were 16, 14, 12, 95% respectively. This case study closely resembled the experimental data as shown in the overall differences, which adds validity to the experimental results.

Overall, the plasma modeling simulation has proven to be extremely useful to understand how the experimental end products are formed. A basic mechanism for the abatement of octafluorocyclobutane and dichlorodifluoromethane was developed and compared to experimental results with no significant differences in product distribution being greater than a factor of 9 for both gases. Verification of the use of additive water was also a key result of the Global_Kin simulations because it showed the importance of added a source of hydrogen for formation of HF and deterred the reformation of PFCs.

All previous surface wave plasma experiments studies can be modeled using Global_Kin with the appropriate reaction databases and well as future etch recipes without conducting experiments.

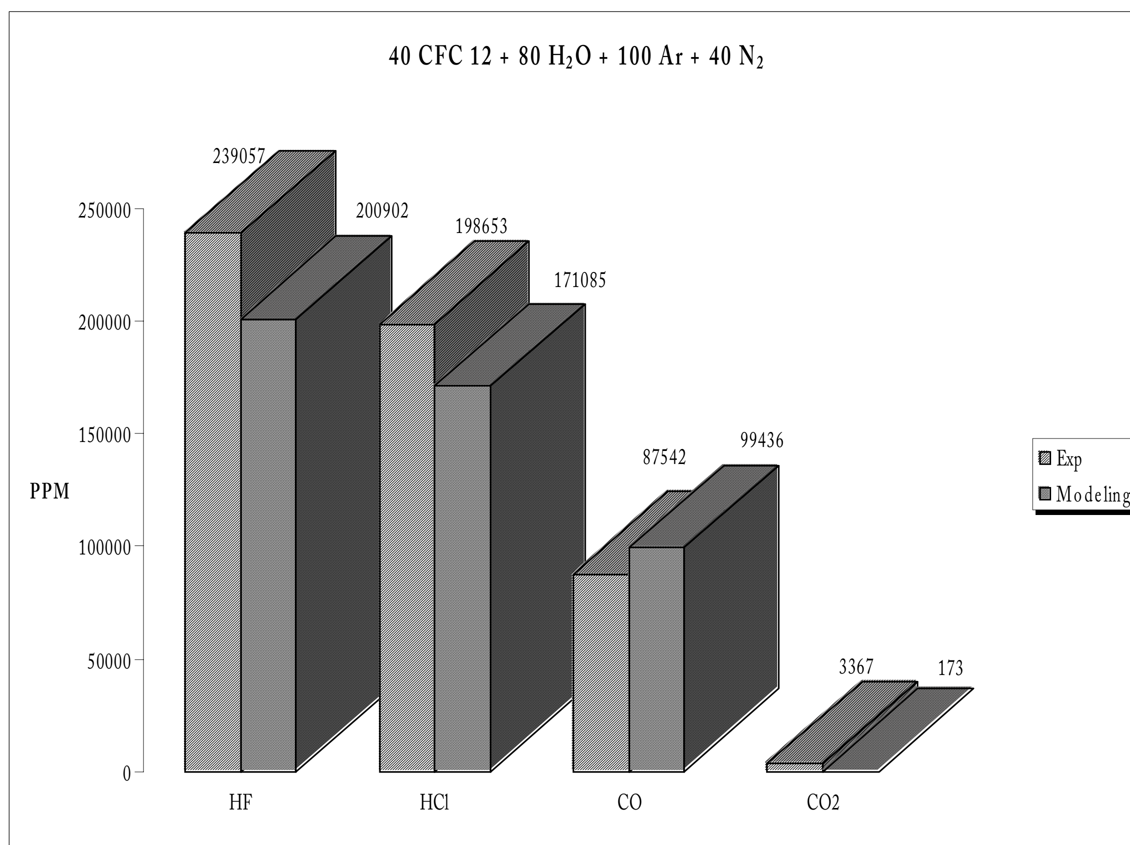


Figure 25: Comparison of CFC 12 data for experimental and modeling byproduct concentrations

CHAPTER VI

SUMMARY AND FUTURE RESEARCH

Summary

This dissertation has been focused on investigating the application of surface wave plasma for effective abatement of perfluorocompounds and chlorofluorocarbons. The primary objective of this dissertation has been to quantitatively evaluate the utility of such technology and mechanisms for it optimization especially with respect to environmental sustainability. In summary I have demonstrated the following: i) in the initial part of this dissertation have successfully applied SWP as effective abatement technology for simulated 300 mm c-C_4F_8 semiconductor manufacturing processes. Optimized abatement in such cases is demonstrated to be better than 99.88% DRE for and is the most effective abatement demonstrated to date. ii) Further applications of SWP abatement for destruction of two CFCs with the largest ozone depleting potentials, CF_2Cl_2 (CFC 12) and $CFCl_3$ (CFC 11) with DREs of > 99.99%. This technology is the first non-thermal plasma technology demonstrated to be fully compliant with OHSA regulations regarding disposal of the CFCs. iii) In the final section of this dissertation, I have successfully applied a zero-dimensional Global_Kin plug flow model to the previous experimental investigations for comparison of end product concentrations as well as investigations into plasma abatement mechanisms. Basic plasma mechanisms were determined for the abatement of both c-C_4F_8 and CF_2Cl_2 with electron-impact being the main dissociation pathway. End product concentration comparisons were

within a factor of 10 for applications. Other advantages of modeling the abatement process include the verification of the importance of additive water for optimal destruction and the lack of PFC of CFC reformation. All of these points illustrate the effectiveness of SWP abatement for application of reduction of semiconductor industrial emissions as well as reduction of CFC stockpiles.

Future Research

As the need for abatement technology grows, so must the progress of the surface wave plasma abatement device. Much engineering on the third generation prototype and testing has occurred in house whereas initial beta testing occurred in an industrial setting. However, designs are in place for a fourth generation device, which should be tested in an actual semiconductor fab to measure the effectiveness of this device, and impact on wafer etch chamber. To successfully implement this technology into the semiconductor industry will require more studies regarding wafer etch process effluents must be conducted. It has been shown that the SWP abatement device is effective at destruction of a simulated manufacturing recipe, but the corresponding beta studies must be repeated in an industrial setting. In the actual etch chamber, the recipe is passed through plasma and the fluorine etches a silicon wafer and the byproducts exit the chamber. Silicon tetrafluoride is a byproduct in this reaction and the possibility of PFC formation is high. For this research project, two plasma abatement systems would be needed. System one would mimic the wafer etch chamber by including a quartz tube to

generate any silicon byproducts that would stem from the wafer etch chamber with applied microwave power. The process effluents from this system should then pass through the second system with the addition of applied power and various amounts of water vapor. Destruction and removal efficiencies studies should be conducted on these experiments as described in this work.

A fourth generation surface wave plasma abatement device is being developed for possible implementation into the semiconductor industry. Possible differences include holes in the brass chimney to help eliminate the need for cooling air, a bent surfaguide and low cost microwave head and sliding short circuit. Other possible studies can include extensive plasma modeling and electron molecule collisions via cross sections interactions.

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APPENDIX A

SAMPLE CALCULATIONS

1. Determine Calibration Curve for CO_2
   - determine ppm range of curve i.e 10 – 80 ppm
   - obtain 1% CO_2(g) balanced in N_2(g)
   - make dilution spreadsheet to calculate ppm at various flow rates
     i. calibration gas concentration ppm * Cal gas flow rate (L)/Total flow rate (L)

     $$10000PPM * \left(\frac{.05L}{30000L} \right) = 16.667$$

   - obtain FTIR and MS using the gas at various flow rates
   - integrate peak areas between 2400-2283.8 cm^{-1} (asymmetric stretch)
   - make a graph of peak area versus ppm
   - insert a trend line to obtain an equation

2. Conversion of Peak Area to ppm for CO_2
   - Integrate 3 independent spectra peak area using Bomem Grams 32 software
   - Average three independent peak areas together
     i. $$\left(\frac{8.463227 + 8.434201 + 8.394024}{3} \right) = 8.430484$$

- Insert average in calibration curve to obtain ppm

    i. PPM = 7.9977*X – 6.3107

    $$(7.9977 * 8.430484) - 6.3107 = 61.11 \text{ ppm of } CO_2$$

3. Obtain DRE for Experiment

- Determine pre-plasma ppm of c-C_4F_8

    i. Total Flow Rate of Reaction

        1. 16 c-C_4F_8 + 90 CO + 12 O_2 + 700 Ar + 40 N_2 + purge/Edwards N_2 = 38000 sccm

        2. $$\left(\frac{16}{38000}\right) = 4.2105E^{-4} * 10^{6} = 421.05 \text{ PPM}$$

- integrate peak area of c-C_4F_8 between 1360-1160 cm^{-1}

- average three independent peak areas

- insert average in calibration curve

- use DRE equation obtain DRE

    i. $$1 - \left(\frac{0.451}{421.05}\right) * 100 = 99.893\%$$

4. Mass Balance the Recipe

i.e. 16 c-C_4F_8 + 12 O_2 + 700 Ar + 85 H_2O + 40 N_2 → aHF + bCO + cCO_2

- Convert all byproducts to ppm

    i. HF – 1632 ppm

    COF2 – 106.15 ppm

CO – 678.1 ppm

CO2 – 94.06 ppm

H2O – 24.82 ppm

- Determine what % of HF is COF_2 (assume all 128 F is in these gases for 16 sccm *c*-C_4F_8 experiments)

    i. $\frac{106.15\, COF_2}{1632\, HF} = .065 * 128 = 8.32$ equivalents

    ii. therefore HF is 112 equivalents

- Take number that HF is and determine number to divide all by (normalization factor)

    i. $\frac{1632\, HF}{112} = 14.57$

- Divide all others by this number

    i. $$CO - \frac{678.09}{14.57} = 46.54$$
    $$CO_2 - \frac{94.06}{14.57} = 6.45$$
    $$H_2O - \frac{24.82}{14.57} = 1.70$$

    ii. 112 HF + 8 COF_2 + 47 CO + 6 CO_2 + 2 H_2O

APPENDIX B

CALIBRATION CURVES

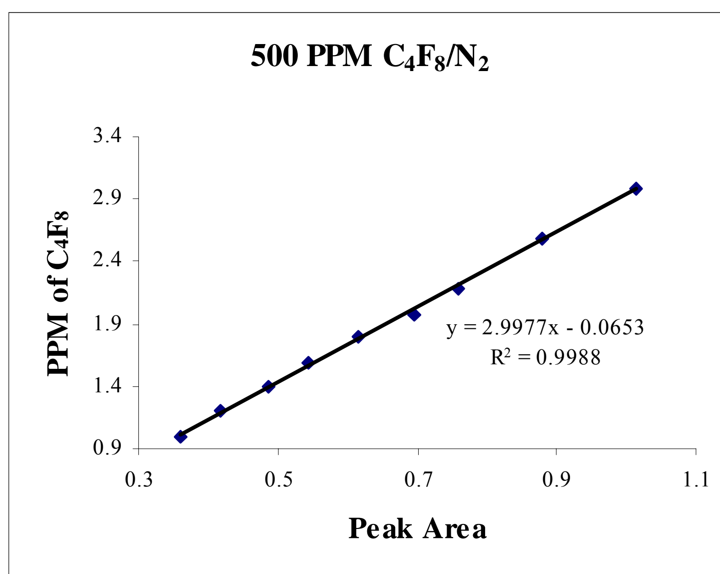

Figure B-1: Octafluorocyclobutane Calibration Curve Between 1-3.4ppm

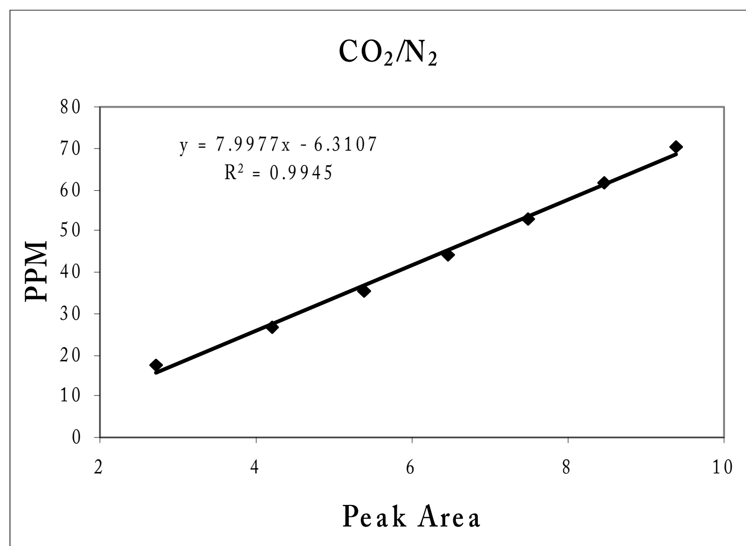

Figure B-2: Carbon Dioxide Calibration Curve Between 10-80ppm

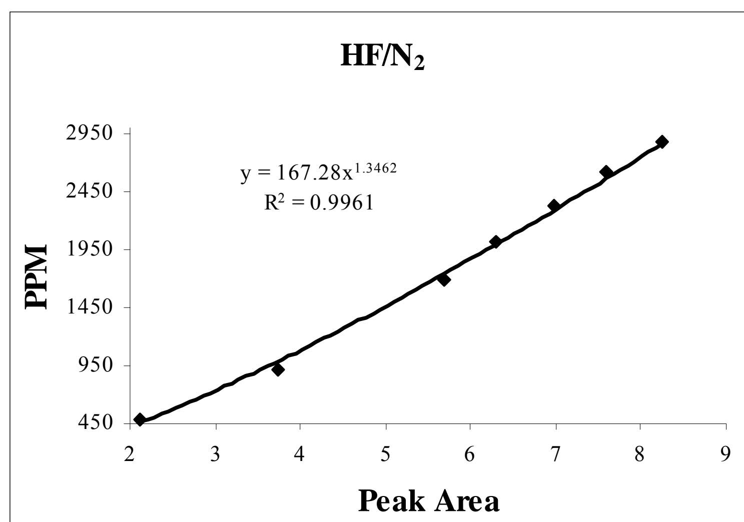

Figure B-3: Hydrogen Fluoride Curve Between 450-3000ppm

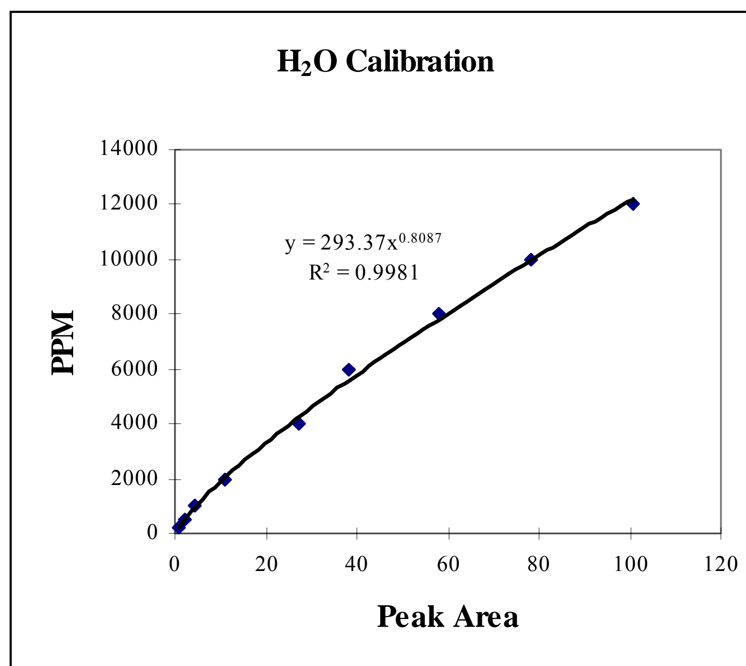

Figure B-4: Water Calibration Curve

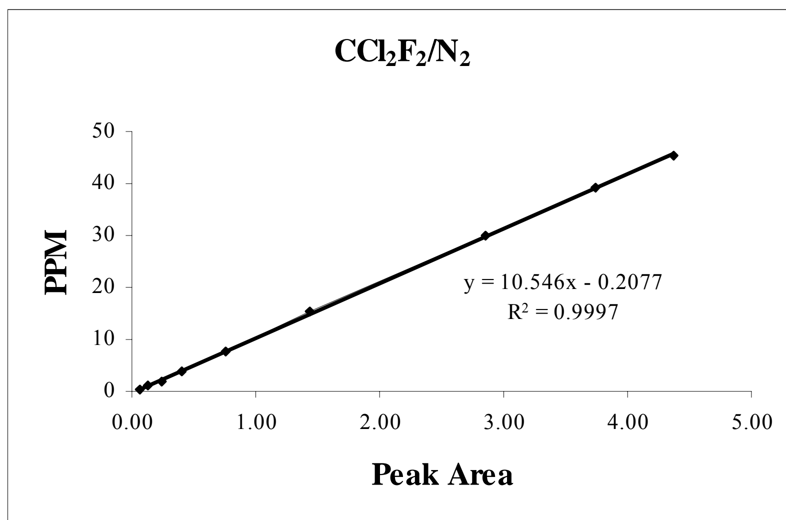

Figure B-5: Dichlorodifluoromethane Calibration Curve

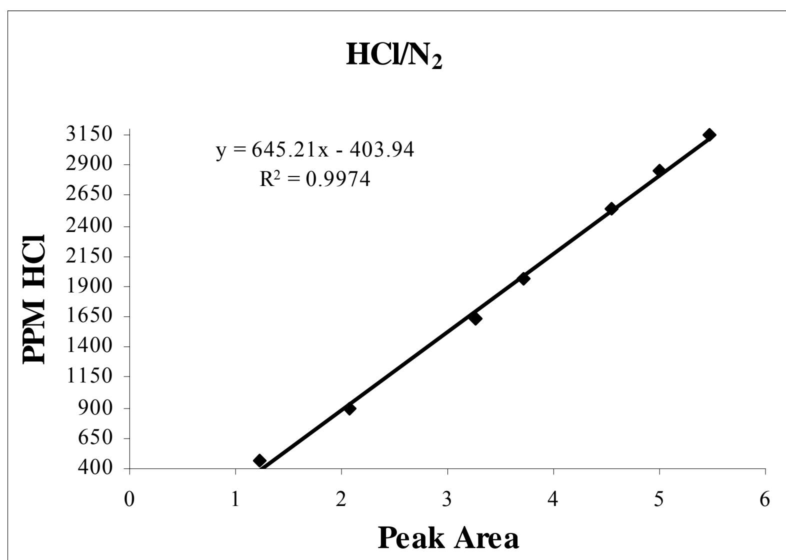

Figure B-6: Hydrogen Chloride Calibration Curve

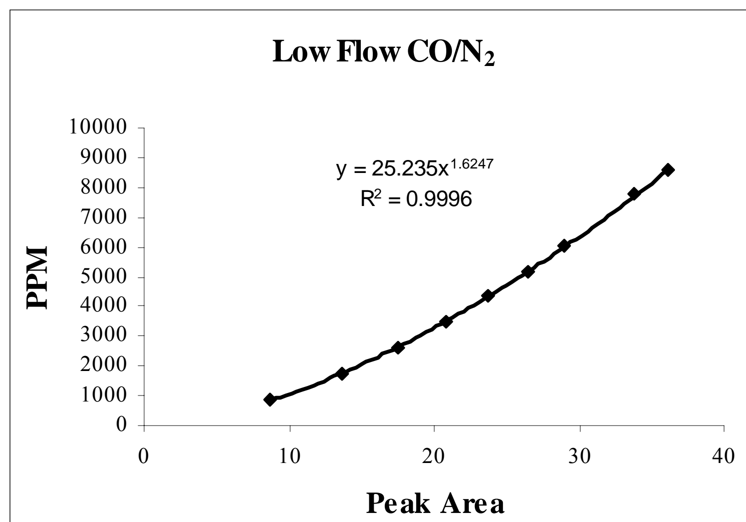

Figure B-7: Carbon Monoxide Calibration Curve for CFC Experiments

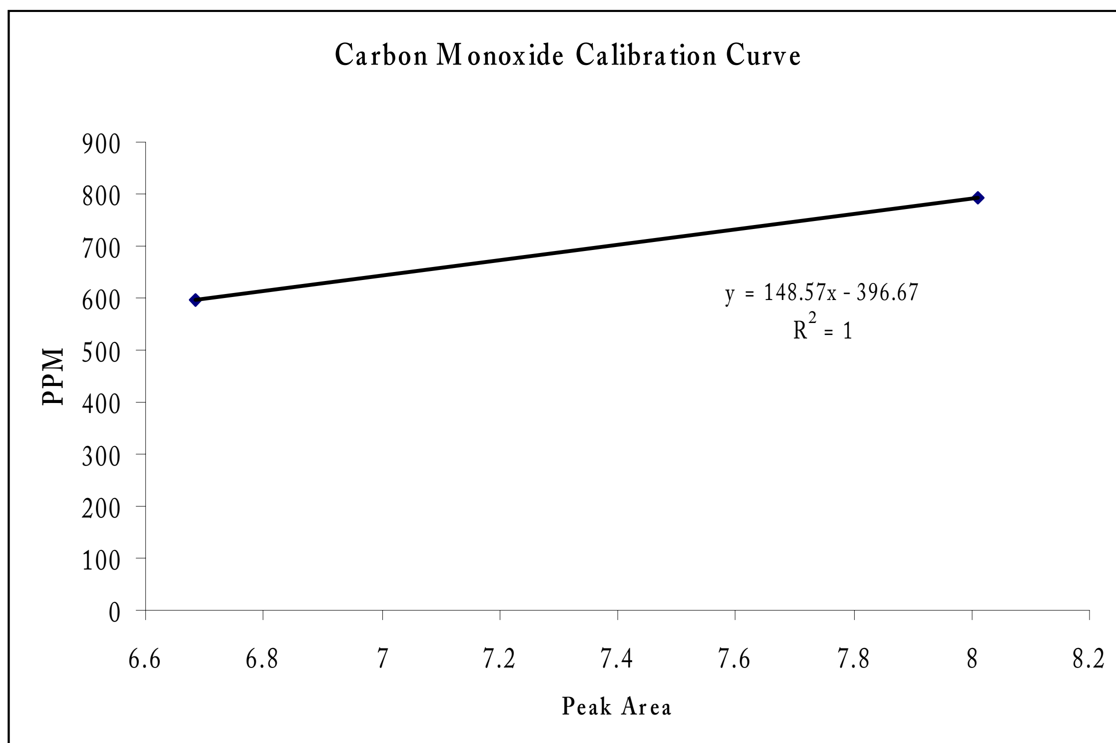

Figure B-8: Extrapolation Carbon Monoxide Calibration Curve

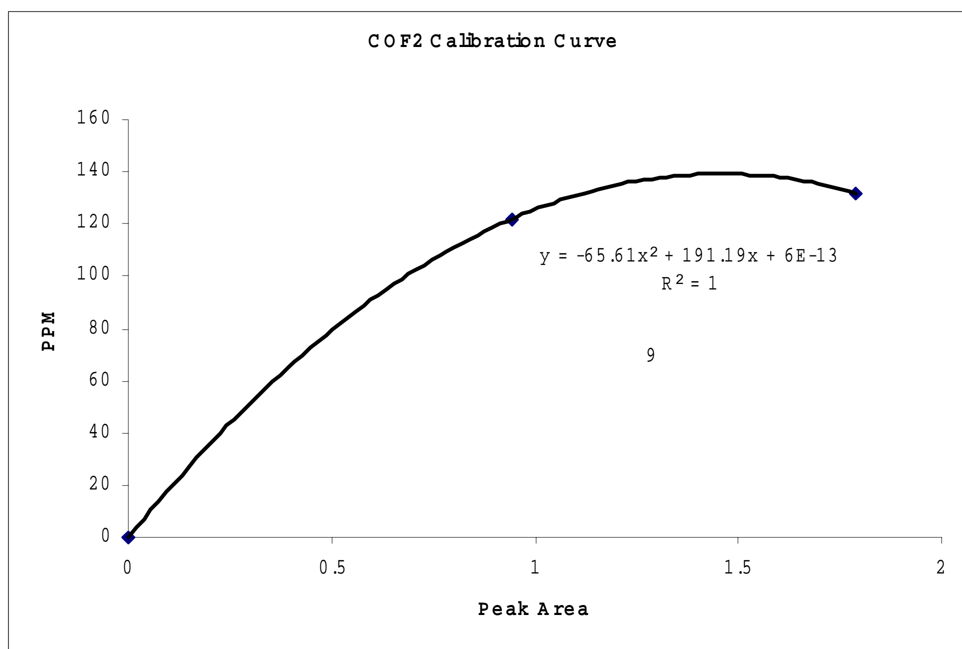

Figure B-8: Extrapolation of Carbonyl Fluoride Calibration Curve

APPENDIX C

GLOBAL_KIN .DAT CHEMISTRY FILE

```
!
! Fluorocarbon species
!
C4F8        :  0  ;     200.00   &    0.0    ]  1  [ 0.0      @C4F8   !
C4F8-       : -1  ;     200.00   &    1.0    ]  1  [ 1.0      @C4F8   !
C4F8-*      : -1  ;     200.00   &    1.0    ]  1  [ 1.0      @C4F8   !
C4F8^       :  1  ;     200.00   &    1.0    ]  1  [ 1.0      @C4F8   !
CF4         :  0  ;      88.00   &    0.0    ]  1  [ 0.0      @CF4    !
CF3         :  0  ;      69.00   &    0.01   ]  1  [ 0.005    @C2F6   !
CF3^        :  1  ;      69.00   &    1.0    ]  1  [ 1.0      @CF3    !
CF3-        : -1  ;      69.00   &    1.0    ]  1  [ 1.0      @CF3    !
CF2         :  0  ;      50.00   &    0.01   ]  1  [ 0.005    @C2F4   !
CF          :  0  ;      31.00   &    0.0    ]  1  [ 0.0      @CF     !
CF^         :  1  ;      31.00   &    1.0    ]  1  [ 1.0      @CF     !
CF2^        :  1  ;      50.00   &    1.0    ]  1  [ 1.0      @CF2    !
F           :  0  ;      19.00   &    0.5    ]  1  [ 0.25     @F2     !
F^          :  1  ;      19.00   &    1.0    ]  1  [ 1.0      @F      !
F-          : -1  ;      19.00   &    1.0    ]  1  [ 1.0      @F      !
F2          :  0  ;      38.00   &    0.0    ]  1  [ 0.0      @F2     !
F2^         :  1  ;      38.00   &    1.0    ]  1  [ 1.0      @F2     !
C           :  0  ;      12.01   &    0.0    ]  1  [ 0.0      @C      !
C^          :  1  ;      12.01   &    1.0    ]  1  [ 1.0      @C      !
C2F3        :  0  ;      81.00   &    0.0    ]  1  [ 0.0      @C2F3   !
C2F3^       :  1  ;      81.00   &    1.0    ]  1  [ 1.0      @C2F3   !
C2F4        :  0  ;     100.00   &    0.0    ]  1  [ 0.0      @C2F4   !
C2F4^       :  1  ;     100.00   &    1.0    ]  1  [ 1.0      @C2F4   !
C2F5        :  0  ;     119.00   &    0.0    ]  1  [ 0.0      @C2F5   !
C2F5^       :  1  ;     119.00   &    1.0    ]  1  [ 1.0      @C2F5   !
C2F6        :  0  ;     138.00   &    0.0    ]  1  [ 0.0      @C2F6   !
C3F5        :  0  ;     131.00   &    0.0    ]  1  [ 0.0      @C3F5   !
C3F5^       :  1  ;     131.00   &    1.0    ]  1  [ 1.0      @C3F5   !
C3F6        :  0  ;     150.00   &    0.0    ]  1  [ 0.0      @C3F6   !
C3F6^       :  1  ;     150.00   &    1.0    ]  1  [ 1.0      @C3F6   !
C3F7        :  0  ;     169.00   &    0.0    ]  1  [ 0.0      @C3F7   !
C3F7^       :  1  ;     169.00   &    1.0    ]  1  [ 1.0      @C3F7   !
C4F7        :  0  ;     181.00   &    0.0    ]  1  [ 0.0      @C4F7   !
C4F7^       :  1  ;     181.00   &    1.0    ]  1  [ 1.0      @C4F7   !
M           :  0  ;       1.00   &    0.0    ]  1  [ 0.0      @M      !
E           : -1  ;  5.444E-04   &    1.0    ]  1  [ 0.0      @E      !
!
! AR
!
AR          :  0  ;     40.00    &    0.0    ]  1  [   0.0    @AR     !
AR*         :  0  ;     40.00    &    1.0    ]  1  [   1.0    @AR     !
AR**        :  0  ;     40.00    &    1.0    ]  1  [   1.0    @AR     !
AR^         :  1  ;     40.00    &    1.0    ]  1  [   1.0    @AR     !
!
! O2
```

```
!
O2            :  0  ;      31.999   &   0.00    ]  1  [ 0.00    @O2    !
O2*           :  0  ;      31.999   &   1.E-5   ]  1  [ 0.01    @O2    !
O2^           :  1  ;      31.999   &   1.00    ]  1  [ 1.00    @O2    !
O2-           : -1  ;      31.999   &   1.00    ]  1  [ 1.00    @O2    !
O             :  0  ;      15.999   &   0.02    ]  1  [ 0.01    @O2    !
O*            :  0  ;      15.999   &   1.0     ]  1  [ 1.00    @O     !
O^            :  1  ;      15.999   &   1.00    ]  1  [ 1.00    @O     !
O-            : -1  ;      15.999   &   1.00    ]  1  [ 1.00    @O     !
!
! COFn
!
CO            :  0  ;      28.00    &    0.0    ]  1  [ 0.0     @CO    !
CO^           :  1  ;      28.00    &    1.0    ]  1  [ 1.0     @CO    !
COF           :  0  ;      47.00    &    0.0    ]  1  [ 0.0     @COF   !
COF2          :  0  ;      66.00    &    0.0    ]  1  [ 0.0     @COF2  !
CO2           :  0  ;      44.00    &    0.0    ]  1  [ 0.0     @CO2   !
FO            :  0  ;      35.00    &    0.0    ]  1  [ 0.0     @FO    !
!
! N2 species
!
N2            :  0  ;       28.00   &    0.0    ]  1  [ 0.0     @N2    !
N2V           :  0  ;       28.00   &    0.25   ]  1  [ 0.25    @N2    !
N2*           :  0  ;       28.00   &    0.5    ]  1  [ 0.5     @N2    !
N2^           :  1  ;       28.00   &    1.0    ]  1  [ 1.0     @N2    !
N             :  0  ;       14.00   &    0.1    ]  1  [ 0.05    @N2    !
N*            :  0  ;       14.00   &    0.1    ]  1  [ 0.05    @N2    !
N^            :  1  ;       14.00   &    1.0    ]  1  [ 1.0     @N     !
!
! N/Flourocarbon
!
CN            :  0  ;       26.01   &    0.0    ]  1  [ 0.0     @CN    !
!
! Hydrogen species
!
H2            :  0  ;        2.00   &    0.0    ]  1  [ 0.0     @H2    !
H2^           :  1  ;        2.00   &    1.0    ]  1  [ 1.0     @H2    !
H             :  0  ;        1.00   &    0.0    ]  1  [ 0.0     @H     !
H2O           :  0  ;       18.00   &    0.0    ]  1  [ 0.0     @H2O   !
OH            :  0  ;       17.00   &    0.0    ]  1  [ 0.0     @OH    !
H-            : -1  ;        1.00   &    1.0    ]  1  [ 1.0     @H     !
H2O^          :  1  ;       18.00   &    1.0    ]  1  [ 1.0     @H2O   !
OH-           : -1  ;       17.00   &    1.0    ]  1  [ 1.0     @OH    !
HO2           :  0  ;       33.00   &    0.0    ]  1  [ 0.0     @HO2   !
H3O^          :  1  ;       19.00   &    1.0    ]  1  [ 1.0     @H2O   !
>                        :          &    1.0    ]  1  [ 1.0     @H     !
HF            :  0  ;       20.00   &    0.0    ]  1  [ 0.0     @HF    !
*
!
! Fluorocarbon reactions
!
E + CF4 > CF3 + F-           : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [   50  !
E + CF4 > CF3- + F           : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  538 !
E + CF4 > CF3 + F + E        : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  506 !
```

```
E + CF4 > CF3^ + F + E + E    : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  507 !
E + CF4 > CF2 + F + F + E     : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  533 !
E + CF4 > CF3^ + F- + E       : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  824 !
E + CF4 > CF + F + F2 + E     : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  829 !
E + CF3 > CF2 + F + E         : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  821 !
E + CF3 > CF3^ + E + E        : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1182 !
E + CF3 > CF2^ + F + E + E    : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  822 !
E + CF3 > CF2 + F-            : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  823 !
E + CF2 > CF + F-             : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1112 !
E + CF2 > CF + F + E          : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1113 !
E + CF2 > CF2^ + E + E        : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1114 !
E + CF2 > CF^ + F + E + E     : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1115 !
E + CF > C + F + E            : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1187 !
E + CF  > CF^ + E + E         : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1188 !
E + C > C^ + E + E            : 6.74E-09 ; 0.6774 & 11.26 ] 0. [ -1   !
E + F > F^ + E + E            : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  1029!
E + C2F6 > CF3^ + CF3 + E + E : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  820 !
E + C2F6 > CF3 + CF3-         : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  819 !
E + C2F6 > C2F5 + F-          : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1148 !
E + C2F6 > CF3 + CF3 + E      : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  536 !
E + C2F4 > CF2 + CF2 + E      : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  537 !
E + C2F4 > C2F4^ + E + E      : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  831 !
E + C2F4 > C2F3^ + F + E + E  : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  832 !
E + C2F4 > CF^ + CF3 + E + E  : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [  1983!
E + C2F5 > CF3- + CF2         : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1143 !
E + C2F5 > CF3 + CF2 + E      : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1146 !
E + C2F5 > CF3^ + CF2 + E + E : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1147 !
E + C2F5 > C2F5^ + E + E      : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [ 1909 !
E + C4F8 > C2F4 + C2F4 + E    : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1984 !
E + C4F8 > C4F8-*             : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1985 !
E + C4F8 > F- + C4F7          : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1986 !
E + C4F8 > C3F5^ + CF3 + E + E: 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1987 !
E + C4F8 > C2F4^ + C2F4 + E + E: 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1988!
E + C4F8 > F^ + C4F7 + E + E   : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1989!
E + C4F8 > CF3^ + C3F5 + E + E : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1990!
E + C4F8 > CF2^ + C3F6 + E + E : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1991!
E + C4F8 > CF^ + C3F7 + E + E  : 0.00E+00 ;  0.00 & 0.000 ] 2.0 [ 1992!
E + C2F3 > CF + CF2 + E           : 1.00E-08 ; 0.906 &  5.0  ] 2.0 [ -1
E + C3F5 > C2F3 + CF2 + E         : 1.81E-08 ; 0.521 & 12.3  ] 2.0 [ -1
E + C3F5 > C2F4 + CF + E          : 1.81E-08 ; 0.521 & 12.3  ] 2.0 [ -1
E + C3F6 > C3F6^ + E + E          : 1.44E-08 ; 0.680 & 10.6  ] 0.0 [ -1
E + C3F6 > C2F3 + CF3 + E         : 1.81E-08 ; 0.521 & 12.3  ] 2.0 [ -1
E + C3F6 > C2F4 + CF2 + E         : 1.81E-08 ; 0.521 & 12.3  ] 2.0 [ -1
E + C3F7 > C2F4 + CF3 + E         : 1.81E-08 ; 0.521 & 12.3  ] 2.0 [ -1
E + C4F7 > C2F4 + C2F3 + E        : 5.71E-08 ; 0.280 &  8.0  ] 2.0 [ -1
E + C4F7 > C4F7^ + E + E          : 1.44E-08 ; 0.680 & 10.6  ] 0.0 [ -1
E + F2 > F- + F                : 0.00E+00 ;  0.00 & 0.000 ] 1.0 [  925!
E + F2 > F2^ + E + E           : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [  931!
E + F2^ > F + F                : 8.00e-08 ; -0.50 & 0.000 ] 2.0 [   -1!
E + CF^ > C + F                : 8.00e-08 ; -0.50 & 0.000 ] 2.0 [   -1!
E + F2^ > F + F                : 8.00e-08 ; -0.50 & 0.000 ] 4.0 [   -1!
E + CF3^ > CF2 + F             : 3.00e-08 ; -0.50 & 0.000 ] 4.0 [   -1!
E + CF2^ > CF + F              : 8.50e-08 ; -0.50 & 0.000 ] 4.0 [   -1!
E + C2F5^ > CF3 + CF2          : 8.00e-08 ; -0.50 & 0.000 ] 4.0 [   -1!
```

```
E + C2F4^ > CF2 + CF2          : 8.00e-08 ; -0.50 & 0.000 ] 4.0 [    -1
E + C2F3^ > CF2 + CF           : 8.00e-08 ; -0.50 & 0.000 ] 5.0 [    -1!
E + C3F5^ > C2F3 + CF2         : 8.00e-08 ; -0.50 & 0.000 ] 5.0 [    -1!
E + C3F6^ > C2F4 + CF2         : 8.00e-08 ; -0.50 & 0.000 ] 5.0 [    -1!
E + C3F7^ > C2F4 + CF3         : 8.00e-08 ; -0.50 & 0.000 ] 5.0 [    -1!
E + C4F7^ > C2F4 + C2F3        : 8.00e-08 ; -0.50 & 0.000 ] 5.0 [    -1!
E + C4F8^ > C2F4 + C2F4        : 8.00e-08 ; -0.50 & 0.000 ] 5.0 [    -1!
F^ + F2 > F2^ + F              : 7.94E-10 ; 0.00 & 0.000 ] 0.0 [     1 !
C + C2F4 > C2F3 + CF           : 1.91E-10 ; 0.00 & 0.000 ] 0.0 [     1 !
C^ + CF3 > CF2^ + CF           : 2.48E-9  ; 0.00 & 0.000 ] 0.0 [     1 !
C^ + C > C^ + C               : 1.00E-9  ; 0.00 & 0.000 ] 0.0 [     !EST
C^ + CF > CF^ + C              : 3.18E-9  ; 0.00 & 0.000 ] 0.0 [     1 !
CF^ + CF3 > CF3^ + CF          : 1.71E-9  ; 0.00 & 0.000 ] 0.0 [     1 !
CF^ + CF4 > CF3^ + CF2         : 1.80E-10 ; 0.00 & 0.000 ] 0.0 [     1 !
CF^ + C2F4 > CF3^ + CF + CF    : 2.60E-10 ; 0.00 & 0.000 ] 0.0 [     1 !
CF^ + C2F4 > C3F5^       : 1.30E-10 ; 0.00 & 0.000 ] 0.0 [     1 ! Ref.4
CF^ + C2F6 > CF3^ + C2F4      : 2.00E-10 ; 0.00 & 0.000 ] 0.0 [     1 !
CF^ + CF > CF^ + CF         : 2.00E-10 ; 0.00 & 0.000 ] 0.0 [     1 !EST
CF2 + CF3 > C2F5               : 1.00E-12 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3 + CF3 + M > M + C2F6    : 3.94E-29 ; 0.00 & 0.000 ] 0.0 [     1!
CF3 + CF3 > C2F6               : 8.30E-12 ; 0.00 & 0.000 ] 0.0 [     1 !
CF2 + CF2 > C2F4               : 7.21E-14 ; 0.00 & 0.000 ] 0.0 [     1 !
CF2^ + C4F8 > C3F5^ + C2F4 + F : 2.10E-11 ; 0.00 & 0.000 ] 0.0 [     1 !
CF2^ + C2F4 > C2F4^ + CF2      : 1.00E-9  ; 0.00 & 0.000 ] 0.0 [     1 !
CF2^ + C2F6 > C2F5^ + CF3: 3.50E-11 ; 0.00 & 0.000 ] 0.0 [     1 ! ESTE.
CF2^ + CF3 > CF3^ + CF2     : 1.48E-09 ; 0.00 & 0.000 ] 0.0 [     1
CF2^ + CF4 > CF3^ + CF3       : 0.40E-09 ; 0.00 & 0.000 ] 0.0 [     1 !
CF2^ + CF > CF3^ + C           : 2.06E-09 ; 0.00 & 0.000 ] 0.0 [     1 !
CF2^ + C > CF^ + CF            : 1.04E-09 ; 0.00 & 0.000 ] 0.0 [     1 !
CF2^ + CF2 > CF2^ + CF2     : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [     1 !EST
CF3^ + C3F5 > C3F5^ + CF3     : 7.04E-10 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3^ + C3F7 > C3F7^ + CF3  : 7.04E-10 ; 0.00 & 0.000 ] 0.0 [     1 !ES
CF3^ + CF3 > CF3^ + CF3        : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3^ + C2F4 > C3F7^      : 3.30E-11 ; 0.00 & 0.000 ] 0.0 [     1 ! Ref.4
CF3^ + C2F6 > C2F5^ + CF4 : 2.50E-12 ; 0.00 & 0.000 ] 0.0 [     1 !Ref.3
CF3- + CF^ > CF3 + CF      : 7.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 ! Est
CF3- + C^ > CF3 + C           : 7.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3- + F^ > CF3 + F           : 7.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3- + F2^ > CF3 + F2          : 5.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3- + CF3^ > CF3 + CF3        : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3- + C2F4^ > CF3 + C2F4      : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3- + C2F3^ > CF3 + C2F3  : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 ! est
CF3- + C2F5^ > CF3 + C2F5     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3- + C3F5^ > CF3 + C3F5  : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 ! EST
CF3- + C3F7^ > CF3 + C3F7  : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 ! EST
CF3- + C4F7^ > CF3 + C4F7  : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 ! EST
CF3- + C4F8^ > CF3 + C4F8  : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 ! EST
CF3- + CF2^ > CF3 + CF2    : 5.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3- + F > CF3 + F-        : 5.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !
CF3- + CF3 > C2F6 + E      : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [     1 !Est.
C2F4^ + C2F4 > C2F4 + C2F4^ : 4.00E-09 ; 0.00 & 0.000 ] 0.0 [     1 !
C2F4^ + C2F4 > C3F5^ + CF3     : 1.00E-11 ; 0.00 & 0.000 ] 0.0 [     1 !
C2F5^ + C2F5 > C2F5 + C2F5^    : 4.00E-09 ; 0.00 & 0.000 ] 0.0 [     1 !
C3F5^ + C3F5 > C3F5^ + C3F5 : 3.00E-9  ; 0.00 & 0.000 ] 0.0 [     1 !EST
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C3F7^ + C2F4 > CF3^ + C4F8 : 9.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !Ref.4
C3F7^ + C3F7 > C3F7^ + C3F7 : 3.00E-9  ; 0.00 & 0.000 ] 0.0 [    1 !EST
F + CF3 > CF4          : 2.00e-11 ; 0.00 & 0.000 ] 0.0 [    1 !Ref.17
F + CF2 > CF3          : 1.80E-11 ; 0.00 & 0.000 ] 0.0 [    1 !Ref.19
F + CF > CF2           : 9.96e-11 ; 0    &  0    ] 0.0 [    1 !Ref.6
F + F + M > F2 + M         : 6.77E-34 ; 0.00 & 0.000 ] 0.0 [    1 !
F + C2F4 > CF3 + CF2    : 4.80E-11 ; 0.00 & 0.000 ] 0.0 [    1 !Ref.21
F + C2F5 > CF3 + CF3         : 1.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
F + C4F7 > C2F4 + C2F4      : 1.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !EST
F + C3F6 > C3F7            : 1.00E-12 ; 0.00 & 0.000 ] 0.0 [    1 !EST
F + C2F3 > C2F4                   : 1.00E-12 ; 0.00 & 0.000 ] 0.0
F + CF3 + M > CF4 + M   : 1.60E-28 ; 0.00 & 0.000 ] 0.0 [    1 !500 mT
F^ + CF > C^ + F2      : 2.71E-9  ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F^ + C > C^ + F         : 1.17E-9  ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F^ + F2 > F2^ + F       : 7.94E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F^ + CF2 > CF^ + F2       : 2.28E-9  ; 0.00 & 0.000 ] 0.0 [    1 !Ref.2
F^ + CF3 > CF2^ + F2     : 2.09E-9  ; 0.00 & 0.000 ] 0.0 [    1 !Ref.2
F^ + CF4 > CF3^ + F2     : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [    1 !IKEZOE
F^ + C2F6 > C2F5^ + F2    : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! EST.
F^ + C2F5 > C2F4^ + F2    : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! EST.
F^ + C2F4 > C2F4^ + F     : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! EST.
F^ + F > F^ + F           : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [    1 !
F- + CF3 > CF4 + E       : 4.00E-10 ; 0.00 & 0.000 ] 0.0 [ 1 !ESTRef.14
F- + CF2 > CF3 + E       : 3.00E-10 ; 0.00 & 0.000 ] 0.0 [ 1 !ESTRef.14
F- + CF > CF2 + E        : 2.00E-10 ; 0.00 & 0.000 ] 0.0 [ 1 !ESTRef.14
F- + C > CF + E          : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [ 1 !ESTRef.14
F- + F > F2 + E          : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [ 1 !ESTRef.14
F- + CF3^ > CF2 + F2     : 8.70E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F- + CF3^ > CF2 + F + F  : 3.00E-07 ; -0.5 & 0.000 ] 0.0 [ 1 !ESTRef.14
F- + CF3^ > F + CF3      : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1
F- + CF2^ > CF + F2      : 9.10E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F- + CF2^ > F + CF2      : 5.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !
F- + CF^ > CF + F        : 9.80E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F- + CF^ > C + F + F     : 7.00E-07 ; -0.5 & 0.000 ] 0.0 [ 1 !ESTRef.14
F- + F2^ > F + F2        : 9.40E-08 ; 0.00 & 0.000 ] 0.0 [    1 !Ref.2
F- + F^ > F + F          : 7.10E-07 ; 0.00 & 0.000 ] 0.0 [    1 !Ref.2
F- + C^ > F + C          : 2.20E-07 ; 0.00 & 0.000 ] 0.0 [    1 !Ref.2
F- + C2F5^ > F + C2F5    : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [    1 !
F- + C2F4^ > CF +CF2 + F2: 8.20E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F- + C2F3^ > F + C2F3    : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! EST
F- + C3F5^ > C2F4 + CF2  : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F- + C3F6^ > C2F4 + CF3  : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! EST
F- + C3F7^ > C2F6 + CF2  : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! EST
F- + C4F7^ > C2F5 + C2F3 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! EST
F- + C4F8^ > C2F6 + C2F3 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [    1 ! EST
F2 + CF2 > CF3 + F       : 8.30E-14 ; 0    & 0     ] 0.0 [    1 !Ref.6
F2 + CF3 > CF4 + F       : 1.88E-14 ; 0.00 & 0.000 ] 0.0 [    1 !
F2 + C2F4 > C2F5 + F     : 3.50E-16 ; 0.00 & 0.000 ] 0.0 [    1 !Ref.16
F2 + C3F6 > C3F7 + F     : 3.50E-16 ; 0.00 & 0.000 ] 0.0 [    1 !EST
F2^ + CF > CF2^ + F      : 2.18E-9  ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F2^ + C > CF^ + F        : 1.04E-9  ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
F2^ + CF2 > CF3^ + F     : 1.79E-9  ; 0.00 & 0.000 ] 0.0 [    1 !Ref.2
F2^ + CF2 > CF2^ + F2    : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [    1 !
F2^ + CF3 > CF3^ + F + F : 1.60E-9  ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.2
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F2^ + CF4 > CF3^ + F + F2 : 1.00E-10 ; 0.00 & 0.000 ] 1.0 [     1 !EST.
F2^ + C2F4 > C2F4^ + F2   : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [     1 ! EST.
F2^ + C2F5 > C2F5^ + F2   : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [     1 ! EST.
F2^ + F2 > F2^ + F2       : 1.00E-9  ; 0.00 & 0.000 ] 0.0 [     1 ! EST.
C4F8-* > C4F8 + E         : 1.00E+5  ; 0.00 & 0.000 ] 0.0 [     1 !EST.
C4F8-* + M > C4F8- + M    : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [     1 !ES
C4F8- + CF^ > C4F8 + CF   : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !Est
C4F8- + C^ > C4F8 + C     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + F^ > C4F8 + F     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + F2^ > C4F8 + F2   : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + CF3^ > C4F8 + CF3 : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + C2F4^ > C4F8 + C2F4 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + C2F3^ > C4F8 + C2F3 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !est
C4F8- + C2F5^ > C4F8 + C2F5 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + C3F5^ > C4F8 + C3F5 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + C3F6^ > C4F8 + C3F6 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + C3F7^ > C4F8 + C3F7 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + C4F7^ > C4F8 + C4F7 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + C4F8^ > C4F8 + C4F8 : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + CF2^ > C4F8 + CF2   : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + F > C4F8 + F-       : 1.00E-09 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8- + C4F8 > C4F8 + C4F8- : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + CF^ > C4F8 + CF    : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !Est
C4F8-* + C^ > C4F8 + C      : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + F^ > C4F8 + F      : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + F2^ > C4F8 + F2    : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + CF3^ > C4F8 + CF3  : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + C2F4^ > C4F8 + C2F4  : 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !E
C4F8-* + C2F3^ > C4F8 + C2F3: 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !est
C4F8-* + C2F5^ > C4F8 + C2F5: 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + C3F5^ > C4F8 + C3F5: 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + C3F6^ > C4F8 + C3F6: 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + C3F7^ > C4F8 + C3F7: 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + C4F7^ > C4F8 + C4F7: 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + C4F8^ > C4F8 + C4F8: 8.00E-08 ; 0.00 & 0.000 ] 0.0 [     1 !EST
C4F8-* + CF2^ > C4F8 + CF2: 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
!
! Ar only reactions
!
E + AR > AR* + E        : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [    2  !
E + AR > AR** + E       : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [    3  !
E + AR > AR^ + E + E    : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [    4  !
E + AR* > AR^ + E + E         : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [    6  !
E + AR* > AR + E              : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [ 274  !
E + AR* > AR** + E             : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [    5  !
E + AR* > AR** + E             : 8.87E-07 ;  0.506 & 1.52 ] 0.0 [  -1  !
E + AR** > AR + E              : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [ 275  !
E + AR** > AR^ + E + E         : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [    7  !
E + AR** > AR^ + E + E         : 1.84E-07 ;  0.614  & 2.663 ] 0.0 [ -1 !
E + AR** > AR* + E             : 0.00E+00 ;  0.00 & 0.000 ] 0.0 [ 277  !
AR* + AR* > AR^ + AR + E : 1.20E-09 ; 0.00 & 0.000 ] 0.0 [     1  ! R39
AR** + AR** > AR^ + AR + E: 1.20E-09 ; 0.00 & 0.000 ] 0.0 [     1  ! R39
AR** + AR* > AR^ + AR + E: 1.20E-09 ; 0.00 & 0.000 ] 0.0 [     1  ! R39
AR** > AR*                : 1.00E+05 ; 0.00 & 0.000 ] 0.0 [ 1  ! 2.E+06
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AR^ + AR > AR^ + AR           : 5.66E-10 ; 0.00 & 0.000 ] 0.0 [    1 !
!
! Ar-Fluorocarbon
!
AR* + CF4 > CF2 + F2 + AR      : 4.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
AR* + CF3 > CF2 + F + AR       : 4.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
AR* + CF2 > CF + F + AR        : 4.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
AR* + C2F6 > CF3 + CF3 + AR    : 4.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
AR* + C2F4 > CF2 + CF2 + AR    : 4.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
AR* + C4F8 > C2F4 + C2F4 + AR: 9.00E-10; 0.00 & 0.000 ] 0.0 [ 1 ! Ref.1
AR^ + CF4 > CF3^ + AR + F:4.79E-10 ; 0.00 & 0.000 ] 0.0 [    1 !REF.4
AR^ + CF4 > CF3^ + F + AR: 7.00E-10;0.00 & 0.000 ] 0.0 [    1 ! FISHER
AR^ + CF3 > CF3^ + AR          : 7.00E-10 ; 0.00 & 0.000 ] 0.0 [    1 !
AR^ + C2F6 > CF3^ + CF3 + AR   : 9.58E-10 ; 0.00 & 0.000 ] 0.0 [    1 !
AR^ + C2F5 > C2F5^ + AR   : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! EST.
AR^ + C2F4 > C2F4^ + AR   : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! EST.
AR^ + C4F8 > C2F4^ + C2F4 + AR:9.00E-10;0.00&0.000]0.0[ 1 !Ref.22, EST.
AR^ + C2F6 > CF3^ + CF3 + AR: 6.00E-10 ; 0.00 & 0.000 ]0.0 [1 !Ref.2,22
CF3- + AR^ > CF3 + AR        : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !
F- + AR^ > F + AR              : 5.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !
C4F8- + AR^ > C4F8 + AR      : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !Est
C4F8-* + AR^ > C4F8 + AR     : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !Est
!
! O2 only reactions
!
E + O2 > O- + O          : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   401 !
E + O2 > O2* + E         : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   407 !
E + O2 > O2* + E         : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   408 !
E + O2 > O + O + E       : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   411 !
E + O2 > O* + O + E      : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   412 !
E + O2 > O2^ + E + E     : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   415 !
E + O2 > O^ + O + E + E  : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   417 !
E + O2 + M > O2- + M     : 3.60E-31 ; -0.5 &  0.0   ]  0.00 [    -1 !
E + O2^ > O + O         : 1.20E-08 ; -0.7 &  0.0   ]  6.88 [    -1 !R36
E + O2^ > O* + O        : 8.88E-09 ; -0.7 &  0.0   ]  4.91 [    -1 !R36
E + O2* > O2 + E         : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [  -407 !
E + O2* > O2^ + E + E   : 1.30e-09 ; 1.1  &  11.1  ]  0.00 [    -1 !R28
E + O > O* + E           : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   935 !
E + O > O* + E           : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   936 !
E + O > O^ + E + E       : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   941 !
E + O* > O + E           : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   943 !
E + O* > O^ + E + E      : 0.00E+00 ; 0.00 &  0.0   ]  0.00 [   944 !
E + O- > O + E + E      : 1.95E-12 ; 0.5  &  3.4   ]  0.00 [    -1 !R29
E + O^ > O*             : 5.30e-13 ; -0.5 &  0.0   ]  0.00 [    -1 !R30
O- + O2^ > O + O2       : 2.00E-07 ; -1.0 &  0.0   ] 10.53 [     1 !R36
O- + O2^ > O + O + O    : 1.00E-07 ; 0.00 &  0.0   ]  5.35 [     1 !R36
O- + O^ > O + O         : 2.00E-07 ; -1.0 &  0.0   ] 12.09 [     1 !R36
O2- + O2^ > O2 + O2     : 2.00E-07 ; -1.0 &  0.0   ] 11.56 [     1 !R36
O2- + O2^ > O2 + O + O  : 1.00E-07 ; 0.00 &  0.0   ]  6.38 [     1 !R36
O2- + O^ > O2 + O       : 2.00E-07 ; -1.0 &  0.0   ] 13.12 [     1 !R36
O- + O2^ + M > O + O2 + M : 2.0E-25 ; -2.5 &  0.0   ] 10.53 [     1 !R36
O- + O^ + M > O + O + M  : 2.00E-25 ; -2.5 &  0.0   ] 12.09 [     1 !R36
O- + O > O2 + E          : 2.00e-10 ; 0.50 &  0.0   ]  0.00 [     1 !R32
O2- + O > O- + O2        : 1.50E-10 ; 0.50 &  0.0   ]  1.03 [     1 !R32
```

```
O2- + O2* > E + O2 + O2  : 2.00E-10 ; 0.50 &  0.0   ]  0.00 [     1 !R32
O + O^ > O + O^          : 1.00E-09 ; 0.50 &  0.0   ]  0.00 [     1 !
O + O^ + M > O2^ + M     : 1.00E-29 ; 0.50 &  0.0   ]  0.00 [     1 !R36
O2 + O2^ > O2 + O2^      : 1.00E-09 ; 0.50 &  0.0   ]  0.00 [     1 !
O^ + O2 > O2^ + O        : 2.00E-11 ;-0.40 &  0.0   ]  0.00 [     1 !R32
O* + O > O + O           : 8.00E-12 ; 0.00 &  0.0   ]  1.97 [     1 !R36
O* + O2 > O + O2*        : 0.16E-11 ; 0.00 & -67.0  ]  0.99 [     1 !R33
O* + O2 > O + O2         : 0.48E-11 ; 0.00 & -67.0  ]  1.97 [     1 !R33
O2* + O > O2 + O         : 2.00E-16 ; 0.00 &  0.0   ]  0.98 [     1 !R34
O2* + O2 > O2 + O2       : 3.00E-18 ; 0.00 &  200.0 ]  0.98 [     1 !R33
O2* + O2* > O2 + O2      : 0.90E-16 ; 0.00 &  560.  ]  1.96 [     1 !R35
O + O + M > O2 + M       : 2.56E-34 ; -0.63 &  0.0  ]  5.18 [    1 !R36A
O + O + M > O2* + M      : 1.93E-35 ; -0.63 &  0.0  ]  4.20 [    1 !R36A
!
! Ar/O2 Reactions
!
AR* + O2 > O + O + AR    : 2.10E-10 ; 0.00 &  0.000 ] 0.0   [     1 R37
AR* + O > O* + AR        : 4.10E-11 ; 0.0  &  0.000 ] 0.0   [    1 ! R38
O- + AR^ > O + AR        : 1.00E-07 ; 0.00 &  0.000 ] 0.0   [     1 !Est
O2- + AR^ > O2 + AR      : 1.00E-07 ; 0.00 &  0.000 ] 0.0   [     1 !Est
AR^ + O2 > O2^ + AR      : 5.10E-11 ; 0.00 &  0.000 ] 0.0   [    1 ! R32
AR^ + O > O^ + AR        : 1.00E-11 ; 0.00 &  0.000 ] 0.0   [  1 ! EST.
O* + AR > O + AR         : 5.00E-13 ; 0.50 &  0.0   ] 0.0   [  1 ! R37
O2* + AR > O2 + AR       : 1.00E-19 ; 0.50 &  0.0   ] 0.0   [  1 ! R37
!
! COFn Only Reactions
!
!E + CO > COV + E              : 0.00E+00 ;  0.00 & 0.000 ] 1.01 [946 !
!E + CO > CO* + E              : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [947 !
E + CO > C + O + E           : 0.00E+00 ;  0.00 & 0.000 ] 2.0  [  948 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  949 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  950 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  951 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  952 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  953 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  954 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  955 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  956 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  957 !
!E + CO > CO* + E            : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  958 !
E + CO > CO^ + E + E         : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  959 !
E + CO > CO^ + E + E         : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  960 !
E + CO > CO^ + E + E         : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  961 !
E + CO > CO^ + E + E         : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  962 !
E + CO > CO^ + E + E         : 0.00E+00 ;  0.00 & 0.000 ] 0.0  [  963 !
CO^ + CO > CO^ + CO          : 1.00E-9  ;  0.00 & 0.000 ] 0.0 [1 ! EST.
CO^ + CO > C^ + CO2        : 1.00E-11 ;  0.00 & 0.000 ] 0.0  1 ! REF.32
!
! O2/COFn/Fluorocarbon Reactions
!
C + O2 > CO + O          : 1.60E-11 ; 0.00 & 0.000 ] 0.0 [    1 ! Ref.8
CF + O > CO + F     : 3.90E-11 ; 0.0 & 0.0 ] 0.0 [ 1 ! Ref.12(5-10Torr)
CF2 + O > COF + F  : 1.63E-11 ; 0.0 & 0.0 ] 0.0 [ 1 ! Ref.10(1-10 Torr)
CF3 + O > COF2 + F : 3.32E-11 ; 0.0 & 0.0 ] 0.0 [ 1 ! Ref.11(1-5 Torr)
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CF3- + O2^ > CF3 + O2          : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !
CF3- + O^ > CF3 + O            : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !
CF3- + CO^ > CF3 + CO      : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 ! EST
CO + O + M > CO2 + M    : 8.27E-34 ; 0.00 & 1510. ] 0.0 [    1 ! Ref.37
COF + CF2 > CF3 + CO           : 3.00E-13 ; 0.00 & 0.000 ] 0.0 [    1 !
COF + CF2 > COF2 + CF          : 3.00E-13 ; 0.00 & 0.000 ] 0.0 [    1 !
COF + CF3 > CF4 + CO           : 1.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
COF + CF3 > COF2 + CF2         : 1.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
COF + COF > COF2 + CO          : 1.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
F^ + O > O^ + F            : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! EST
F^ + O2 > O2^ + F       : 7.14E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.43
F^ + O2 > O^ + FO       : 5.04E-11 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.43
F- + CO^ > F + CO    : 4.00E-7  ; -0.5 & 0.00 ] 0.0 [ 1 ! EST (Ref.14)
F- + O2^ > F + O2    : 4.00E-07 ; -0.5 & 0.00 ] 0.0 [ 1 ! EST (Ref.14)
F- + O^ > F + O       : 4.00E-07 ; -0.5 & 0.00 ] 0.0 [ 1 ! EST (Ref.14)
F- + O > F + O + E    : 1.00E-10 ; 0.00 & 0.00 ] 0.0 [ 1 ! EST (Ref.14)
C4F8- + CO^ > C4F8 + CO   : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !EST
C4F8- + O2^ > C4F8 + O2   : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !EST
C4F8- + O^ > C4F8 + O     : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !EST
C4F8-* + CO^ > C4F8 + CO  : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !EST
C4F8-* + O2^ > C4F8 + O2   : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !EST
C4F8-* + O^ > C4F8 + O     : 3.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !EST
O + CF3 > COF2 + F             : 3.10E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O + CF2 > COF + F              : 1.40E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O + CF2 > CO + F + F           : 4.00E-12 ; 0.00 & 0.000 ] 0.0 [    1 !
O + CF > CO + F          : 6.64e-11 ; 0.0  &   503 ] 0.0 [    1 ! Ref.6
O + C2F4 > CF2 + CF2 + O : 2.66e-12 ; 0.0  &   310 ] 0.0 [    1 ! Ref.7
O + COF > CO2 + F              : 9.30E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O + FO > O2 + F                : 5.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O + F + M > FO + M       : 1.00E-33 ; 0.00 & 0.000 ] 0.0 [    1 ! EST.
O* + CF4 > O + CF4             : 1.80E-13 ; 0.00 & 0.000 ] 0.0 [    1 !
O* + COF2 > O + COF2           : 5.30E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O* + COF2 > F2 + CO2           : 2.10E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O* + CF3 > COF2 + F            : 3.10E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O* + CF2 > COF + F             : 1.40E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O* + CF2 > CO + F + F          : 4.00E-12 ; 0.00 & 0.000 ] 0.0 [    1 !
O* + CF > CO + F               : 2.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O* + COF > CO2 + F             : 9.30E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O* + FO > O2 + F               : 5.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 !
O^ + CF4 > CF3^ + FO   : 1.40E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF. 23
O^ + CF3 > CF3^ + O      : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! EST.
!O^ + C2F6 > CF3^ + CF3 + O: 0.89E-09 ; 0.00 & 0.000 ] 0.0 [ 1 ! REF.40
!O^ + C2F6 > C2F5^ + OF : 0.33E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.40
O^ + C2F6 > C2F5^ + F + O : 0.13E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF5
O^ + C2F6 > CF3^ + CF3 + O: 1.47E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF5
O^ + C2F4 > C2F4^ + O      : 1.30E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! R
O^ + C3F6 > C3F6^ + O     : 1.24E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF5
O^ + C3F6 > C2F4^ + CF2 + O: 0.29E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF
O^ + C3F6 > C3F5^ + F + O : 0.38E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF5
O^ + C4F8 > C3F5^ + CF3 + O: 0.76E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF5
O^ + C4F8 > C4F8^ + O    : 1.22E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF5
O^ + C4F8 > C4F7^ + F + O : 0.28E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF5
O- + CF^ > O + CF          : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !Est
O- + C^ > O + C            : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [    1 !EST
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O- + F^ > O + F             : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + F2^ > O + F2           : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + CF3^ > O + CF3         : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C2F4^ > O + C2F4       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C2F3^ > O + C2F3       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !est
O- + C2F5^ > O + C2F5       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C3F5^ > O + C3F5       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C3F6^ > O + C3F6       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C3F7^ > O + C3F7       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C3F6^ > O + C3F6       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C4F7^ > O + C4F7       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C4F8^ > O + C4F8       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + CF2^ > O + CF2         : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + CO^ > O + CO           : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + O2^ > O + O            : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + F > O + F-             : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O- + C4F8 > O + C4F8-       : 1.00E-10 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + CF^ > O2 + CF         : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !Est
O2- + C^ > O2 + C           : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + F^ > O2 + F           : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + F2^ > O2 + F2         : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + CF3^ > O2 + CF3       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + C2F4^ > O2 + C2F4     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + C2F3^ > O2 + C2F3     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !est
O2- + C2F5^ > O2 + C2F5     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + C3F5^ > O2 + C3F5     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + C3F6^ > O2 + C3F6     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + C3F7^ > O2 + C3F7     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + C3F6^ > O2 + C3F6     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + C4F7^ > O2 + C4F7     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + C4F8^ > O2 + C4F8     : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + CF2^ > O2 + CF2       : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + CO^ > O2 + CO         : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + O2^ > O2 + O2         : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
O2- + F > O2 + F-           : 1.00E-07 ; 0.00 & 0.000 ] 0.0 [     1 !EST
!O2 + CF3 > CF3O2         : 1.37E-13 ; 0.00 & 0.00 ] 0.0 [ 1 !150mTorr
O2 + CF > COF + O         : 3.30E-11 ;  0.0 &  906 ] 0.0 [    1 ! Ref.6
O2^ + CF4 > CF3^ + O2 + F : 8.45E-17 ; 1.2043 & 41739. ] 2.0[1 ! REF.40
O2^ + C2F4 > C2F4^ + O2   : 0.98E-09 ;  0.00 & 0.000] 0.0 [    1 ! REF5
O2^ + C2F5 > C2F5^ + O2   : 1.00E-10 ;  0.00 & 0.000] 0.0 [    1 ! EST.
O2^ + C2F6 > CF3^ + CF3 + O2: 3.03E-17 ; 1.3571 & 34783.]0.0[1 ! ReF.40
O2^ + C2F6 > C2F5^ + F + O2 :7.88E-14 ; 1.8571 & 34783. ]0.0[1 ! ReF.40
O2^ + C3F6 > C3F6^ + O2   : 1.08E-09 ;  0.00 & 0.000] 0.0 [    1 ! REF5
O2^ + C3F6 > C2F4^ + CF2 + O2 : 0.18E-09 ;  0.00 & 0.000] 0.0 [ 1 !REF5
O2^ + C3F6 > C3F5^ + F + O2: 0.14E-09 ;  0.00 & 0.000] 0.0 [    1 !REF5
O2^ + C4F8 > C4F8^ + O2  : 1.55E-09 ;  0.00 & 0.000] 0.0 [    1 ! REF5
O2^ + C4F8 > C2F4^ + C2F4 + O2: 4.48E-10 ;0.00 & 0.000 ]0.0 [1 ! REF.23
O2^ + C4F8 > C3F5^ + CF3 + O2: 1.15E-09 ; 0.00 & 0.000 ] 0.0 [1 !REF.23
O2- + C4F8 > C4F8- + O2 : 0.46E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.23
CO^ + CF4 > CF3^ + COF  : 7.00E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.32
CO^ + C2F4 > C2F4^ + CO : 1.10E-09 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.42
CO^ + C3F6 > C2F4^ + CF2 + CO: 4.76E-10 ; 0.00 & 0.000 ] 0.0 [1 !REF.42
CO^ + C3F6 > C3F5^ + F + CO: 4.93E-10 ; 0.00 & 0.000 ] 0.0 [ 1 ! REF.42
CO^ + C3F6 > C3F6^ + CO : 7.31E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.42
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CO^ + C4F8 > C3F5^ + CF3 + CO: 4.86E-10 ; 0.00 & 0.000 ] 0.0 [1 !REF.42
CO^ + C4F8 > C3F6^ + CF2 + CO: 4.68E-10 ; 0.00 & 0.000 ] 0.0 [1 !REF.42
CO^ + C4F8 > C4F7^ + F + CO: 7.02E-10 ; 0.00 & 0.000 ] 0.0 [ 1 ! REF.42
CO^ + C4F8 > C4F8^ + CO     : 1.44E-10 ; 0.00 & 0.000 ] 0.0 [1 ! REF.42
CO^ + C2F6 > CF3^ + CF3 + CO : 4.51E-10 ; 0.00 & 0.000 ] 0.0 [1 ! REF.
CO^ + C2F6 > C2F5^ + F + CO : 6.49E-10 ; 0.00 & 0.000 ] 0.0  1 ! REF.42
CO^ + O > O^ + CO       : 1.40E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.32
CO^ + O2 > O2^ + CO     : 1.20E-10 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.32
!
! Ar/COFn
!
AR^ + CO > CO^ + AR      : 4.00E-11 ; 0.00 & 0.000 ] 0.0 [    1 ! REF.32
!
! N2 only reactions
!
E + N2 > N2V + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 620  !
E + N2 > N2V + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 621  !
E + N2 > N2V + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 622  !
E + N2 > N2V + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 623  !
E + N2 > N2V + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 624  !
E + N2 > N2V + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 625  !
E + N2 > N2V + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 626  !
E + N2 > N2V + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 627  !
E + N2 > N2* + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 628  !
E + N2 > N2* + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 629  !
E + N2 > N2* + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 630  !
E + N2 > N2* + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 631  !
E + N2 > N2* + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 632  !
E + N2 > N + N + E           : 0.00E+00 ; 0.00 & 0.00 ] 4.85 [ 633  !
E + N2 > N2^ + E + E         : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 634  !
E + N2V > N2 + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 874  !
E + N2V > N2* + E            : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 875  !
E + N2V > N2^ + E + E        : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 876  !
E + N2* > N2V + E            : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 878  !
E + N2* > N2 + E             : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 879  !
E + N2* > N2^ + E + E        : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 880  !
E + N2^ > N + N              : 1.00E-07 ; -0.5 & 0.00 ] 9.0  [  -1  !
E + N > N* + E               : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 1079 !
E + N > N* + E               : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 1080 !
E + N > N^ + E + E           : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 1081 !
E + N* > N + E               : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 1083 !
E + N* > N^ + E + E          : 0.00E+00 ; 0.00 & 0.00 ] 0.00 [ 1085 !
N + N + M > N2* + M          : 1.00E-32 ; 0.00 & 0.00 ] 0.00 [    1 !
N + N + M > N2 + M           : 1.00E-32 ; 0.00 & 0.00 ] 1.0  [    1 !
N* + N2 > N + N2             : 2.00E-14 ; 0.00 & 0.00 ] 0.00 [    1 !
N* + N + M > N2* + M         : 2.00E-32 ; 0.00 & 0.00 ] 0.00 [    1 !
N^ + N > N^ + N              : 5.00E-10 ; 0.00 & 0.00 ] 0.00 [    1 !
N2V + M > N2 + M             : 1.00E-14 ; 0.00 & 0.00 ] 0.20 [    1 !
N2* + N2 > N2 + N2           : 1.90E-13 ; 0.00 & 0.00 ] 0.00 [    1 !
N2* + N > N2 + N             : 1.00E-13 ; 0.00 & 0.00 ] 0.00 [    1 !
N2* + N* > N2 + N            : 1.00E-13 ; 0.00 & 0.00 ] 0.00 [    1 !
N2* + N2* > N2 + N2*         : 1.36E-09 ; 0.00 & 0.00 ] 0.00 [    1 !
N2^ + N > N^ + N2       : 5.00E-12 ; 0.00 & 0.00 ] 0.00 [    1 ! Izekoe
N2^ + N* > N^ + N2          : 1.00E-10 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
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N2^ + N2 > N2^ + N2        : 5.00E-10 ; 0.00 & 0.00 ] 0.00 [    1
!
! Ar/N2 Reactions
!
AR* + N* > N^ + AR + E        : 5.00E-10 ; 0.00 & 0.00 ] 0.00 [    1 !
AR* + N > N* + AR             : 1.00E-12 ; 0.00 & 0.00 ] 0.00 [    1 !
AR* + N2* > N2^ + AR + E      : 5.00E-10 ; 0.00 & 0.00 ] 0.00 [    1 !
AR* + N2 > N2 + AR            : 3.60E-11 ; 0.00 & 0.00 ] 0.00 [    1 !
AR* + N2V > N2 + AR           : 3.60E-11 ; 0.00 & 0.00 ] 0.00 [    1 !
AR^ + N2 > N2^ + AR           : 1.00E-11 ; 0.00 & 0.00 ] 0.00 [    1 !
AR^ + N2V > N2^ + AR          : 1.00E-11 ; 0.00 & 0.00 ] 0.00 [    1 !
AR^ + N2* > N2^ + AR          : 1.00E-11 ; 0.00 & 0.00 ] 0.00 [    1 !
AR^ + N > N^ + AR             : 1.00E-11 ; 0.00 & 0.00 ] 0.00 [    1 !
AR^ + N* > N^ + AR            : 1.00E-11 ; 0.00 & 0.00 ] 0.00 [    1 !
!
! CnFn/N2 Reactions
!
CF + N > CN + F         : 3.90e-11 ; 0.00 & 0.00 ] 0.00 [    1 ! Ref.12
CN + N > C + N2         : 3.00E-10 ; 0.00 & 0.00 ] 0.00 [    1 ! Ref.44
CF2 + N > CN + F + F   : 3.90E-11 ; 0.00 & 0.00 ] 0.00 [    1 ! Ref. 18
CF3 + N > CN + F + F2  : 1.80E-11 ; 0.00 & 0.00 ] 0.00 [    1 ! Ref. 19
CF3- + N^ > CF3 + N     : 3.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
CF3- + N2^ > CF3 + N2     : 3.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
F- + N^ > N + F           : 2.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
F- + N2^ > N2 + F         : 3.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
CF3- + N^ > N + CF3       : 2.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
CF3- + N2^ > N2 + CF3     : 2.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
C4F8- + N2^ > C4F8 + N2   : 1.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
C4F8- + N^ > C4F8 + N     : 1.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
C4F8-* + N2^ > C4F8 + N2  : 1.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
C4F8-* + N^ > C4F8 + N     : 1.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
N^ + C2F4 > C2F4^ + N      : 1.40E-09 ; 0.00 & 0.00 ] 0.00 [    1 !
REF5
N^ + C2F6 > CF3^ + CF3 + N: 1.21E-09 ; 0.00 & 0.00 ] 0.00 [    1 ! REF5
N^ + C2F6 > C2F5^ + F + N  : 0.49E-09 ; 0.00 & 0.00 ] 0.00 [    1 ! REF
N^ + C3F6 > C3F6^ + N     : 0.82E-09 ; 0.00 & 0.00 ] 0.00 [    1 ! REF5
N^ + C3F6 > C2F4^ + CF2 + N: 1.00E-09 ; 0.00 & 0.00 ] 0.00 [   1 ! REF5
N^ + C4F8 > C4F8^ + N    : 1.75E-09 ; 0.00 & 0.00 ] 0.00 [    1 ! REF5
N^ + C4F8 > C3F5^ + CF3 + N: 0.65E-09 ; 0.00 & 0.00 ] 0.00 [  1 ! REF5
N2^ + CF4 > CF3^ + F + N2: 8.00E-10; 0.00 & 0.00 ] 0.00 [    1 ! Izekoe
N2^ + C2F4 > C2F4^ + N2  : 0.46E-09 ; 0.00 & 0.00 ] 0.00 [    1 ! REF5
N2^ + C2F4 > CF^+ CF3 + N2: 0.25E-09 ; 0.00 & 0.00 ] 0.00 [    1 ! REF5
N2^ + C2F4 > CF3^+ CF + N2: 0.13E-09 ; 0.00 & 0.00 ] 0.00 [    1 ! REF5
N2^ + C3F6 > C2F4^ + CF2 + N2:0.77E-09 ; 0.00 & 0.00 ] 0.00 [  1 ! REF5
N2^ + C3F6 > C3F5^ + F + N2: 0.69E-09 ; 0.00 & 0.00 ] 0.00 [   1 ! REF5
N2^ + C4F8 > C3F5^ + CF3 + N2: 0.41E-09 ; 0.00 & 0.00 ] 0.00 [ 1 ! REF5
N2^ + C4F8 > C3F6^ + CF2 + N2: 0.34E-09 ; 0.00 & 0.00 ] 0.00 [ 1 ! REF5
N2^ + C4F8 > C4F7^ + F + N2: 1.04E-09 ; 0.00 & 0.00 ] 0.00 [   1 ! REF5
N2^ + C2F6 > C2F5^ + F + N2: 0.92E-09 ; 0.00 & 0.00 ] 0.00 [   1 ! REF5
N2^ + C2F6 > CF3^ + CF3 + N2: 0.35E-09 ; 0.00 & 0.00 ] 0.00 [  1 ! REF5
!
! N2/COFn Reactions
!
N2^ + CO > CO^ + N2    : 7.00E-11 ; 0.00 & 0.00 ] 0.00 [    1 ! Izekoe
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N^ + CO > CO^ + N      : 5.00E-10 ; 0.00 & 0.00 ] 0.00 [    1 ! Izekoe
!
! N2/O2 Reactions
!
N2^ + O2 > O2^ + N2     : 1.00E-10 ; 0.00 & 0.00 ] 0.00 [    1 ! Izekoe
N2^ + O > O^ + N2       : 1.40E-10 ; 0.00 & 0.00 ] 0.00 [ 1 Izekoe(NO^)
N^ + O2 > O2^ + N       : 6.00E-10 ; 0.00 & 0.00 ] 0.00 [    1 ! Izekoe
O- + N^ > O + N           : 1.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
O- + N2^ > O + N2         : 1.00E-07 ; 0.00 & 0.00 ] 0.00 [    1 ! EST
!
! H2/H2O Electron Impact
!
E + H2 > H + H + E             : 0.00E+00 ; 0.00 & 0.0  ] 3.0  [  17  !
E + H2 > H2^ + E + E           : 0.00E+00 ; 0.00 & 0.0  ] 0.0  [  18  !
E + H2 > H + H + E             : 0.00E+00 ; 0.00 & 0.0  ] 3.0  [  19  !
E + H2 > H + H + E             : 0.00E+00 ; 0.00 & 0.0  ] 3.0  [  20  !
E + H2^ > H + H                : 1.00E-07 ; -0.5 & 0.00 ] 9.0  [  -1  !
E + H2O > OH + H-              : 0.00E+00 ; 0.00 & 0.0  ] 3.0  [ 1044 !
E + H2O > OH + H + E           : 0.00E+00 ; 0.00 & 0.0  ] 3.0  [ 1045 !
E + H2O > O* + H2 + E          : 0.00E+00 ; 0.00 & 0.0  ] 3.0  [ 1046 !
E + H2O > H2O^ + E + E         : 0.00E+00 ; 0.00 & 0.0  ] 0.0  [ 1047 !
E + H2O^ > O + H2              : 1.00E-07 ; -0.5 & 0.00 ] 9.0  [  -1  !
!
! H Heavy Particle  Reactions
!
AR* + H2 > AR + H + H            : 2.10E-10 ; 0.00 & 0.0000 ]  1  ! EST.
AR* + H2O > AR + OH + H          : 2.10E-10 ; 0.00 & 0.0000 ]  1  !
AR^ + H2 > AR + H2^              : 1.00E-09 ; 0.00 & 0.0000 ]  1  !
AR^ + H2O > AR + H2O^            : 1.40E-09 ; 0.00 & 0.0000 ]  1  !
F^ + H2 > H2^ + F                : 1.20E-09 ; 0.00 & 0.0000 ]  1  !
F^ + H2O > H2O^ + F              : 7.97E-11 ; 0.00 & 0.0000 ]  1  !
F- + H > E + HF                  : 1.60E-09 ; 0.00 & 0.0000 ]  1  !
H- + H > E + H2                  : 1.80E-09 ; 0.00 & 0.0000 ]  1  !
H- + H2O > OH- + H2    : 3.70E-09 ; 0.00 & 0.0000 ]  1  ! IKEZONE (HO-)
H- + AR^ > H + AR                : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H- + CF3^ > H + CF3              : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H- + O2^ + M > HO2 + M           : 1.20E-25 ; 0.00 & 0.0000 ]  1  !
H- + O^ + M > OH + M             : 1.20E-25 ; 0.00 & 0.0000 ]  1  !
H- + F^ + M > HF + M             : 1.20E-25 ; 0.00 & 0.0000 ]  1  !
H- + F2^ > H + F2                : 5.00E-08 ; -0.5 & 0.0000 ]  1  !
H- + C2F4^ > H + C2F4            : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H- + C2F5^ > H + C2F5            : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
OH- + H > E + H2O      : 1.40E-09 ; 0.00 & 0.0000 ]  1  ! IKEZONE (HO-)
OH- + O > E + HO2      : 2.00E-10 ; 0.00 & 0.0000 ]  1  ! IKEZONE (HO-)
OH- + AR^ > OH + AR              : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
OH- + CF3^ > OH + CF3            : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
OH- + O2^ > OH + O2              : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
OH- + O^ > OH + O                : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
OH- + F^ > OH + F                : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
OH- + F2^ > OH + F2              : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
OH- + C2F4^ > OH + C2F4          : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
OH- + C2F5^ > OH + C2F5          : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2^ + O2 > O2^ + H2              : 7.56E-09 ; 0.00 & 0.0000 ]  1  !
H2^ + C2F6 > CF3^ + CF3 + H2     : 5.00E-10 ; 0.00 & 0.0000 ]  1  ! EST.
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H2^ + H2O > H2 + H2O^            : 3.60E-09 ; 0.00 & 0.0000 ]  1  !
H2^ + CF3- > H2 + CF3            : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2^ + F- > H2 + F                : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2^ + O- > H2 + O                : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2^ + H- > H2 + H                : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2^ + OH- > H2 + OH              : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2O^ + CF3- > H2O + CF3          : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2O^ + F- > H2O + F              : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2O^ + O- > H2O + O              : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2O^ + H- > H2O + H              : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2O^ + OH- > H2O + OH            : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H2O^ + H2O > H3O^ + OH           : 1.70E-09 ; 0.00 & 0.0000 ]  1  !
H3O^ + E > H2O + H               : 2.00E-07 ; 0.00 & 0.0000 ]  1  !
H3O^ + H- > H2 + H2O             : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H3O^ + O- > OH + H2O             : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H3O^ + F- > H2O + HF             : 1.00E-07 ; 0.00 & 0.0000 ]  1  ! EST.
H3O^ + CF3- > H2O + HF + CF2     : 1.00E-07 ; 0.00 & 0.0000 ]  1  ! EST.
H3O^ + OH- > H2O + H + OH        : 1.00E-07 ; 0.00 & 0.0000 ]  1  !
H + H + M > H2 + M               : 8.10E-33 ; 0.00 & 0.0000 ]  1  !
H + OH + M > H2O + M             : 1.56E-31 ;-1.21 & -295.3 ]  1  !
H + O + M > OH + M               : 4.33E-32 ; 0.00 & 0.0000 ]  1  !
H + O2 + M > HO2 + M             : 1.94E-32 ;-0.70 & -144.2 ]  1  !
H + HO2 > O + H2O                : 3.85E-11 ; 0.46 &  677.9 ]  1  !
H + HO2 > H2 + O2                : 2.34E-11 ; 0.59 &  320.8 ]  1  !
H + HO2 > OH + OH                : 1.58E-10 ; 0.00 &  365.2 ]  1  !
H + CF3 > CF2 + HF               : 9.00E-11 ; 0.00 & 0.0000 ]  1  !
H + CF2 > CF + HF                : 3.90E-11 ; 0.00 & 0.0000 ]  1  !
H + CF > C + HF                  : 1.90E-11 ; 0.00 & 0.0000 ]  1  !
H + F2 > F + HF                  : 1.53E-11 ; 0.00 & 0.0000 ]  1  !
H + COF > CO + HF                : 1.93e-10 ; 0.00 & 0.0000 ]  1  !
C + O2 > CO + O                  : 3.30E-11 ; 0.00 & 0.0000 ]  1  !
H2 + F > HF + H                  : 1.43E-10 ; 0.00 &  528.0 ]  1  !
H2 + O* > OH + H                 : 1.10E-10 ; 0.00 & 0.0000 ]  1  !
OH + F > O + HF                  : 3.32E-11 ; 0.00 & 0.0000 ]  1  !
OH + CF3 > COF2 + HF             : 3.32E-11 ; 0.00 & 0.0000 ]  1  !
OH + CF2 > COF + HF              : 6.64E-12 ; 0.00 & 1762.5 ]  1  !
OH + CF > HF + CO                : 6.64E-11 ; 0.00 &  503.0 ]  1  !
OH + CO > H + CO2                : 1.18E-13 ; 0.98 & -94.03 ]  1  !
HO2 + F > O2 + HF                : 8.28E-11 ; 0.50 & 0.0000 ]  1  !
HO2 + CF3 > COF2 + HF + O        : 1.66E-11 ; 0.00 & 0.0000 ]  1  !
HO2 + CF2 > COF2 + OH            : 1.66E-11 ; 0.00 & 1762.5 ]  1  !
HO2 + O > OH + O2                : 3.00E-11 ; 0.00 & 0.0000 ]  1  !
HO2 + OH > H2O + O2              : 5.00E-11 ; 0.00 & 0.0000 ]  1  !
H2O + F > OH + HF                : 1.11E-11 ; 1.50 & 0.0000 ]  1  !
H2O + O* > OH + OH               : 2.50E-10 ; 0.00 & 0.0000 ]  1  !
!
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VITA

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