VUV spectroscopy of RF plasma sources.

Jan. Li

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VUV SPECTROSCOPY OF RF PLASMA SOURCES

by

JAN LI

A Thesis
submitted to the
Faculty of Graduate Studies and Research
through the Department of
Physics in Partial Fulfillment
of the requirements for the Degree
of Master of Science at the
University of Windsor

Windsor, Ontario, Canada

1995
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ABSTRACT

In this experiment we observe the spectra from RF discharges through SF₆, CF₄ and CH₄ and some mixtures of these and helium over the wavelength range of 115-315 nm.

In the spectra of SF₆, strong sulphur atomic lines were observed to cover the wavelength range of 120-195 nm. Fluorine features should be even stronger, but no fluorine lines were observed because their wavelengths are shorter than 100 nm and are cut off by the MgF₂ window on the detector. The intensity-pressure variations of SI lines have been established in chapter 4 as well as the relative intensity ratios for lines within multiplets. Strong oxygen lines and SO (A-X) and (B-X) systems show up at 240-300 nm. Some SiI lines are prominent especially in 1% SF₆ in He mixtures. These are explained as the product of the reaction between active F atoms and the glass discharge walls. Hydrogen Lyman α, NI lines, N₂ and NO γ and β systems were also observed as impurities. The intensities were found to vary directly with the power input. SO band-intensities were observed to build up much more rapidly with time than S line-intensities within the discharge.

Three strong CO systems ( "Fourth Positive", "Third Positive" and "3A") dominate the spectra of CF₄. The CO features were so strong that only a few carbon lines were observable even in 1% of CF₄ and He mixtures. The CO is most probably formed from the interaction of C atoms from the break up of CF₄ in the discharge and O₂ released from the glass walls of the discharge vessel by an F-etching process. Some background continua were identified as due to CF₄' and CF₃ / CF₂ by comparison with other spectra obtained following electron, ion, photon and metastable atom impact. The intensity-pressure variations of the various features were also established. A calculation was carried out of the Franck-Condon Factors of the 3A system and was compared with the measurements.
Strong HI Lyman $\alpha$ emission was observed from CH$_4$ discharge together with the H$_2$ Lyman and Werner systems.
This work is lovingly dedicated to my father Li Guofu and my mother Zhao Yin for their endless love and support.
ACKNOWLEDGMENTS

I would like to extend my utmost appreciation and thanks to my supervisor, Dr. J.W. McConkey, for his patient guidance and generous support. His beautiful humanity has provided a very friendly and comfortable environment in his group and has made the life of last few years much more enjoyable.

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Low pressure glow discharge plasmas have been used extensively in semiconductor fabrication for many years, for dry etching and for the deposition of thin films. They have also been widely used for surface modifications of polymers (d'Agostino et al. (1990) and Hollander et al. (1994)) to change such properties as wettability and adhesion.

Since all important low pressure plasmas emit VUV radiation (McOmber et al., 1992) and since much of this radiation is sufficiently energetic to cause modifications to surface layers by breaking bonds or initiating surface chemistry, it is important to characterize the spectral emissions from these plasmas. Fluorine containing molecules are widely used in etching reactors because of the efficient etching properties of fluorine atoms and fluorine containing radicals. Hydrocarbon discharges are widely used for diamond film deposition.

The vacuum ultraviolet (VUV) and ultraviolet (UV) emission (115 nm < $\lambda$ < 315 nm) from RF discharges through SF$_6$, CF$_4$ and CH$_4$ have been investigated as a function of source pressure and RF power.

In chapter 2, the apparatus is described and the operation of the Charge-Coupled Device (CCD) detection system discussed in detail. Use of the strong Si lines and CO bands for calibration purposes is discussed in chapter 3. The reciprocal dispersion of the detection system as a function of wavelength is determined. The relative quantum efficiency of the detection system is established using the molecular branching ratio technique. Chapter 4, 5 and 6 discuss the results obtained for SF$_6$, CF$_4$ and CH$_4$ respectively while some conclusions are presented in Chapter 7.
II. EXPERIMENTAL SET-UP

A schematic of the experimental set-up is shown in Fig.2-1. The apparatus consists of a discharge tube, a gold mirror, a reflection monochromator, and a CCD spectroscopic detection system. The first two components were located in the main chamber, while the latter two were located in the monochromator chamber. Each of these components is discussed in more detail below.

The sample gas(SF₆, CF₄, or CH₄ etc.) was leaked into the discharge tube from which it flowed into the main vacuum chamber. As shown in Fig.2-2, the photons emitted axially from the discharge tube were reflected by the gold mirror into the monochromator. The CCD detector was used to observe the reflected and dispersed photons in the exit focal plane of the monochromator over the wavelength range 115 to 315 nm.

2.1 Vacuum System

Two Edwards E04 oil diffusion pumps were employed to pump down the main chamber and the monochromator chamber. These were backed by an E2M40 two stage rotary pump, whose pumping speed was 44m³/hr. The measured ultimate pressure at the rotary pump inlet was a few mtorr. The base pressure, as measured on a ion gauge, was 8 × 10⁻⁷ torr. This was achieved without using the cold trap on the system.

The main chamber was made from non-magnetic stainless steel and constructed with nine ports (Donaldson, 1972 ). The axes of the eight ports had a common intersection point where the mirror was located.
Figure 2-1 Block diagram of experimental setup.

2.2 Gas Handling System

High purity gases (99.99%) were used in the experiment. Sometimes the gas under study (SF₆, CF₄ or CH₄) was mixed with various quantities of He. Fig.2-3 gives a schematic for the gas handling system.

The following procedures were followed to get a gas mixture at a pressure of 100 mtorr with 10% of SF₆ and 90% of He. First SF₆ was allowed to flow into chamber through needle valve N1. After the pressure, as read on the capacitance manometer ("CM"), had been stable at 10 mtorr for 3~5 minutes, the needle valve N2
Figure 2-2 Schematic of the experimental apparatus used in the RF discharge experiments.
was open to let He in until the final pressure became stable at 100 mtorr. CM gave a reading of the absolute gas pressure just prior to the discharge vessel.

2.3 Discharge Source

The radio frequency discharge source was developed by Slevin and Stirling (1981). The mounting of the discharge tube and RF cavity has been given by Wang (1991). This source has been used in the laboratory for several years primarily to provide intense beams of atom hydrogen or oxygen.

The discharge tube is a 220 mm long, 18 mm diameter Pyrex tube surrounded by a water cooling jacket (Fig. 2-2). The coaxial resonator cavity, 70 mm diameter and 89 mm height, is powered via a 25-turn helical inner conductor. The outer part of the cavity is made from high conductivity oxygen free copper. The cavity is driven by an
impedance matched RF generator, which supplies 20–40 watts of RF power at a
frequency of 35 MHz. The frequency could be adjusted over a small range to optimise
the tuning of the system.

Distilled water is used to cool the discharge tube, and transfer the heat to a
heat-exchanger from which heat is carried away by tap water. The flow rate of water
through the cooling jacket is monitored by a flow sensor, which shuts off the RF
generator, water pump and two solenoid valves if the flow rate drops too low. This
protects the discharge from overheating and provides some protection against leaks
from the cooling system into the vacuum chamber.

Figure 2-4 Layout of the Seya-Namioka monochromator.
2.4 Monochromator

A McPherson half meter Seya-Namioka VUV spectrometer (Fig.2-4) was used to disperse the light from the discharge. Its optical element was a gold-coated concave grating with 1200 grooves per millimetre, blazed at 150 nm, with linear reciprocal dispersion of around 20 Å/mm at the exit slit (see Section 3.1). The only mechanism needed for wavelength adjustment was rotation of the grating, which was accomplished by a stepping motor. The spectrometer was designed to focus the image of the entrance slit onto the exit slit with unit magnification. In our experiment, the entrance slit width was set to be 0.1 mm. The height of the image was about half centimetre. For our purposes, the exit slit assembly was replaced by a special mount designed to position the CCD detector tangential to the Rowland circle where focusing of the entrance slit occurred.

2.5 CCD Detection System

The Charge-Coupled Device (CCD) chip was a specially selected Grade I Tektronix TK 512 CB/AR. This was chosen for its high sensitivity, low dark current and large total capacity per pixel (see later). The full performance characteristics are given in Table 2-1. The CCD array consisted of 512 x 512 pixels. In order for the device to work at the VUV wavelengths of the present study, the CCD was housed in a vacuum-sealed region with a MgF2 window (cut off at 115 nm) and the chip was also coated with a fluorescing substance (Metachrome II) to down convert the incoming VUV photons into the visible spectral region. To reduce the dark current, the chip was thermally connected to a liquid nitrogen reservoir via a temperature controlling device. Normally the system was operated at -120°C. Fig.2-5 shows a
### Table 2-1

**CCD PERFORMANCE CHARACTERISTICS**

(Manufacturer's Specifications)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCD Manufacturer:</td>
<td>Tektronix</td>
</tr>
<tr>
<td>CCD Architecture:</td>
<td>Full Frame Back Illuminated</td>
</tr>
<tr>
<td>MPP Mode</td>
<td>No</td>
</tr>
<tr>
<td>Active Pixel Count:</td>
<td>512 x 512</td>
</tr>
<tr>
<td>Optical Fill Factor:</td>
<td>100%</td>
</tr>
<tr>
<td>Pixel Size (µm):</td>
<td>27 x 27</td>
</tr>
<tr>
<td>Full image Size (Bytes):</td>
<td>524,288</td>
</tr>
<tr>
<td>Typical Linear Full Well Capacity (e/pixel)</td>
<td>500,000</td>
</tr>
<tr>
<td>Typical CCD Readout Noise (e-RMS) at (kHz)</td>
<td>8 (40), 35 (200)</td>
</tr>
<tr>
<td>Typical Dark Current (e/sec/pixel)</td>
<td>60 (-30°C), 12 (-40°C), 0.02 (-110°C)</td>
</tr>
<tr>
<td>Typical % Quantum Efficiency at 700 nm</td>
<td>80</td>
</tr>
<tr>
<td>Typical % QE at 300 nm METACHROME II-COATED CCD:</td>
<td>35</td>
</tr>
<tr>
<td>Stabilized Temp. in Peltier Cooled Camera Head:</td>
<td>-30°C</td>
</tr>
<tr>
<td>Minimum Stabilized Temp. in Liquid Nitrogen Cooled Camera Head:</td>
<td>-110°C</td>
</tr>
<tr>
<td>Linear Error</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

---

![Diagram](image)

**Figure 2-5** Section view of CCD Camera head.

8
section view of the device. For our application the lens and shutter assembly were removed so that the camera body could be bolted directly onto the vacuum spectrometer.

2.5.1 Theory of Operation

Referring to the CCD 9000 user's manual (Photometrics, 1990), the CCD imager is made from silicon. In crystalline silicon, each atom is covalently bonded to its neighbours. Incident photons of wavelengths shorter than 1100 nm can break the bonds and generate electron-hole pairs. The number of photons can be found by counting the number of electrons generated. Photons of wavelength greater than 1100 nm are not able to break the bonds. However, high energy particles, X rays, and cosmic rays can break thousands of bonds. Hence excessive exposure to much high energy radiation can damage the crystal lattice.

Bonds can also be broken by thermal agitation. The electron-hole pair generation rate can be reduced by lowering the temperature. The unwanted charge produced by thermal agitation is called dark current, because it is produced in the absence of light.

Once the electrons are produced, they are collected in a potential well (Fig. 2-6). A thin layer of silicon dioxide is grown on a section of silicon and a conductive gate structure is applied over the oxide. Applying a positive electrical potential to the gate

![Figure 2-6 CCD potential well details](image-url)
creates a depletion region where free electrons generated by incoming photons can be stored. Practically a potential well is able to collect a million electrons before it is filled. Note that the electrons freed by thermal agitation and by high energy particles are indistinguishable from those generated by photon interaction.

By fabricating a series of oxide and conductive gate structures with multiple phase, we are able to move the potential wells with the collected electrons. As displayed in Fig.2-7, the potential wells are propagated in the direction shown when an appropriate sequence of potentials is applied to the gates. The loss of charge during the transfer is negligible. The typical charge transfer efficiency is 0.99999 for a scientific-grade CCD imager. By this means, packets of charges are transferred to registers where the charge number is counted and recorded for subsequent computer analysis. For the two dimensional CCD array, charges are transferred column by column and then row by row to get a 512x512 matrix of charge numbers. This allows spectra to be

Figure 2-7 Diagram illustrating charge transfer mechanism in CCD device.
obtained either in the form of an image of the charge distribution on the CCD or as summed rows or columns.

2.5.2 Technical Performance

i. Sensitivity: Within the visible spectral range, the photon to electron conversion factor is less than unity and it varies as a function of wavelength. At a given wavelength, the creation of charge from incident light is intrinsically linear.

For wavelengths less than 400 nm, the gate structure attenuates the incoming light. To solve this problem, the CCD was uniformly thinned to approximately 10 μm with acid etching techniques. As shown in Fig.2-8, an image can be focused on the backside of the parallel register where there is no gate structure. In addition, a down converter METACHROME™ II is used to coat the back surface of the back-illuminated CCD. This absorbs photons with short wavelength and emits photons at 560 nm (Fig.2-9). Therefore the sensitivity of the CCD increases significantly in the ultraviolet wavelength over what it would be in the absence of “thinning” and coating. The down converter is transparent between 400 and 1000 nm.

Figure 2-8 Diagram of “thinned”, back illuminated CCD device.

Figure 2-9 Diagram illustrating a CCD with a down converter.
Figure 2-10 Quantum efficiency of the CCD over the range 200-900 nm. (Manufacturer’s specification)
The quantum efficiency of the CCD over the range 200 to 900 nm has been provided by the manufacturers and is shown in Fig.2-10. We note that no data were available from the manufacturer for wavelengths less than 200 nm. Our measurements (see Section 3.2) indicate that good sensitivity is achieved right down to the MgF₂ cut off at 115 nm.

ii Operating Temperature: Since thermal charges accumulate with time, it is necessary for long exposures to cool the CCD down to -120°C. It is pointless to cool the device to even lower temperatures because, even though dark current is reduced, the overall performance of the CCD is degraded due to poorer charge transfer efficiency. At a temperature of -110°C, the dark current was tested to be about 0.397 electrons per pixel per hour.

iii Uniform Background: It should be noted that the analog processor card in the CE200A Camera Electronics Unit can digitise only positive voltages. To ensure that only positive signals are obtained, a DC offset, or bias, is added to all CCD charge packets. Thus any spectra recorded have a uniform background which must be subtracted off in subsequent analysis.

iv Spurious Features: When very low light signals are recorded, (necessitating the use of long exposure times of perhaps many hours), it is possible to observe features on the spectral image which are caused by the arrival of cosmic rays. They show up as short, very intense, tracks on the recorded image (Fig.2-11) and thus produce strong spurious peaks when rows or columns of pixels are summed. To remove these spurious peaks from the data, a computer program, “SPIKES”, was written (personal communication Darrach, 1992). This program compares the counts in each pixel with those in the neighbouring pixels. If an excessive difference is recorded, this count is cancelled and assigned a value which is the average of the counts on neighbouring pixels.
For short exposures using more intense sources, a different procedure was used to identify spurious peaks. Two or more spectra were always recorded consecutively using identical experimental parameters. Features which appeared on one spectrum and not on the other were discarded as spurious.

![Image](image.png)

Figure 2-11 Image acquired by CCD using "Image" exposure method. A 100 eV electron beam through an N₂ gas target was used as the source. Very low light levels were observed in this exposure, less than 100 photons per pixel. The white dots on the picture are due to background noise. Short continuous tracks due to cosmic rays are evident in the lower right corner of the picture.
2.5.3 Software

There are three major software packages used in this experiment: CCD9000 software, Lab Calc and Quattro Pro.

**CCD9000** is the software designed specifically for the purpose of CCD camera control. It provides the functions of setting the CCD orientation, the exposure time and sequence, the observation track size, the method of storing and displaying the data etc.

The orientation was arranged so that wavelength dispersion occurred horizontally. The exposure time for most of the experiments was 50 sec. Multiple exposures could be accomplished by the proper sequence option setting but in this experiment it was done manually. Due to the property of the optical system, the height of the image was less than one centimetre and just covered part of the CCD array. A track, a subarray with the full width of the CCD, was specified as 240 rows high to cover the image. The additional rows were disregarded in the data summing procedure since they only contributed noise to the spectrum.

Concerning data storage and display, three methods are available: “Image”, “Co-add”, and “Average”. When the Image method is selected, the track is acquired and displayed as a grey-scale image, with every pixel shown. (See Fig.2-11) This method was used in the first instance since it gave a direct visual image, which was helpful for the identification of features. Moreover, it was the only practical method if the exposure time was long and modification of individual pixel counts was necessary to eliminate the spurious effects. Files taken with the Image method were relatively large (about 250 kilobytes each) and labelled with an extension “*.TDF”. When the Co-add method was selected, pixel values from the CCD were summed vertically in the host computer and displayed as a line trace. The display showed a plot of intensity against wavelength. This method was normally used since the spectra were the major focus of my experiments and most of my exposure times were only 50 seconds. If the
Average method is selected, pixel values are summed, divided by the track size, and then displayed as a line trace. This Average method was not used.

Although the CCD9000 software provides some functions like spectroscopic calibration, uniform background subtraction etc., it was found to be relatively inconvenient compared to other software when dealing with a large amount of spectra. Therefore, it was not chosen for calibration etc. Another drawback of the CCD9000 is that it does not provide direct input / output conversion with the commonly used ASCII code file. Its own file saving function sometimes simply did not work. LabCalc was found to be the most reliable output, where files were saved in a compact format, 2304 bytes each, with extension "*.SPC".

**LabCalc**, an advanced scientific data processing software package, is provided by Galactic Industries. For our spectra, it provided functions such as calibration, peak picking, multi-mode display, drawings, plotting, and so on. One of its most useful features is the user’s capability to write programs for processing the data. A complete programming language, Array Basic™, is built into the LabCalc Arithmetic module, which includes many pre-programmed functions for the most common operations on scientific data. The program "SPIKES" (mentioned earlier) to eliminate spurious features, was written with this Array Basic language. In the experiment, this program eventually summed pixel values vertically and produced a line trace spectrum.

As advanced, flexible data processing software, LabCalc provides a lot of options in every application, which, on the other hand, may seem too complex for a new user. LabCalc is not as well-developed as other commercial software and is still far from user-friendly.

However, I was able to take advantage of LabCalc’s ability to convert a variety of data files. The "*.SPC" files were converted to ASCII files or Lotus 1-2-3’s
"*.WK1" files, which were then readable by another commercial software package, Quattro Pro.

Quattro Pro is a user-friendly worksheet software package developed by Borland Inc. The usage is straightforward and allows much freedom for the users to customise. The Quattro Pro for Windows version has a multi-page workbook feature. This "three dimension" feature was important in the present instance, since the data contained intensity variation with both wavelength and pressure in each section. This feature could not be found in any other scientific data processing software.

The data calibration, background subtraction, and almost all of the data analysis were done with the help of this software. The only significant disadvantage using Quattro Pro was its drawing performance, which was slow compared to any scientific graphics software and limited the display of error bars and character fonts. Sometimes, it was necessary to use some other scientific software just for presentation of the data. For example, Grafer for Windows and Origin were sometimes used.
III. CALIBRATION OF THE VUV DETECTION SYSTEM

In any spectroscopic investigation, careful calibration of the detection system has always been the first priority before any further data analysis. In the present case, careful wavelength measurements allowed the reciprocal dispersion of the spectrometer to be obtained over the whole observed wavelength range. The relative quantum efficiency of the detection system was established using the molecular branching ratio technique.

3.1 Reciprocal Dispersion

The CCD imager has dimensions of 10.25 mm × 10.25 mm with 512 × 512 pixels. It can cover a wavelength range of about 20 nm with the current grating, so the resolution is about 0.04 nm (± one pixel). The MgF₂ window on this device limited its operation to wavelengths longer than 115 nm. A series of spectra were taken from 120 nm up to 300 nm. The set-up was such that each spectrum overlapped its neighbour by 2.5 nm. This enabled accurate identification of spectral features to be carried out.

The reciprocal dispersion, usually given in Å/mm, varies slightly over a given wavelength region when a grating is used as the dispersion element. This follows from the basic diffraction formula, \( n\lambda = d\sin\theta \), where \( \theta \) is the angle of diffraction. From measurements of the wavelength of known atomic lines of Sulphur, Helium and Hydrogen, as well as the molecular bands of CO and CO\(^+\), the dispersion was found to vary slowly over the wavelength range(Fig.3-1). The dispersion increases from 19.5 Å/mm up to about 21.3 Å/mm over the wavelength range from 120 nm to 305 nm. Table A-1 (Appendix. 1) includes the detailed information of spectral features which were used for calibration purposes. Fig.3-1, together with any known features, enables
Figure 3-1 Reciprocal dispersion of the Seiya-Namioka spectrometer.
all features in any particular spectrum to be calibrated. This greatly assisted the identification of unknown spectra.

The following points should be noted:

i. In general, the atomic lines were much sharper than the molecular bands. Therefore the atomic lines enabled more accurate measurements to be obtained.

ii. Calibration features separated as widely as possible within the spectrum, preferably by more than 100 pixels, were used to establish the data of Fig.3-1. If closely spaced features were considered, the width of the pixels themselves tended to influence the accuracy of the data. This is reflected in the error bars on some of the data points in Fig.3-1.

iii. The error bars on Fig.3-1 were established from the accuracy in establishing the pixel numbers of the centre of the observed line. This error was ±1 pixel for atomic features and ±2 for molecular bands.

iv. The upward slope of the data points towards longer wavelength in Fig.3-1 indicates that measurements taken at either end of a spectrum could give quite different values for the reciprocal dispersion. The difference was found to be approximately 4%. This is one reason why some scatter is observed in the data, Fig.3-1.

3.2 Relative Quantum Efficiency

The relative spectral sensitivity of this optical system was obtained from measurements of the relative intensities of molecular bands—the so-called “molecular branching ratio” technique.
3.2.1 Theoretical Background

Referring to the original analysis of McConkey (1969), the measured emitted intensity of a vibrational band is given by:

\[
I_{v',v''} = C k_{v',v''} N_v E^3_{v',v''} R^2 c q_{v',v''} \quad \text{(photons/sec)} \quad (3-1)
\]

where \(C\) is a constant, \(k_{v',v''}\) is the relative sensitivity of the detection system, \(N_v\) is the population of the upper vibrational level \(v'\), \(v''\) is the lower vibrational level, \(E_{v',v''} = \hbar c / \lambda_{v',v''}\) is the energy difference between \(v'\) and \(v''\), \(R_c\) is the average value of the electronic transition moment, and \(q_{v',v''}\) is the Franck-Condon factor. Usually \(R_c\) varies slowly within a given band system and thus can be regarded as effectively constant. Therefore,

\[
I_{v',v''} \propto k_{v',v''} N_v q_{v',v''} / \lambda^3_{v',v''} \quad (3-2)
\]

Since the molecules were excited in the RF discharge tube, it is difficult to calculate relative \(N_v\) for upper vibrational levels. However the intensities of vibrational bands originating from the same upper level can be rewritten as:

\[
I_{v',v''} \propto k_{v',v''} q_{v',v''} / \lambda^3_{v',v''} \quad (3-3)
\]

or relative sensitivity:

\[
k_{v',v''} \propto I_{v',v''} \lambda^3_{v',v''} / q_{v',v''} \quad (3-4)
\]

The wavelength and the known Franck-Condon factors for the de-exciting transitions, are used to predict the relative intensities of different vibration bands from the same upper level. The relative sensitivity \(k_{v',v''}\) is then obtained directly from the ratio of the observed to predicted band intensities.

3.2.2 Measured Sensitivity

The well known CO systems observed from the CF₄ discharge, covering almost the whole wavelength range of observation, enabled the calibration of the relative sensitivity of our optical system (the grating system + CCD detector).
The CO third positive system covered the higher wavelength range, 266 nm ~ 313 nm, while the CO fourth positive system covered the range 138 nm ~ 222 nm. Because of the broad extent of the spectral region to be calibrated and because each spectrum only extended over 20 nm, a large number of spectra had to be taken for calibration purpose. During this long experimental period, the condition of the RF discharge could vary. Thus the different spectra had to be normalised relative to one another. This was accomplished by overlapping each spectrum with its neighbours.

After the renormalization of intensities, different bands from the same upper vibrational level were compared using the method discussed in the last section. To get better statistical accuracy, only strong bands were chosen for calibration. Each vibrational progression gave a series of relative sensitivities covering a certain wavelength range. At the end, all these series of relative sensitivities were renormalized and combined as in Fig.3-2. Table A-2 (Appendix 1) includes the detailed information of the spectral features which were used for calculation purposes.

Note that the sensitivity peaks at 150 nm and falls off rapidly towards the longer wavelengths. This is due to the fact that the grating is blazed for this wavelength. The CCD quantum efficiency variation is expected to be small in the VUV spectral region as it depends on the fluorescent efficiency of the Metachrome II coating on the CCD itself. However, it is clear from Fig.2-10 that significant fluctuations with wavelength can sometimes occur. If a smooth curve is drawn through the data points on Fig.3-2, it is clear that some points lie significantly off the line. The absorption of the air, which could leak into the CCD head, could have a minor effect. It is well known that most of the absorption of air in the VUV region is due to the O₂ Schumann-Runge system (Fig.3-3), which is peaked at 140-150 nm with much structure above 175 nm. We see little sign of any absorption occurring except perhaps at 178.2 nm (CO Fourth Positive (4,7) band), where an anomalous point is observed.
Figure 3-2 Relative detection sensitivity. The dashed line indicates estimation.
Figure 3-3 Absorption cross section for $O_2$ between
(a) 1250 and 1750 Å (b) 1700 and 1950 Å.

on Fig. 3-2. Another factor which could lead to an anomalous data point on Fig. 3-2 could be a molecular band perturbation causing a spurious Franck-Condon factor; Equation (3-4).
As far as the errors of data in Fig.3-2 is concerned, only strong bands in the system were chosen to minimise the statistical errors. Typical noise levels were ±3%. To estimate the magnitude of the error from this source, relative sensitivities were estimated for the bands of the v'=4 sequence under different pressures and thus experimental conditions within the discharge. These results are summarised plotted in Fig.3-4. From Fig.3-4, we estimated the errors in the sensitivity from this source to be ±10%.

Note that the gap, between the CO third & fourth positive systems (220 nm ~ 260 nm), was estimated from the trends of the data on both sides of the gap and is indicated by a dashed line on Fig.3-2. Actually, the CO 3A system, involving a single upper level (v'=0), was observed within this region, but no published Franck-Condon factors were available. The fourth positive bands in this range were too weak to be used for calibration purposes. Assuming the relative sensitivity curve, Fig.3-5, it was possible to obtain relative Franck-Condon factors for the CO 3A system using:

\[ q_{v'\nu'} \propto I_{v'\nu'} \lambda_{v'\nu'}^3 / k_{v'\nu'} \]  

(3-5).

The results are presented in Chapter 5 along with calculations of these Franck-Condon factors using the known spectroscopic data of the two states involved.
Figure 3-4 Relative sensitivities for CO fourth positive bands of \(v' = 4\) sequence under different pressures. Data are normalized to the (4,10) band at 199 nm. The vertical extent of the data points indicates the variations observed.
Figure 3-5 Relative sensitivity curve estimated for bands of CO 3A system.
IV. VACUUM ULTRAVIOLET SPECTROSCOPIC STUDIES OF SF₆ IN RF DISCHARGES

4.1 Introduction

Over the past years, there has been considerable interest in low-pressure discharges in SF₆ for etching different materials in electronic circuit fabrication (d'Agostino et al., 1981; Picard et al., 1986; Coulon et al., 1991) and for the deposition of thin films. In the presence of contaminants such as water vapour and oxygen, SOF₂, SO₂F₂, SF₄, and SO₂ were found in the discharge (Van Brunt et al., 1990 and 1994). Spectroscopic studies of SF₆ have been done using a variety of experimental techniques such as corona discharge (Zengin et al., 1991), ultraviolet (UV) (Liu et al., 1951 and Duncan et al., 1954), vacuum ultraviolet (VUV) (Blecchenschmidt et al., 1972), X ray (Lavilla et al., 1966 and 1972), photoelectron (Gelius et al., 1974), electron-impact (Trajmar et al., 1977) and mass (Dibeler et al., 1948) spectroscopies. A previous study done in our group by Forand, Becker and McConkey used electron impact to investigate the dissociation mechanisms (Forand et al., 1986a).

However, there is little known about the VUV radiation from the RF discharge. In this work, we present the UV and VUV spectra from RF discharges through SF₆ and its mixtures with helium. The intensity-pressure variation of various observed spectral features as well as intensity-power variations will be discussed in detail below.
4.2 Results and Discussion

Fig.4-1 shows a typical spectrum from a pure SF₆ RF discharge covering the entire observed spectral range. A pressure of 250 mtorr was used in the source with an RF power rating of 30W. A clear break occurs in the spectrum at about 195 nm. Below this wavelength most of the features are atomic lines, dominated by the first spectrum of sulphur. Above 195 nm the features are clearly molecular in nature and consist of three main features, two of which near 255 and 300 nm, have been identified as the $A^3\Pi - X^3\Sigma$ and $B^3\Sigma - X^3\Sigma$ systems of SO respectively. The third feature is due to NO $\gamma$ ( $A^2\Sigma^+ - X^2\Pi$ ) and $\beta$ ( $B^2\Pi - X^2\Pi$ ) systems.

Intensity variation as a function of RF power input has been established by observing the spectra in the wavelength range, 112-132 nm, using a fixed pressure of 220 mtorr (Fig.4-2). The intensities of all the different features were observed to increase monotonically with increasing power. Hence, almost all the following spectra for SF₆ were taken with the same RF power input (30 watt).

4.2.1 Atomic Features

i. Identification

In Fig.4-1, the spectrum at wavelengths shorter than 195 nm is essentially an atomic line spectrum. Most of them are identified as atomic sulphur lines. Fig.4-3, 4-4, 4-5 show the observed spectra together with the standard S lines from National Institute of Standards and Technology (NIST) database of atomic lines obtained through the computer internet access. Note the close correspondence between our data and the NIST spectra.

* Unless further specified, the spectra present in this thesis were taken at the discharge power of 30 watt, the discharge frequency of 35.045 Mhz and the exposure time of 50 seconds.
Figure 4-1  Output spectral intensity versus wavelength for SF\(_6\) discharge (250 mtorr). Note that the data have not been corrected for variations in detector sensitivity with wavelength.
Figure 4-2 Variation of output SF$_6$ spectral intensity with input RF power for the features indicated. (220 mtorr)
Figure 4-3  Output intensity versus wavelength over 112-132 nm.
The positions of known SI features are indicated by vertical bars. Other features are as indicated.
Figure 4-4  Output intensity versus wavelength over 131-150 nm. The positions of known SI features are indicated by vertical bars. Other features are as indicated.
Figure 4-5  Output intensity versus wavelength over 160-210 nm. The positions of known SI features are indicated by vertical bars. Other features are as indicated.
Table 4-1 Identifications of SI emissions following
RF discharge through SF6 using NIST data.

( Note that the intensities have not been corrected for variations
in detector sensitivity with wavelength. )

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<th>2J'+1</th>
<th>Term</th>
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Table 4-1 gives the detailed configurations of these S transitions. Most of the lines are due to transitions to one or another of the levels of the ground configuration $3p^43P$, $1D$ or $1S$. In view of the fact that the S spectrum is excited so strongly, it is certain that the F spectrum is equally strong below 100 nm. This is supported by the e-beam excited spectra of Forand et al. (1986a), where both S and F lines are strongly evident. All of this indicates that surfaces being exposed to etchant SF$_6$ plasmas are subject also to intense irradiation of hard VUV photons.

Besides S lines, there are some other atomic lines observed: H Lyman-α (121.6 nm), the O resonance triplet (130.22, 130.48, 130.60 nm) which overlaps S lines, and N lines (120.0 nm triplet, 149.3, 149.5, 174.2, 174.5 nm). These are typical impurity lines from air or water vapour and are probably due to outgassing from the walls of the discharge vessel. Virtually no F lines appear because of the energy level structure of neutral F. Any transitions to the ground states of F lie at wavelengths shorter than 100 nm and so lie outside the short wavelength cut off of our detection system. No F$^+$ lines were observed probably due to the very high excitation threshold for those features.

In the spectrum of 1% SF$_6$ and 99% He mixture (Fig.4-6), there are some He atomic lines (272.32, 276.38, 282.91, 294.51 nm). The N lines seem to be much stronger than those in pure SF$_6$ (Fig.4-1), as are the S(5$^2S_2 \rightarrow 3P_{1,2}$) lines at 190 nm. In addition, a series of Si lines show up around 251-252 nm (Fig.4-7). Inner shell excitation of Si (to the 1s$^2$2s$^2$2p$^6$3s$^1$3p$^3$ 3D$^0$ configuration) gave rise to features at 220.80, 221.09, 221.17, 221.67 and 221.81 nm. Two other Si lines were also observed at 212.41 and 288.16 nm. These Si lines are also observed from low pressure discharges in pure SF$_6$ (4 mtorr), pure CF$_4$ (1.9 mtorr) or 1% CF$_4$ + He mixtures. This evidence strongly suggests that etching of the walls of the discharge vessel is occurring, releasing Si and O$_2$ into the discharge. Reaction of these species with other
Figure 4-6  Spectrum taken with 1% SF₆ in He at total pressure of 1 torr. Features are as indicated. Note that the spectrum has not been corrected for variations of detector sensitivity with wavelength.
Figure 4-7 Spectrum taken with 1% SF₆ in He.
The positions of known Si I lines are indicated by vertical bars. See text for further details.
species in the discharge produces much of impurity spectra observed. (See below for
detailed discussion.) In higher pressure discharges the Si atomic features are swamped
by other stronger features.

ii. Pressure Variation

Examples of the variation of the intensities of specific spectral features as a
function of discharge pressure are shown in Fig.4-8 and 4-9. The Lyman-α
impurity line displays a monotonic fall off with increasing pressure (Fig.4-10a) as
might be expected. Similar characteristic is shown by the impurity lines of N and
O.

We have picked out a few representative features and plotted their intensity
as a function of source pressure keeping other parameters such as discharge power
constant. The lines at 138.5-139.6 nm are of special interest since they involve
inner shell excitation, \(3s^23p^4 3P \rightarrow 3s^13p^5 3P^0\). A typical intensity-pressure curve for
this series is shown in Fig.4-10b. Other inner shell features share the same character.
Compared with a nearby non-inner-shell excited feature at 140.15 nm (\(3s^23p^4 3P \rightarrow
3s^23p^5 5s^1 3S^0\), Fig.4-10c), the inner shell excited lines demonstrate a peak intensity at
somewhat lower pressures (below 100 mtorr) with a more rapid fall off in intensity
as the pressure is increased. To excite electrons from atomic inner shells, high
energy electrons are needed. The intensity behaviour probably reflects the varying
discharge conditions as the pressure is varied with fewer electrons in the high
energy tail of the distribution at higher pressures.

Considering other S features, a number of points should be noted. The \(^3S^0 \rightarrow
^3P, ^3S^0 \rightarrow ^3P_1, ^1P_1 \rightarrow ^1S_0\) and \(^1D_2 \rightarrow ^1D_2\) transitions, (at 182, 147, 169 and 167 nm
), all of which involve different final states within the sulphur ground
configuration, display very similar intensity versus source pressure curves (Fig.4-
11) with a broad maximum occurring in the region of 150 mtorr. These are rather
Figure 4-8 Spectral output from pure SF₆ discharge as a function of discharge pressure over range 112-132 nm.
Figure 4-9 Spectral output from pure SF₆ discharge as a function of discharge pressure over range 126-146 nm.
Figure 4-10 Variation of output intensity with pressure in pure SF$_6$ discharges for the features indicated. See text for further details.
Figure 4-11 Variation of output intensity with pressure for the Si lines indicated. See text for further details.
similar to the behaviour observed in Fig.4-10c for 140.15 nm ( \(^{3}S^{0} \rightarrow ^{3}P\) ). The pressure variation curve for the 190 nm ( \(^{5}S \rightarrow ^{3}P_{2}\) ) transition (Fig.4-12) looks more like that for the inner shell transitions, i.e. relatively stronger at lower pressure. We note that the two lines at 190.03 and 191.47 nm are extremely strong in a 1% SF\(_{6}\) mixture.

It is of interest to see how the relative intensities of lines within a given multiplet vary as the pressure in the discharge is changed. In Fig.4-13 we consider the \(3s^{2}3p^{3}(^{4}S^{0})4s^{3}S_{1}^{0} \rightarrow 3s^{2}3p^{4}^{3}P_{2,1,0}\) multiplet with transitions occurring at 180.7 nm (\(\Delta J = +1\)) 182.0 nm (\(\Delta J = 0\)) and 182.6 nm (\(\Delta J = -1\)). The intensity ratios of the different features are presented. A similar ratio curve is shown in Fig.4-14 for the \(4s^{5}S_{2}^{0} \rightarrow ^{3}P_{2,1}\) multiplet with transitions at 190.0 and 191.5 nm (\(\Delta J = 0\) and -1 respectively). The same upper state is involved for a particular multiplet with transitions to different lower states. If the relative intensities were governed solely by the statistical weighting of the lower state, then we would expect the relative intensities of the 180.7, 182.0 and 182.6 nm lines to be in the ratio 5:3:1. The ratio of the intensities of the first two lines was indeed found to approach 1.67, as predicted, at the very low pressure (4 mtorr, see Fig.4-13), but other ratios were rather lower than predicted and varied quite strongly with pressure. For the case of \(4s^{5}S_{2}^{0} \rightarrow ^{3}P_{2,1}\) transitions, the ratio of the 190.0 and 191.5 nm line intensities should be 5:3, which was only realized at the highest pressure, 600 mtorr (Fig.4-14).

The observed pressure variations could be due to a number of factors:

1. The lines are expected to be heavily self absorbed as they all represent transitions to the ground state. The amount of trapping of resonance radiation which was obtained would depend strongly on whether a good statistical equilibrium had been established within the discharge. If not, the absorption and
Figure 4-12: Variation of output intensity with pressure for the SI line multiplet indicated. See text for further details. 100 seconds exposures were used.
Figure 4-13 Ratio of lines intensities within the SI multiplet at 180 nm.

Figure 4-14 Ratio of lines intensities within the SI multiplet at 190 nm. See text for further details.
emission line profiles could be quite different and thus the final observed intensities of the different lines would become unpredictable.

2. Since the central axis of the discharge, along which observation is made, defines an axis of symmetry for the system, it is quite possible that optical polarization effects could be contributing. Thus if the lines emitted from the discharge were differently polarized, they would suffer different effects on reflection from the mirror and the grating of the spectrometer. These two optical elements combine to make the detection system significantly polarization sensitive.

4.2.2 Molecular Features

The spectra above 195 nm are typical molecular features with band heads on top of a continuous background (Fig.4-1). These molecular features are actually more significant than might be inferred from Fig. 4-1 because the overall sensitivity of the system decreases as the wavelength increases from the blaze (150 nm) towards longer wavelengths (see Fig. 3-2).

Fig.4-15 illustrates how the molecular features vary with source pressure. On this figure we have identified the various systems, namely: SO (B^3Σ^- X^3Σ^-), SO (A^3Π - X^3Σ^-), NO γ (A^2Σ^- - X^2Π ) and NO β (B^3Π - X^2Π ) systems. Intensity-pressure curves for representative bands within these systems are shown in Fig.4-16.

The identification of the different systems is shown in Fig.4-17 to 4-19. The known band heads are shown as vertical bars below the observed spectra. We note the very good correspondence between the data sets. Comparison spectral data were obtained from Pearse and Gaydon (1976) for NO and SO (B-X ) systems and Colin (1969) for SO (A-X) system. The NO γ system has distinctive double headed bands.
Figure 4-15 Variation of output from SF₆ discharges in wavelength range 200-320 nm for various pressures. Pressures are 4, 19, 69, 114, 247, 452 and 830 mtorr, increasing from bottom to top of diagram. The main spectral features are indicated.
Figure 4.16 Variation of intensities of various molecular features in SF₆ discharge with pressure.

- a: SO(A-X) system
- b: SO(B-X) system
- c: NOγ bands
Figure 4-17 SO (A-X) bands excited in an SF₆ discharge at 250 mtorr pressure. The positions of known features are indicated by vertical bars.
Figure 4-18 SO (B-X) bands excited in an SF₆ discharge at 250 mtorr pressure. The positions of known features are indicated by vertical bars. 10 minutes exposure was used.
Figure 4-19 NO $\gamma$ system excited in an SF$_6$ discharge at 452 mtorr pressure. The positions of known features are indicated by vertical bars.
which facilitates identification. A triple headed band was observed at 240 nm but is so far unidentified.

The presence of NO is probably due to small N₂ and O₂ impurities in the parent gas. These NO systems were not observed in the discharge when another SF₆ gas source was used.

We note that the intensity-pressure variations of the two SO systems (Fig.4-16) were quite different, indicating that different production channels were operative for the SO A and B states. Note that at pressures higher than 110 mtorr, the overlapped NO features become significant and effect the intensity-pressure curves.

The strong SO emissions clearly dominate the spectrum in the 250-300 nm region and so features such as observed by Jabbour et al. (1988), and Blanks and Becker (1987) following electron impact excitation of SF₆ in a crossed beams experiment, are probably obscured. The SO is formed within the discharge as a result of reactions between oxygen, released from the walls of the pyrex tube by the active F species from the discharge, and sulphur also present within the active discharge. Typical reactions follow:

\[ \text{SF}_6 \rightarrow \text{S} + 6\text{F}, \quad x\text{F} + \text{SiO}_2 \rightarrow 2\text{O} + \text{Si} + \text{F}_x (\text{or SiF}_x), \quad \text{S} + \text{O} + \text{M} \rightarrow \text{SO} + \text{M} \]

where M is a third body to conserve energy and momentum. This phenomenon is well known and has been noted by Clyne et al. (1973). The observations of Si atomic lines mentioned earlier and of the SO development with time (see below) also support this explanation. This is a further example of the effectiveness of F-species in etching or other surface reactions.

The features at 298 and 315 nm (Fig.4-15) are well known N₂ bands. Their intensity-pressure variation demonstrates a sharp peak at 450 mtorr somewhat similar to that of NO (Fig.4-16c).
Below 195 nm a few small, unidentified but clearly molecular, structures were observed around 118 nm (Fig.4-8). This is shown in more detail in Fig.4-20 where a long (60 minutes) exposure has been taken. Six closed spaced features are seen between 114 and 121 nm. Their intensity-pressure variation is very similar to those of S lines.

4.2.3 Time Development of Spectra

It is interesting to observe the time development of different features before the discharge stabilizes. A series of spectra were taken immediately after the RF discharge was switched on, focusing on the 140-160 nm and 245-265 nm regions to study the atomic features and molecular bands respectively. The results are shown in Fig.4-21. We note that it takes about two minutes for the discharge to stabilize. The S lines increased their intensity by about thirty percent as the discharge warmed up. However, the SO (A-X) continuum increased dramatically in intensity, by a factor of 2.4 over what was obtained initially. This shows that it takes time for the interaction of active F with the glass walls and subsequent discharge chemistry to build up the SO density inside the discharge.
Figure 4-20 Unidentified molecular spectrum near 118 nm excited in pure SF₆ discharge at 250 mtorr pressure. Known features are indicated. 60 minutes exposure was used.
Figure 4-21 Time development of the intensities of SO(A) and SI(B) features after initiation of discharge through SF₆ at 250 mtorr.
V. VACUUM ULTRAVIOLET SPECTROSCOPIC STUDIES OF CF₄ IN RF DISCHARGES

5.1 Introduction

The CF₄ molecule is of special interest because of its use in plasma etching and deposition applications. In the present observation, an RF discharge experiment was performed with the objective of detecting the UV and VUV spectra directly from CF₄ low pressure glow discharges. The intensity pressure variation of various spectroscopic emissions from pure CF₄ were studied. An investigation was also carried out of the emissions of CF₄-He mixtures. The visual brightness of the discharge was observed to increase with pressure with a maximum at about 400–800 mtorr. The discharge was observed to become weaker as pressure was further increased.

The main observed features, the background continua and the intensity pressure/mixture variation will be discussed below in detail. Calculations of Franck-Condon factors for the CO 3A system were also carried out and compared with the results of the measurements.

5.2 Results and Discussion

5.2.1 Main Features

Fig.5-1 shows a spectrum of a pure CF₄ RF discharge at 240 mtorr covering the whole observed wavelength range 110-315 nm. A strong signal of the impurity, CO, dominated most of the spectra. This is seen in Fig.5-1 which shows the main spectral features observed and indicates the complete dominance of the impurity
Figure 5-1  Output spectral intensity versus wavelength for CF$_4$ discharge (240 mtorr). The main features are indicated. Note that the data have not been corrected for variations in detector sensitivity with wavelength. See text for further details.
emissions. Since the resolution of the system was 0.04 nm, it was easy to distinguish
the molecular bands from atomic lines. Three well known CO systems, fourth positive
system ( A^1\Pi -- X^1\Sigma ' ), 3 A system ( c^3\Pi -- a^3\Pi ) and third positive system ( b^3\Sigma ' -- a^3\Pi ),
were identified to cover almost the whole spectrum. As an example, part of the CO
fourth positive system is enlarged and shown in Fig.5-2 with identification. These CO
features were very strong, dominating everything else except for a little hint of a
carbon atomic line at 156.0 nm ( Fig.5-2 ) and two narrow CO_2^+ bands ( A^2\Sigma ' -- X^2\Pi )
at 288.3, 289.6 nm ( Fig.5-3 ). Several continua at 130-180 nm and 200-300 nm were
observed as weak background radiation. These were identified as due to CF_4^+ and
CF_3^+ ( and/or CF_2^+ ) and are discussed in detail below ( See Section 5.2.2 ).

On the other hand, many more features show up in the spectra from the mixture
of CF_4 ( 1% ) and He ( 99% ) at 1000 mtorr ( Fig.5-4 ). This is mainly because the
intensity of the CO bands drops down to just about three per cent of that of pure CF_4
in Fig.5-1. He was chosen as an inert gas since it has only a few lines in the observed
wavelength range: four He lines at 272-295 nm ( Fig.5-8 ). A very strong sharp line of
H Lyman \alpha shows up at 121.5 nm with its weak second order image at 243.0 nm.
There is a weak nitrogen line at 120.0 nm from air impurity, and the oxygen lines
around 130 nm appear quite strongly ( Fig.5-5,6 ). The CO' first negative system ( B
^2\Sigma -- X^2\Sigma ) was identified in the wavelength range 210-251 nm ( Fig.5-9 ). This system
was also present in the pure CF_4 spectra. A few Carbon lines were identified at 119.3,
135.5, 156.1, 165.7, 193.1 and 209.2 nm ( CII ), though in some cases, eg. 135.5,
156.1, 165.7 nm, these were overlapped with other atomic features or molecular
bands. The two lines at 174.47 and 174.55 ( Fig.5-7 ) were assigned to NI. The 196
nm feature, as well as other NO band heads present in SF_6 (Fig.4-19), shows up in all
CF_4 spectra, under different conditions of pressure and gas mixture, but not in CH_4.
Figure 5-2 150-175 nm spectral region indicating the various bands of the CO(A-X) 4th Positive System which are indicated (240 mtorr)
Figure 5-3 230-320 nm spectral region indicating the (c-a) 3A and (b-a) 3rd Positive systems of CO which were observed. Note also the CO$_2^+$ features.
Figure 5-4 Spectrum output versus wavelength from a discharge through 1% CF$_4$ in He at a total pressure of 1 torr. The main features are as indicated. Note that the spectrum has not been corrected for variations of detector sensitivity with wavelength.
Figure 5-5 Spectral output from a discharge through 1% CF₄ in He at 1 torr pressure in range 110-135 nm. Features are as indicated.
Figure 5-6 Spectral output from a discharge through 1% CF$_4$ in He at 1 torr pressure in range 126-146 nm. Features are as indicated.
Figure 5-7 Spectral output from a discharge through 1% CF₄ in He at 1 torr pressure in range 155-175 nm, illustrating the strong CO 4th Positive System. Portions of known CO features are indicated by vertical lines. Other features are indicated.
Figure 5-8 Spectral output from a discharge through 1% CF₄ in He at 1 torr pressure in 270-295 nm range. Portions of the He(π₃P-2σ₁S) systems, the CO 3rd Positive band (0,0) and the CO₂⁺(A-X) bands are indicated.
Figure 5-9 Spectra from a discharge through 1% CF₄ in He at 1 torr pressure. Main features are indicated.
Some of the CO impurity entered the discharge as an impurity in the CF₄ gas source (quoted as 0.0003% of CO and 0.04% of CO₂ in 99.9% of CF₄). However, most of the CO was presumably generated within the discharge following etching of the walls of the discharge vessel. It is suggested that the following reactions occurred,

\[ x \text{ F} + \text{SiO}_2 \rightarrow 2 \text{ O} + \text{Si} + F_x \text{(or SiF}_x \text{)} \quad \text{and} \quad \text{C} + \text{O} + \text{M} \rightarrow \text{CO} + \text{M}' , \]

where \( M \) is a third body to conserve energy and momentum. This explanation is also supported by Clyne et al. (1973), who observed appreciable SiF₄ and O₂ from a microwave discharge in a mixture of CF₄ (1%) and Ar (99%) using a mass spectrometer. Some SiI lines have been identified around 252 nm (Fig.5-9), similar to those found in 1% SF₆ mixture (Fig.4-7). We were not able to observe any features due to SiF₆ (\( n = 1, 2 \)).

A measurement of CO band intensity as a function of time, after the discharge was switched on, demonstrated a fairly rapid increase in intensity over a time period of about 50 seconds to a relatively constant value (Fig.5-10). This suggested that after this interval the discharge had stabilised with the walls reaching a temperature significantly higher than room temperature.

The emissions from CO will not be discussed further in this chapter except in connection with the calculation of the Franck-Condon factors for the CO 3A system (See Section 5.2.4). CO’s main usefulness was that it provided a very convenient means of establishing the relative quantum efficiency of the detection system via the “Molecular Branching Ratio” technique. This was discussed in Chapter 3.

5.2.2 Background Continua of CF₄⁺⁺ and CF₃⁺

Optical emissions of CF₄ in the visible, ultraviolet (UV), and vacuum ultraviolet (VUV) range can be used for diagnostic purposes and have been investigated by several groups following electron (Müller et al., 1992; Van Sprang et al., 1978 and Hesser et al., 1967), ion (Müller et
Figure 5-10 Time development of CO 4th Positive feature at 156 nm following initiation of discharge through CF₄ at the pressure of 300 mtorr.
al, 1994; Sasaki et al., 1986 and Aarts, 1985), photon (Lee et al., 1986) and metastable atom (Tsuji et al., 1992) impact. Hesser and Dressler (1961) observed three continuous emission bands excited by 200 eV electrons with maxima at 160, and 230/290 nm (Fig.5-11c). When lower energy (100 eV) electrons were used, the peak at 230 nm became relatively less intense compared to the peak at 290 nm (Van Sprang et al., 1978). Aarts (1985) showed a similar spectrum using 1 keV He⁺ impact (Fig.5-11b). An additional band at 189 nm was also observed in this work. The continuous bands 200-400 nm with maxima at 230 and 290 nm were also studied using 55.1 nm photon excitation (See Fig.5-11a) by Lee et al. (1986). Again two broad features in the 200-350 nm region were observed.

Originally Hesser and Dressler (1961) suggested that the 200-400 nm continua were generated by CF₃⁺. Following 100 eV electron impact on CF₄, van Sprang et al. (1978) assigned the CF₄⁺(B ²E) state as the upper state of the continuum at 230/290 nm and the CF₄⁺(C ²T₂) state for the band at 160 nm. Maier and Thommen (1981) criticised this assignment after they observed no coincidences in a photon/ion coincidence experiment following VUV photon impact on CF₄. These authors were in favour of Hesser’s assignment, CF₃⁺. Unfortunately their photon energy was less than 20 eV so that the CF₄⁺ C and D states could not be excited. In 1985, Aarts (1985) explained the observed continuum as due to a transition between the CF₄⁺( C ²T₂) state and the ground state CF₄⁺ ( X ²A₁). This repulsive potential ground state quickly dissociates into vibrationally highly excited CF₃⁺ and a fluorine atom. The 160 nm band was generated by a similar process involving the CF₄⁺(D) state. This was supported by Müller et al. (1993), who performed a photon/fragment-ion coincidence experiment using 2 MeV H⁺, He⁺, and He⁺⁺ impact on CF₄ and CHF₃. In the case of CF₃⁺ the photons in the 200-500 nm continuum were quantitatively coincident with CF₃⁺ fragments. Muller et al. argued that the
Figure 5-11 Spectral obtained from CF₄ under various excitation conditions:
(a) Using 55.1 nm photon excitation; (b) Using 1 keV He⁺ impact;
(c) Using 200 eV electrons; (d) Present discharge through CF₄ at 240 mtorr.
See text for further details.
continuum could not be assigned to excited CF$_3^-$, because no coincidences between photons in 200-500 nm range and CF$_3^-$ were observed when CF$_3$H was used as a target. Thus it was very unlikely to be occurring with CF$_4$ also. It seems likely that the explanation given by Aarts is the correct one, i.e. the continuum at 160 nm and 200-500 nm are due to CF$_4^-$ transitions.

In our spectra, the continuous bands mentioned above are present as background radiation. Fig.5-11d shows our spectrum from the RF discharge at a pressure of 447 mtorr and compares it with the spectra obtained using the other modes of excitation. The strong features of the CO fourth positive system (discussed earlier) tend to mask the structure at 160 nm and the 189 nm feature is absent or very weak. The peak at 230 nm, however, is in good agreement with the data from the other experiments, though the peak at 290 nm seems to be absent. This may be due to the low sensitivity of our detection system at this wavelength. We note that the relative intensities of the features at 230 and 290 nm vary with different impact electron energy. This implies that these bands originate either from a mixed or different upper state of the same radiating species or from different excited species. This is not in agreement with the suggestion of Muller et al. (1992). They observed a CF$_4$ excitation threshold of 23.5±2 eV and a second onset around 40 eV independent of spectral position within the band. This indicated a unique precursor for the whole 230/290 nm feature, but also highlighted the fact that it was being excited by two different mechanisms. Presumably in our discharges, somewhat different excitation mechanisms are involved.

All the spectra, which were taken using different pressures of pure CF$_4$ or under different mixtures of CF$_4$ in He, appeared similar to the one shown in Fig.5-11d., except for the one taken with 1412 mtorr of pure CF$_4$ (Fig.5-12c). This spectrum displayed a broad peak at 255 nm, where the CO impurity features were
Figure 5-12 Spectral obtained from CF$_4$ under various excitation conditions:
(a) He after glow excitation in presence of both ions and metastables;
(b) He after glow excitation in presence of metastables only;
(c) Present discharge through CF$_4$ at 1412 mtorr.
See text for further details.
relatively weak. We note that it was much more pronounced than the background continua near 230 nm or, indeed, at 160 nm. Comparison with the emission spectra of CF$_4$ excited in He afterglow (Tsuki et al., 1992) (Fig.5-12a and b) suggests that this 255 nm peak could be assigned to CF$_3$(2$^2$A$_1′$--X 1$^2$A$_2″$) and/or CF$_2$( A$^1$B$_1$-X 1$^1$A$_1$). Fig.5-12a shows an emission spectrum of CF$_4$ in the He afterglow at a He buffer gas pressure of 750 mtorr, where He(2$^3$S), He$^+$, and He$_2^+$ were present as He active species. We note that CF(A$^2$Σ$^−$--X$^2$Π; ν$′$=0,1 and B$^2$Δ--X$^2$Π; ν$′$=0,1) transitions are superimposed upon the continuous band. When He$^+$, and He$_2^+$ were removed by using the collector grids, the CF(A-X and B-X) emissions disappear and the continuum intensity is reduced by 50% (Fig.5-12b). This implies that all the CF(A-X) and CF(B-X) emissions result from ionic interactions, whereas both He(2$^3$S) and ionic active species participate in the formation of the continuous CF$_3$(2$^2$A$_1′$--X 1$^2$A$_2″$) and/or CF$_2$( A$^1$B$_1$--X 1$^1$A$_1$) band. A very similar spectrum without the CF features was given by the interaction of CF$_4$ and Ar($^3$P$_2$), Ar$^+$, Ar$^{2+}$ (Tsuki et al., 1992) or by 92.3 nm photon absorption by CF$_4$(Lee et al., 1986). For the latter case, the emission band was observed at a lower wavelength, below 200 nm. In our experiment, none of the structure which was observed could be identified with the CF emission. It appears that the very high pressure CF$_4$ discharge features are rather similar to those produced by rare gas metastables. (Fig. 5-11b,c)

5.2.3 Pressure and Mixture Variation

With the discharge power fixed at 25 watts, spectra were obtained from the RF discharge at pressures of 1.9, 14, 37, 136, 447, 810, 1412 mtorr. These pressures were measured by a capacitance manometer just prior to the discharge vessel. The visual brightness of the discharge was observed to peak at 400–800 mtorr. The intensities of every band of the CO fourth positive system were monitored as a
function of pressure. The results were normalised and were essentially identical for all bands. All curves maximise at 400~800 mtorr. A typical pressure variation curve (using band ( 2, 2 ) at 157.6 nm ) is shown in Fig.5-13. Similar measurements were carried out for the bands of the CO third positive system ( Fig.5-13 ) as well as for the background continua of CF₄⁺/CF₃⁺ at 200~300 nm ( Fig.5-14 ). The results were just like those for the fourth positive system.

Sample spectra in the range 215~235 nm are shown in Fig.5-15 to display intensity change via pressure variation. We note that in Fig.5-15, the CO⁺ features seem to be quite uniform under different pressures. This may reflect the fact that even though the CO density is smaller at lower pressures, the effective electron temperature is higher, thus providing more collisional excitation of CO⁺. The opposite effect is true at higher total pressures.

Spectra are shown in Fig.5-16 for different CF₄-He mixtures. At the same total pressure of 800 mtorr, the CO signal from a 20% CF₄ discharge is much stronger than when only 5% CF₄ is used. This may be due to the effect of He preventing the active F atoms from interacting with the walls of the discharge vessel and releasing oxygen. This supports the argument that most of the CO was generated within the discharge.

5.2.4 Calculation of Franck-Condon Factors for the CO 3A System

A series of relatively weak features, the CO 3 A system ( c³Π--a³Π ), were present at 229~272 nm in our spectra ( Fig.5-3 ). All the five features observed are from the same upper vibrational level, v' = 0, to different lower vibrational levels: v"= 0, 1, 2, 3, 4. As discussed in Chapter 3, the relative Franck-Condon Factors for these bands have been established from the analysis of the experimental data. Here we discuss the theoretical calculation of these relative Franck-Condon Factors.
Figure 5-13 Intensity versus $\tau_{F_1}$ pressure of the representative bands of the CO 4th Positive and 3rd Positive Systems.
Figure 5-14 Intensity versus CF₄ pressure of the CF₄/CF₃⁺ background continua at 200-300 nm. See text for further details.
Figure 5-15 Spectra taken at different CF₄ pressures (indicated on right of diagram) in the spectral region 215-235 nm. The main spectral features of CO 4th Positive and CO⁺ 1st Negative systems are indicated.
Figure 5-16 Spectra taken at different CF<sub>4</sub>/He mixtures. Percentage of CF<sub>4</sub> is indicated to the right of diagram. Total pressures are 1000, 800, 400, 800, 310 and 240 mtorr counting from the bottom of the diagram.
The intensities of diatomic molecular bands in emission or absorption are proportional to the Franck-Condon Factors $q_{v', v''}$:

$$ q_{v', v''} = |\int_0^\infty d r \psi_i^*(v') \psi_2(v'')|^2 $$

(5-1)

$v'$ is the upper vibrational level and $v''$ is the lower vibrational level. The subscript “1” represents the upper electronic level and “2” the lower electronic level throughout this section. The so-called overlap integral is defined as:

$$ (v', v'') \equiv \int_0^\infty d r \psi_i^*(v') \psi_2(v'') $$

(5-2)

The wave function $\Psi_i$ for state $i$, depends on the shape of the molecular potential energy curve. Most conveniently, this is taken as a Morse potential. The Morse potential of an electronic state $i$ is given by:

$$ U_i(r) = D_i [1 - \exp(-a_i (r - r_{e_i}))]^2 $$

(5-3)

where $D_i$ is the dissociation energy, $r_{e_i}$ is the equilibrium position. The factor $a_i$, containing the information on the shape of the potential curve, usually is different between upper state $\psi_1$ and lower state $\psi_2$. It is very difficult to calculate explicitly the overlap integral for different $a_i$. The most accurate way is to use numerical methods, but this is very complicated and time consuming. An approximation method was introduced by Fraser and Jarmain (1953) to calculate this overlap integral. They introduced a mean value “$a$” as an approximate value for both $a_1$ and $a_2$. Two new potentials using the mean value $a$, $U_1'(r)$ and $U_2'(r)$, are constructed to replace the original Morse potentials, $U_1(r)$ and $U_2(r)$. All the calculation are based on these approximations.

A lengthy calculation is carried out by Fraser et al. (1953), and the results are quoted from their appendix. The ratio of the overlap integrals of the (0,1) and (0,0) molecular bands is
\[
\frac{(0,1)}{(0,0)} = -\frac{N_2^{(1)}}{N_2^{(0)}} \left[1 - \rho_2 \frac{(K_2 - 2)}{(K - 2)} \right]
\] (5-4)

Similarly for the (0,2) and (0,3) bands, we have:
\[
\frac{(0,2)}{(0,0)} = +\frac{N_2^{(2)}}{N_2^{(0)}} \left[1 - 2\rho_2 \frac{(K_2 - 3)}{(K - 2)} + \rho_2^2 \frac{(K_2 - 3)(K_2 - 4)}{(K - 2)(K - 3)} \right]
\] (5-5)
\[
\frac{(0,3)}{(0,0)} = -\frac{N_2^{(3)}}{N_2^{(0)}} \left[1 - 3\rho_2 \frac{(K_2 - 4)}{(K - 2)} + 3\rho_2^2 \frac{(K_2 - 4)(K_2 - 5)}{(K - 2)(K - 3)} - \rho_2^3 \frac{(K_2 - 4)(K_2 - 5)(K_2 - 6)}{(K - 2)(K - 3)(K - 4)} \right]
\] (5-6)

where \(N_i\), \(\rho_i\), \(\lambda_i\), \(\lambda\), \(K_i\), \(K\), a etc. are constants defined below,
\[
\frac{N_2^{(v')}}{N_2^{(v'-1)}} = \left[\frac{(K_2 - v')}{v'} \cdot \frac{(K_2 - 2v' - 1)}{(K_2 - 2v' + 1)}\right]^{1/2}, \text{ then } \frac{N_2^{(2)}}{N_2^{(0)}} = \frac{N_2^{(3)}}{N_2^{(1)}} = \frac{N_2^{(1)}}{N_2^{(0)}} \text{ etc.}
\] (5-7)

\[
\rho_2 = \frac{\lambda_1}{\lambda_2}, \quad \lambda = \frac{1}{2}(\lambda_1 + \lambda_2); \quad K = \frac{1}{2}(K_1 + K_2)
\]

\[
\lambda_1 = K_1 \exp\left(a \, r_{c1}\right), \quad \lambda_2 = K_2 \exp\left(a \, r_{c2}\right);
\]

\[
a = (a_1 + a_2)/2;
\]

\(a_1\), \(a_2\), \(K_1\) and \(K_2\) can be written in terms of the known molecular spectroscopic constants.
\[
a_i = 2\pi \omega_{ei} \sqrt{\frac{\mu}{2D_i}} \cdot \frac{c}{h} \quad \text{(Graybeal, 1988) Equation (12.34))}^*
\]

\[
K_1 = (a_1/a)^2 \omega_{c1} / (\omega_{c}x_c)_1;
\]

\[
K_2 = (a_2/a)^2 \omega_{c2} / (\omega_{c}x_c)_2;
\]

where \(\omega_c\), \(\omega_{c}x_c\) are vibration parameters, \(D\) is the dissociation energy from the bottom of the potential well and \(\mu\) is the reduced mass of CO.

As far as the CO 3A system (\(c^3\Pi - a^3\Pi\)) is concerned, the upper electronic state 1 is \(c^3\Pi\) and the lower state 2 is \(a^3\Pi\) (Ginter et al., 1969). \(\omega_{c2}\) and

\[\text{In practice, } a_i = 1.2177 \times 10^7 \omega_{ei} \sqrt{\frac{\mu}{D_i}} \quad \text{(Hersberg et al., 1950)(III, 160);} \text{ where } \mu \text{ is the reduced mass in atomic-mass unit (a.m.u.), } D_i \text{ is in cm}^3 \text{ unit, as are } \omega_{c2} \text{ and } a_i.\]

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$(\omega_c x_c)_{2}$ for state $\alpha^3\Pi$ can be obtained from NIST's data series (Krupenie, 1966). It should be noted that in this approximation method, the dissociation energy $D_1$ obtained from the equation

$$D = \frac{\alpha_c^2}{4\omega_c N_c},$$

(5-8)

should be used. The exact value of this dissociation energy, found in the NIST data tables (Krupenie, 1966), on the other hand, introduces a serious error and should not be used. This point was discovered when carrying out test calculation for the $N_2$ second positive system. The Franck-Condon Factor values calculated using the $D$ value from Equation (5-8), agreed excellently with those using numerical methods, while the ones using the exact value for $D$ showed significant differences from the accepted results.

The rotational structure of the upper electronic level $c^3\Pi$ is known (Ginter et al., 1969) and $\omega_{el}$ can be calculated to within 10 percent uncertainty using

$$\omega_{el} = \sqrt{\frac{4B_{el}^3}{D_{el}}} \quad (\text{Graybeal, 1988}) \quad \text{Equation (12.5))} \quad (5-9)$$

where $B_{el}$ and $D_{el}$ are rotational parameters taken from Ginter et al. (1969). However, since only the spectra due to the $v' = 0$ sequence were observed, $(\omega_c x_c)_1$ could not be found and hence $D_1$ could not be established using Equation (5-8). An alternate method was therefore used to estimate $D_1$ based on the known excitation energy of CO ($c^3\Pi$), the known dissociation energy of CO into ground state fragment (Herzberg et al., 1950), and the calculated separated atom energies assuming dissociation occurred to $\text{C} \left( ^3\text{P} \right)$ and $\text{O} \left( ^1\text{S} \right)$. The calculated relative Franck-Condon Factors are compared with the measured relative intensities in Table 5-1.
Table 5-1. CO 3A System Franck Condon Factors

<table>
<thead>
<tr>
<th>$\nu'-\nu''$</th>
<th>Measured</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Area</td>
<td>Peak Height</td>
</tr>
<tr>
<td>0-0</td>
<td>0.603</td>
<td>0.430</td>
</tr>
<tr>
<td>0-1</td>
<td>1.000</td>
<td>1.000</td>
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<tr>
<td>0-2</td>
<td>0.800</td>
<td>0.798</td>
</tr>
<tr>
<td>0-3</td>
<td>0.775</td>
<td>0.690</td>
</tr>
<tr>
<td>0-4</td>
<td>0.915</td>
<td>0.722</td>
</tr>
</tbody>
</table>

We note that there is some disagreement between the calculated Franck-Condon Factors and the measured ones. One of the major reasons, as mentioned earlier, is due to the error introduced by the method used to establish the dissociation energy, $D_1$. Another possible reason comes from the error in the measured intensities of the bands. For the 3A system, some overlap with fourth positive and CO' features occurred. Some radiation trapping may have occurred with the (0,0) transition. The metastability of the lower $\alpha^3\Pi$ state (LeClair et al., 1994) could allow a significant build up of $\nu''=0$ population within the discharge. This may help to explain the anomalous relative intensity of this feature.
VI. VACUUM ULTRAVIOLET SPECTROSCOPIC STUDIES OF CH₄ IN RF DISCHARGES

6.1 Introduction

Methane (CH₄) and other hydrocarbons have been widely used in industry for the production of diamond like coatings using plasma assisted deposition techniques. It has been found that the presence of hydrogen plays a crucial role in diamond growth on surfaces (Madison et al., 1994) and there should be a correlation between the quality of the coatings produced and the concentration of atomic hydrogen present in the plasma during deposition (Cheshire et al., 1994). The radiation from the discharge may also affect the surface structure and hence the diamond film quality. In the present work, the VUV spectra from RF discharges through CH₄ have been studied and HI and H₂ features were found to dominate the spectra in the observed VUV region.

The electron impact excitation of methane has been extensively studied by several groups (Shyn, 1991; Pang et al., 1987 and Aarts, 1970). Vacuum ultraviolet (VUV) emission features (from 10 to 200 nm) were found to be entirely due to atomic dissociation fragments (Cl, CII and H) by Pang et al. (1987), following 200 eV electron impact. The CH (A-X, 430 nm) system was found by Aarts (1970) with onset threshold for electron impact at about 15 eV. This is outside our spectral range of observation. A study of CH absorption was carried out by Herzberg et al. (1969) in the ultraviolet and vacuum ultraviolet using the flash photolysis of diazomethane. CH (D-X), (E-X), (F-X) and (D-B) systems were found at 169, 156, 154 and 300 nm respectively.

In the present work, HI and Cl lines are identified, but the H₂ Werner and Lyman-band systems are found to dominate the spectra below 165 nm. At higher wavelengths the CO and CO⁺ impurity features are evident.
6.2 Results and Discussion

Fig.6-1 shows a spectrum of the CH₄ RF discharge covering the entire observed wavelength region. HI Lyman α is found to be extremely strong at 121.57 nm probably resulting from direct disassociative excitation of CH₄. A clear break occurs in the spectrum at about 165 nm. Below this wavelength the features are strong and clearly molecular in nature (Fig.6-2). These are identified as the H₂ Werner and Lyman-band systems (See below for detailed discussion.). From 165 to 220 nm the features are due to the CO fourth positive bands. The CO⁺ first negative system also shows up at 220-230 nm, as does the CO third positive system at 280-313 nm. We note that these CO features are much weaker than those in CF₄, since they can only be due to a small amount of impurity in the parent gas. The second order spectrum of HI Lyman α as well as of the H₂ Werner and Lyman-band systems show up at 240-315 nm.

The identification of the H₂ Werner and Lyman-band systems from 114 to 165 nm is established via a comparison with the high resolution spectra of H₂ obtained by 100 eV electron impact (Liu et al., 1995). A typical comparison is shown in Fig.6-3, which covers the range 130-135 nm. Clearly the one to one correspondence is extremely good. This is the case over the whole spectral range up to 165 nm indicating that electron impact excitation of H₂, produced following dissociation of CH₄, is a dominant process within the discharge. We note that the features such as shown in Fig.6-3 are largely isolated rotational lines, not band heads.

The CI features in the spectra were very weak. The 193.1 nm line was superimposed on the weak CO band. Although the CH⁺ [(D²Π - X ²Π), (E²Π - X ²Π)] and (F²Π - X ²Π) bands were found in absorption spectra in the range 154-169 nm by Herzberg (1969), there was no clear evidence for them in our spectra. Further, neither

* Electronic data obtained through personnel communication.
Figure 6-1  Output spectral intensity versus wavelength from RF discharge through CH$_4$ at the pressure of 245 mtorr. The main spectral features are indicated. Note that the data have not been corrected for variations in detector sensitivity with wavelength.
Figure 6-2 Spectrum from CH₄ under same conditions as in Fig.6-1, illustrating the strong development of H₂ Lyman and Werner systems.
Figure 6.3 Comparison spectra indicating close correspondence between present data (top curve) and 100 eV electron impact data of H₂ (Liu et al., 1995) (bottom curve).
the CH ($D^2Π - B^2Σ^+$) system nor the CH$_2$ features observed by Herzberg were present in this work.

In conclusion, the spectra of CH$_4$ in this spectral region from RF discharges are mainly due to H and H$_2$. Some CO and CO$^+$ impurity features were also observed.

The intensity-pressure variation of the various features was established with spectra taken at 50, 100, 250 and 500 mtorr(Fig.6-4). The intensities of the H$_2$ features were found to increase monotonically with pressure. The HI Lyman $α$ feature was strongest at 50 mtorr and fell off a little in intensity towards the higher pressures. The CO features had a maximum intensity around 250 mtorr while the CO$^+$ intensity was observed to decrease as the pressure went up.
Figure 6-4 CH₄ spectra taken at 50, 100, 250 and 500 mtorr. The main features are as indicated.
VII. CONCLUSIONS

VUV and UV spectra from RF discharges through SF₆, CF₄ and CH₄ gases have been studied in the wavelength region 115-315 nm. Many intense emissions have been found in the observed region indicating that there is much energetic radiation generated by the RF discharges. During the glow discharge plasma etching process, the discharge gases as well as the surface layers are expected to be heavily influenced by these radiations.

It is observed that features due to dissociation products, S, H and H₂, etc., dominated the observed spectra, indicating that very considerable dissociation of the multi-atom parent molecules is occurring within the discharge followed by much plasma chemistry.

Significant oxygen-bearing impurities, SO, NO and CO, have been identified in the discharge, showing the active etching properties of the fluorine atoms and radicals, releasing SiO₂ from the walls into the discharge. Use of the impurity band systems, to provide a relative calibration of the sensitivity of the detection system with wavelength, has been demonstrated. The Franck-Condon factors for the CO 3A system have been calculated and compared with measured band intensities.
# APPENDICES

## Table A-1 Spectral Data Using for Dispersion Calculation Purposes

<table>
<thead>
<tr>
<th>Centre</th>
<th>Calibration Lines</th>
<th>Wavelength Separation (nm)</th>
<th>Spectral Features</th>
<th>Measured Reciprocal Dispersion (A/mm)</th>
<th>J'-J&quot;</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
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<td>121.57</td>
<td>129.57</td>
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<td>g2S-2Po</td>
<td>1/2-3/2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>129.57</td>
<td>209</td>
<td></td>
<td>3P-3P*</td>
<td>2-2</td>
<td>19.50</td>
</tr>
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<td>131.65</td>
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### CO 3rd Positive System

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REFERENCES

Blechschmidt D., Haensel R., Koch E.E., Nielsen V. and Savawa T.
Chem.Phy.Lett. 1433 (1972)
Cheshire R.C., Kornas V., Dobele H.F., Donnelly, Dowling D., Graham W.G.,
d'Agostino R., “Plasma Deposition, Treatment and Etching of Polymers” (Academic,
Boston,1990)
Donaldson F.G., Ph.D. Thesis, University of Windsor (1972)
Forand J.L.M., Ph.D. Thesis, University of Windsor (1986b)
Herzberg G., “Molecular Spectra and Molecular Structure I. Spectra of Diatomic
Molecules” (van Nostrand Reinhold, New York,1950)
Supplement (To be published) (1995)

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Jan Li, also named Jian Li, was born in 1970 in Guangzhou, Guangdong, People's Republic of China. He graduated from Zhixin High School, Guangzhou, in 1988 and went on to Tsinghua University, Beijing, P.R.C. to study in engineering. After finished three years and half studies, he transferred to University of Windsor in January, 1992, where he got his Honour B.Sc. in Physics in 1994. He is currently a candidate for the Master's degree in Physics at University of Windsor and hopes to graduate in July, 1995.