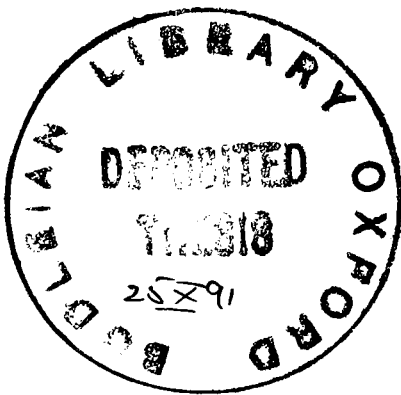


Studies of the Chemistry of Plasmas
used for Semiconductor Etching

A Thesis submitted for the Degree of
Doctor of Philosophy



By

Matthew John Toogood

Merton College, Oxford

Hilary Term, 1991

Abstract

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Optical diagnostic techniques have been developed and then used to investigate the chemistry of reactive species formed in CF_4 / O_2 rf parallel plate discharges, similar to those employed in semiconductor material processing.

Oxygen atoms were detected by two photon laser induced fluorescence (LIF), and the technique was found to have a number of experimental caveats owing mainly to the high laser intensities required. In particular, amplified spontaneous emission (ASE), was observed from laser excitation of oxygen, and was found to influence the spontaneous fluorescence signal and thus question the use of LIF for ground state concentration measurements in these systems. The spin orbit states of the $3p\ ^3\text{P}$ level were resolved for the first time, both in using high resolution excitation experiments and also as a consequence of detecting ASE. Spin orbit temperatures of less than 50° above ambient were observed. The absolute concentration of oxygen has been found to be $7.4 \pm 1.4 \times 10^{13} \text{ cm}^{-3}$ in a 50 mTorr, 100 W, 85% O_2 / CF_4 plasma.

Optical emission was also used to study fluorine atoms and to examine the use of the actinometered emission technique as a measure of ground state concentrations. The latter was investigated directly by comparison with LIF measurements of O and CF_2 , and in many cases shown to be a poor representation of the ground state concentration.

To investigate the chemical and physical processes in the plasma, time resolved methods are required and a new technique, time resolved actinometry, has been developed, tested by comparison with LIF measurements and then used to study the kinetics of fluorine atoms. Results have shown the importance of wall reaction rates on the magnitude of the fluorine atom concentrations, and the sensitivity of these concentrations to the nature of the surface, particularly in the presence of oxygen and silicon. Oxygen has also been shown to be removed predominantly at the surface but the influence of gas phase reactions with CF_x radicals is apparent in discharges containing low percentages of O_2 .

Studies on an afterglow type, electron cyclotron resonance reactor have been carried out as a comparison to the parallel plate system, and high excitation and dissociation levels have been observed from differences in the emission intensities and from measured values of the absolute CF and CF_2 concentrations.

The use of LIF as a diagnostic for CF has been investigated by probing the predissociation of the $\text{A}^2\Sigma^+$ state. Emission from the $\text{A}^2\Sigma^+ (\nu = 2)$ level has been seen for the first time, and a J independent predissociation mechanism, with a rate of $3 \times 10^9 \text{ s}^{-1}$ has been observed.

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To Brads
and all of my family

Contents

<u>Chapter One</u>	<u>Introduction</u>	
1.1	Introduction	1
1.2	Physical Processes	5
1.2.1	General Physics of the Plasma	5
1.2.2	Temperature and EEDF	8
1.2.3	α and γ Regimes	10
1.2.4	Excitation and Production Rates	11
1.3	Chemical Processes	13
1.3.1	Production Processes	14
1.3.2	Removal Processes	15
1.3.3	Models for CF_4 & CF_4 / O_2 Plasmas	17
1.4	Diagnostic Techniques	19
1.4.1	Surface Diagnostics	20
1.4.2	Diagnostics of Chemical Processes	21
1.4.3	Diagnostics of Physical Processes	30
	References	33
 <u>Chapter Two</u>	 <u>Experimental Apparatus</u>	
2.1	The Plasma Chamber	38
2.2	Laser System	41
2.3	Detection and Data Acquisition	43
2.3.1	Optical Emission	45
2.3.2	LIF and ASE	46
2.4	The Flow Cell Apparatus	49
	References	51
 <u>Chapter Three</u>	 <u>LIF Studies of Oxygen Atoms</u>	
3.1	Introduction	52
3.2	LIF of Oxygen Atoms	53
3.2.1	Theory of Two Photon LIF of Oxygen	56
3.2.2	Experimental Observations of Oxygen	58
3.3	Competing Processes	64
3.4	Amplified Spontaneous Emission	72
3.4.1	Dependence of ASE on Concentration	73
3.4.2	Effect of ASE on Fluorescence Yields	75
3.4.3	Polarization Effects	81
3.4.5	Other Observations	83
3.5	Absolute Oxygen Atom Concentration	85

3.5.1	Absolute Concentration measurements	86
3.5.2	Quenching of $3p^3P$ by O_2 and CF_4	89
	References	91
<u>Chapter Four</u>	<u>Spectroscopy of CF</u>	
4.1	A – X Transition of CF	93
4.2	Predissociation	96
4.2.1	General Theory	97
4.2.2	Experimental Investigation	101
4.2.3	Interpretation	104
4.3	Predissociation in CF	105
4.4	Experimental Observations of CF	108
4.4.1	LIF of the CF A($\nu = 2$) – X band	108
4.4.2	Measurement of the Rate of Predissociation	116
4.5	Conclusions	121
	References	123
<u>Chapter Five</u>	<u>Actinometered Optical Emission</u>	
5.1	Introduction	125
5.2	Theoretical Basis for Actinometry	126
5.3	CF_2 : LIF and Actinometered Emission	128
5.3.1	Steady State Studies	128
5.3.2	Time Dependent Studies	135
5.4	Oxygen Atom Actinometry	146
5.4.1	Steady State Measurements	148
5.4.2	Time Dependent Measurements	153
	References	161
<u>Chapter Six</u>	<u>Time Resolved Actinometry</u>	
6.1	Introduction	163
6.2	The Technique	165
6.3	Validation of the Technique : CF_2 Kinetics	167
6.4	Fluorine Atom Kinetics	169
	References	181
<u>Chapter Seven</u>	<u>Plasma Chemistry</u>	
7.1	Introduction	182
7.2	Chemistry of Fluorine	186
7.2.1	CF_4 Plasma	186
7.2.2	CF_4 / O_2 Plasmas	191

7.2.3	SF ₆ Plasmas	195
7.2.4	Fluorine in the Presence of Silicon	198
7.3	Chemistry of Oxygen	201
	References	212
<u>Chapter Eight</u>	<u>Afterglow Reactors</u>	
8.1	ECR Plasma Reactor	213
8.2	Experimental	214
8.3	Results	217
8.3.1	Optical Spectroscopy from the ECR Region	217
8.3.2	LIF Spectra of CF and CF ₂	220
8.3.3	The Parametric Study	224
8.4	Discussion	232
8.4.1	The ECR Region	237
8.4.2	The Downstream Region	237
8.4.3	Fluorine Atom Concentration	238
8.4.4	Excitation Rate	239
8.4.5	Conclusion	239
	References	240
Appendix One		
	Oxygen Atom Titration	241
Appendix Two		
	Reactions of Importance to Fluorine and Oxygen Atoms	243
Appendix Three		
	Data for Chapter Eight	245

Chapter One

Introduction

1.1 Introduction

A gas phase plasma is a state whose extensive universal abundance contrasts with the low level of its general perception and understanding. It constitutes much of interstellar space and is present in fluorescent lamps around the world. Plasma technology has been applied to a variety of industrial processes, including the generation of power by nuclear fusion and the processing of materials. Yet, in spite of this, there is a high degree of black art and empiricism associated with the application and interpretation of plasmas.

The physics of a plasma, a partially ionized gas, has been investigated for many years but much of the thrust has been on systems which are chemically inert or have limited chemistries, such as argon or hydrogen. This is partly a result of the high complexities of these systems, even without the complications of chemical processes. Discharges containing more complex molecular species have been used to prepare reactive species. This has enabled kinetic and spectroscopic studies to be carried out on the species, but for such systems, the mechanisms of production were not of primary interest.

The invention of the integrated circuit sparked off a vast technological effort, which now sees complex gas phase plasmas being used to produce the intricate sub – micron patterns required in todays semiconductor and electronics industry¹, and it is these plasmas which are the subject of this thesis. The chemical and physical processes taking place in the molecular plasmas are now areas of great investigation, particularly as the demands of the industry are constantly becoming more severe. This requires optimal performance from these so called dry technologies, which necessitates a thorough understanding, founded on a quantitative rather than empirical approach.

Conceptually, plasma based material processing is simple, and involves the generation of reactive species in a discharge, which either react with surface atoms

to release volatile products, (etching), or react and stick to the surface, (deposition). A number of attempts have been made to model these plasmas, but knowledge of the physics, chemistry, surface and material science of the system is necessary for a full comprehension, and much collaboration between disciplines is required. These plasmas generate a large number of different species; ions, atoms, radicals, electrons as well as the feedstock molecular species, and all in a variety of states. The parameter space associated with such a mixture and the interdependence of these parameters often makes the interpretation of experimental results difficult. As a consequence, much research has limited itself to investigating single processes by studying the process in isolation. Thus, gas phase rate constants of importance to fluorocarbon plasmas have been measured in flow cells, electron excitation cross sections have been obtained using electron beam techniques and surface reactions have been studied under high vacuum conditions. Although these measurements are useful, the data need to be related to real plasma systems, where all the interactions connected with these processes are present. As will be shown, the surface chemistry and reaction rates in fluorocarbon plasmas have a dramatic influence on the composition and hence performance of the plasma, but under typical operating conditions the surface is far from the clean single crystal environment used in many surface science experiments.

In view of this, a variety of experimental techniques have been developed to investigate directly the many types of plasma used. Unfortunately, many of these involve analysis of the plasma outside the operating conditions of processing plasmas or require the plasma to be distorted in some way. Thus, the major aim of the work for this thesis was to develop and adapt optically based diagnostics to produce techniques which are capable of in — situ, non — perturbative measurements of the species present inside a commercial plasma reactor.

To gain maximum benefit from such measurements, models of the system are required, but the system is very complex, with coupled interactions between electric fields, and charged and neutral species. No complete model has yet been developed and indeed, for a model to produce a worthwhile understanding of the relationships

between the various processes, there needs to be some simplification in the representation. This may lead to a number of models being applied to different aspects of the same overall system. Assumptions and simplifications will distort and put limitations on these models, but if these can be evaluated then a great deal of useful information can be extracted from the experimental data.

In this study, both simple limited, and more complex models were used to assist in the interpretation of the experimental data, which were obtained from laser induced fluorescence (LIF), and optical emission spectroscopy (OES), studies of fluorocarbon based plasmas, similar to those used in the industrial process of silicon etching. These plasmas, CF_4 and CF_4 / O_2 mixtures, are produced by applying a radio frequency (rf) electric field between two parallel plates. They generate atomic species such as fluorine and oxygen, and radical species such as CF and CF_2 , all of which have been detected and investigated in this work.

LIF is a diagnostic which, with careful experimental technique can provide direct measurement of the ground state concentration of a particular species, with spatial and temporal resolution. It is however restricted by the large number of species for which it is inappropriate. This may be a result of low fluorescence yields due to fast non – radiative relaxation processes, (as for CF_3) or technological limitations of available tunable laser sources, (as for F). By contrast OES is virtually universally applicable, but this lack of selectivity can also be a disadvantage, if the behaviour of a single species can not be extracted due to masking by emission from another. The plasma itself radiates over a wide range of wavelengths due to the electron excitation of species present. It is thus a ready source for emission studies and experimentally it is relatively simple to obtain optical emission signals, without the need of expensive and delicate equipment, such as lasers. It is because of this that optical emission spectroscopy has been extensively used in the study of processing plasmas.

The interpretation of such studies however, is not simple, because emission is produced by radiative decay from electronically excited states and thus the intensity of emission is related to the concentration of the excited state. In typical processing

plasmas, it is the ground state species which have $10^4 - 10^6$ times higher concentrations, that are of importance and interest. In an attempt to utilize this universal technique, Coburn and Chen² developed the technique of actinometry, which relates the emission intensity to the ground state concentration by adding a small amount of inert gas, called the actinometer, to the processing mixture. Emission from this chemically inert species is used as a measure of the electron excitation in the plasma, and thus by normalizing the emission from the species of interest to the actinometer signal, it is hoped that information on the relative ground state concentration of the species of interest can be obtained. For actinometry to be suitable, a number of criteria need to be met, and much of the work in this thesis has involved investigation into the applicability of these criteria. This has entailed direct comparisons between actinometered optical emission studies, which produce corrected measurements of the excited state, and laser induced fluorescence, which directly measures the ground state, to find regions where actinometry is valid.

The fluorine atom is one species for which actinometry appears to hold, and the important role it plays in the etching of silicon combined with the absence of techniques capable of measuring the ground state, led to the development of a new experimental method which we have called time resolved actinometry, (TRA). This technique, which is based only on optical emission, was developed so that measurements of the temporal variation of concentration could be taken, which allows direct investigation into the fundamental plasma processes. The technique was tested by comparison with time resolved LIF studies.

Measured decay rates, by LIF and TRA, have been used to aid interpretation of the processes taking place inside a plasma, but the steady state concentrations and particularly the absolute values of these, can also produce valuable information and can be used to test the available models. Accurate absolute concentrations are hard to obtain from optical techniques without lengthy calculations using a large number of assumptions and approximations. LIF can be a quantitative technique, but even so a comparative method of measurement assists in reducing potential

errors. In this study, the absolute concentration of atomic oxygen was measured, by comparing the signal from a CF_4 / O_2 plasma with that from a known concentration of oxygen in an optically identical flow cell.

After the development of suitable diagnostics and their use to obtain experimental data, an attempt to interpret and understand the key physical and chemical processes taking place can be made. It should be noted that these diagnostics are not limited to the systems on which they were developed, but can be used on a range of plasma systems, as shown in this thesis.

The plasma can also be used as a method of generating reactive species, on which particular studies can be carried out. The predissociation of the CF radical and amplified spontaneous emission from laser excited oxygen atoms are two examples of such studies which were investigated in this work.

1.2 Physical Processes

1.2.1 General Physics and Architecture of the Plasma

A plasma is a partially ionized gas, containing electrons and ions (positive and negative) as well as radicals, atoms and molecular species. For the plasmas considered in this study an external electric field is applied to an electrode, which accelerates the charged particles and so acts as an energy source to the plasma. This source is necessary to sustain the plasma as wall and gas phase recombinations remove species from it. The degree of ionization inside typical processing plasmas is one part in 10^5 , (ie. 10^{10} charged pairs cm^{-3} for a 50 mTorr plasma), which is several orders of magnitude lower than the concentrations of neutrals, both molecules and radicals.

The higher mobility of the electrons compared to ions means that an isolated surface in the plasma will develop a negative charge and hence potential, which increases until the electron and ion fluxes to the surface balance. This potential is known as the floating potential, V_f , and is negative with respect to the space or plasma potential, V_s , which has the effect of containing all but the highest energy electrons and sustaining the plasma. The small fraction of electrons with energies

greater than $e.V_s$ can escape from the plasma region, and they become absorbed on the walls, but diffusion and electric fields cause this reduction in electron density to be localized to the sheath region, with quasi-neutrality being maintained in the bulk of the plasma. Thus, the sheath is a positive space charge region (ion density > electron density), but the density of ions is also lower than in the bulk, owing to acceleration of the ions by the sheath potential. Electron impact generation of excited state species which decay by photoemission also decreases in this region, hence the sheath is also known as the dark space.

The electric fields present in the plasma are largely confined to the sheath, with most of the applied rf voltage being dropped over the small sheath length. The thermal motion of the electrons allow fields of the order of $(k.T_e/e.L)$ to be present in the bulk of the plasma, (where T_e is the electron temperature and L is the dimension of the chamber), and such fields will cause acceleration of ions towards the sheath-plasma boundary, as the sheath does not totally shield potentials in a plasma. The variation of voltage across a discharge is shown schematically in figure 1.1 and illustrates these features. The large drop in V_{rf} causes much energy to be dissipated in the sheath region, by accelerating ions towards the electrode and electrons out of the sheath.

With a capacitively coupled rf power supply, the variation in electron and ion mass produces a dc offset. Since no net dc current must flow, to counteract the faster response of the electron to the field, a negative bias is formed relative to the plasma. The size of this d.c. bias is dependent on the geometry of the system and the electrical circuit. Current density of the positive ions can be thought of as uniform at both electrodes and so the smaller electrode acquires a larger accelerating voltage over the sheath^{4,5}. In inductively coupled plasma sources, there are no electrodes and so no bias is formed and as will be seen, this can be a useful feature.

The rate of diffusion depends on diffusion coefficients and spatial concentration gradients. In a plasma, the higher mobility of the electrons might be expected to result in rapid electron diffusion compared to the ion diffusion rate. However, any movement of electrons causing a depletion in electron density,

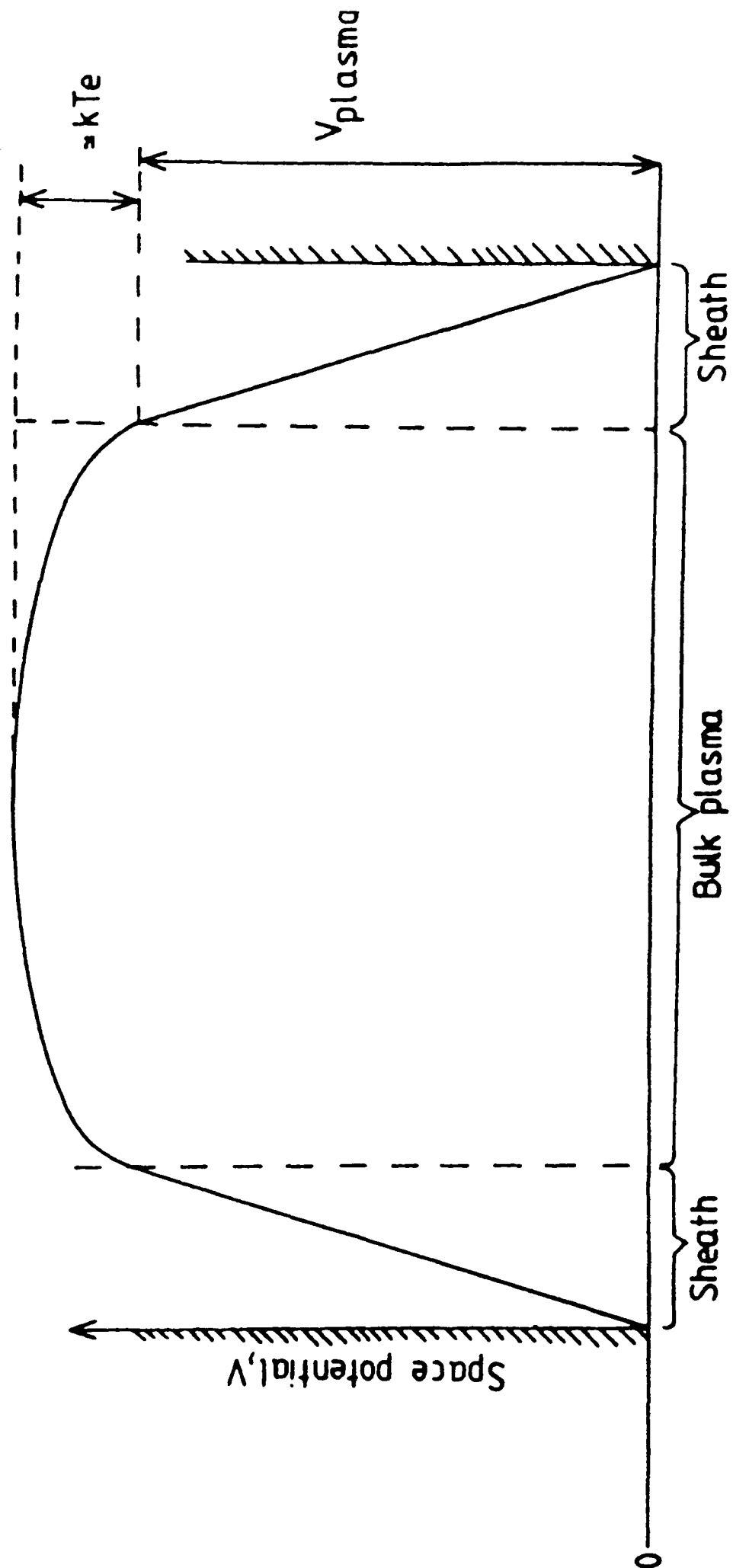


Figure 1.1 Schematic representation of the variation of potential between two electrodes in a parallel plate discharge, (effects of externally applied fields not shown in the figure).

produces a potential which has the effect of retarding the electrons and accelerating the ions until equal diffusion rates are obtained. This behaviour, known as ambipolar diffusion, will apply to all motion in the plasma region and becomes particularly apparent in the plasma afterglow (ie. in the absence of applied fields, for example after plasma extinction), where diffusion limited loss rates of ions and electrons are seen to be the same⁶.

1.2.2 Temperatures and the Electron Energy Distribution Function

The electrons, being much lighter than any ions present, respond more quickly to the field and pick up more energy. Their low relative mass also results in poor elastic energy transfer to the ions, molecules and radicals, while the latter tend to share energy more efficiently. Thus, electrons have mean energies of 2 – 8 eV, (equivalent to temperatures of $2.4 - 9.6 \times 10^4$ K), whereas ions are at translational temperatures just above ambient, (300 – 400 K), except near the sheaths where large electric fields accelerate them. Energy is also unequally distributed between the degrees of freedom of molecular species, such that the vibrational temperature is higher than the rotational and translational values, which are in thermal equilibrium with the walls of the reactor. This is a result of both the excitation and quenching rates for the vibrational and rotational energy levels, in particular the relatively poor vibrational – translational, (V – T), energy transfer rates and low cross sections for electron impact excitation of rotational levels.

An electron temperature can strictly only be assigned if a Maxwell – Boltzmann distribution of electron energies is present, but a mean energy, $\langle \epsilon \rangle$, can always be found. An important factor for T_e , or $\langle \epsilon \rangle$, is the field divided by the pressure, $\frac{E}{P}$. In simple terms, the field accelerates the electrons and so tends to increase $\langle \epsilon \rangle$, whereas high pressure means high collisional frequencies and loss of energy to the colder atomic and molecular species, which leads to a decrease in $\langle \epsilon \rangle$, thus high values of $\frac{E}{P}$ will tend to give high $\langle \epsilon \rangle$. It should be noted that an increase in the power delivered to the plasma does not necessarily cause an increase in $\langle \epsilon \rangle$, since it can result in a rise in rf current as well as rf voltage. Generally, an

increase in power leads to an observed increase in plasma density, and hence in rf current, therefore $\langle \epsilon \rangle$ can be found to be virtually independent of rf power⁶.

The precise electron energy distribution function, (EEDF), found in a plasma is clearly dependent on the plasma parameters, such as power and pressure, but it is also influenced by the gas composition. Different gases with specific cross sections for excitation, ionization, electron attachment and elastic scattering, result in differing EEDF⁷. Furthermore, the energy distribution and electron density can show significant spatial and temporal variations, and the electron velocity distribution can be anisotropic⁸. These latter variations are often summed to produce an average energy distribution, $f(\epsilon)$ and a mean electron density, n_e . This analysis can be misleading when localized regions of high electron energy result in significant spatial and temporal variation in the excitation and production of species.

The full description of $n_e(r,t)$ and $f(\epsilon,r,t)$ can be calculated by determining the response of electrons and ions to the spatially and temporally varying electric fields, which in turn are influenced by the motion of the ions and electrons. The density and momentum distributions can be obtained by an iterative solution to the partial differential equation known as the Boltzmann equation^{9,10}. This contains a term relating to the specific cross sections for electron interactions with all the molecular species, and is thus unique to the gas mixture and conditions studied. Some attempts have been made to solve the Boltzmann equation, although a number of simplifications are often required^{11,12,13}. For example, Kushner^{8,11} solved the Boltzmann equation for an rf plasma in CF_4 / O_2 mixtures, but he obtained values for the electron energy and density which have been shown to be higher than experimental results.

Monte – Carlo trajectory calculations have also been performed to simulate rf discharges^{14,15}, where single electron trajectories are averaged to obtain macroscopic characteristics. Kushner *et al.*¹⁴ has applied this to a silane plasma and presented a temporally averaged, but spatially resolved electron energy distribution. The prediction was that a bimodal distribution was present, with the

bulk of the electrons associated with a low mean energy, and a high energy tail localized near the plasma / sheath boundary. This tail was shown to be responsible for much of the excitation, ionization and dissociation present. Other models have predicted a similar spatial behaviour^{3,16} and these theoretical calculations have been supported by experimental observations, spatially resolved optical emission^{17,18} and Langmuir probe studies⁸, which have suggested the presence of enhanced electron density in this region.

1.2.3 α and γ Regimes

The high energy tail of the distribution is formed from secondary electrons produced by ion bombardment of the electrode surfaces, and from acceleration of the bulk electrons by the oscillating plasma / sheath boundary, the so called wave riding mechanism¹⁶. The relative contributions of these excitation mechanisms to the overall energy distribution and more explicitly to the mechanism for sustaining the plasma, has been an area of some debate. Some models suggested that secondary electrons were not required to produce a maintainable plasma¹⁹, whilst others involved detailed calculations of ion trajectories and energies^{20,21} and relied on high secondary energy electrons to cause the necessary ionization³. There is also experimental evidence for the presence of both sources of high energy electrons^{17,22}.

The secondary electron yields are dependent on the nature of the surface and the ions, as well as the impact energy, and so it is likely that the relative importance of the mechanisms may depend on the plasma conditions. Recent theoretical modelling has illustrated that there are two regimes for generating a plasma^{23,24,25} and that it is possible to go through a transition from one regime to the other¹⁶. This was in fact first established in 1958 by Levitskii²⁶.

Low pressures and high rf powers result in high sheath voltages, which cause many electrons to be emitted from the electrode and accelerated by the sheath voltage into the plasma, where they undergo ionizing collisions. This is termed the "secondary electron regime" or the γ regime. The other regime, characterized by low rf power and low ion bombardment of the electrode, is sustained due to power

deposition to the bulk electrons by sheath heating. This is caused by an oscillating plasma / sheath boundary and the regime is known as the "wave riding" or α regime.

The experimental characteristics of the regimes have been shown to be different. The variation of plasma density with rf voltage rises more rapidly in the γ regime, and a more significant amount of excitation and ionization takes place within the bulk of the plasma for this regime²². The mean electron energy has been shown experimentally to decrease on going from the α to the γ regime, as does the sheath length²⁴. Power dispersion in the plasma has been shown to be predominantly due to electrons for the wave riding regime and to ions for the secondary electron regime^{16,27}, although it was also noted that 50 % of the power from the generator could be lost in the rf matching unit. The phase of the rf cycle during which excitation is most intense has also been used to demonstrate the differences¹⁷.

The fields present in the bulk of the plasma can sometimes be sufficient to produce electrons with energies above the threshold of excitation processes, particular where negative ions and fast diffusional losses are present¹⁶. This mechanism is common in dc discharges.

1.2.4 Excitation and Production Rates

It can be seen that a complete model of the electron dynamics in the plasma is very complex and requires a great deal of fundamental physical data. Thus for molecular plasmas, where the plasma chemistry is of particular interest, the EEDF is often approximated to a functional form. The Maxwell – Boltzmann distribution is sometimes used, but the Druyvesteyn distribution²⁸, with its depleted high energy tail due to inelastic collisions, is generally considered to be more appropriate for molecular plasmas.

Maxwellian distribution

$$f(\epsilon).d\epsilon = \left[\frac{4\epsilon}{\pi \cdot (kT_e)^3} \right]^{\frac{1}{2}} \cdot \exp(-\epsilon/kT_e).d\epsilon \quad 1.1$$

Druyvesteyn distribution

$$\begin{aligned}
 f(\epsilon).d\epsilon &= \frac{2}{\Gamma(3/4)} \cdot \left[\frac{\Gamma(5/4)}{\Gamma(3/4) \cdot \langle \epsilon \rangle} \right] \cdot (\epsilon)^{\frac{1}{2}} \cdot \exp \left(- \left[\frac{\Gamma(5/4)}{\Gamma(3/4) \cdot \langle \epsilon \rangle} \right] \cdot \epsilon^2 \right) \\
 &= 1.2072 \cdot \frac{(\epsilon)^{\frac{1}{2}}}{\langle \epsilon \rangle^{1.5}} \cdot \exp(-0.547[\epsilon/\langle \epsilon \rangle]^2) \cdot d\epsilon
 \end{aligned} \tag{1.2}$$

These functional forms can be taken together with the cross sections for various electron processes to calculate the rates of such phenomena. Thus, the rate of production is given by

$$\frac{dP}{dt} = n_e \cdot N \cdot \int_0^\infty \left(\frac{2\epsilon}{m_e} \right)^{\frac{1}{2}} \cdot f(\epsilon) \cdot \sigma(\epsilon) \cdot d\epsilon \tag{1.3}$$

where N is the precursor density, ϵ the electron energy, m the electron mass, $f(\epsilon)$ the normalized EEDF and $\sigma(\epsilon)$ the energy dependent cross section. Strictly, the rate illustrates spatial and temporal variation but for simplicity, it is often calculated using the spatial and temporal averaged equation shown here.

Absolute measurements of the cross sections are hard to obtain, but a number of excitation and ionization processes associated with CF_4 ^{29,30,31} and O_2 ³² have been either measured or calculated. This enables the electron impact production and excitation rates to be estimated and these are used in chapter 7. The general form of these cross sections is that they have a threshold energy above which the cross section rises to a maximum and then slowly falls, (see figure 5.15). It has been shown that, because the typical mean electron energies obtained in these plasmas are lower than most threshold energies, it is the position of the threshold and not the detailed high energy form, which affects the relative process rates.³³ The approximation and averaging of the EEDF combined with the poor overlap of electron energy and cross section, mean that these calculations can only be considered as rough approximations. In – situ measurements of electric fields and ion energies by LIF³⁴ and other optical diagnostics³⁵, have increased the understanding and helped improve the modelling of the physics of the plasmas, but for molecular gases much work is still required.

1.3 Chemical Processes

The chemical processes of interest in a plasma are those which involve the production or loss of neutral species, in contrast with details of the electron dynamics and electric fields, which characterize the physical processes. When the production and loss processes have rates which are constant with time, the concentration of the species in the plasma will also tend towards a constant, steady state level. Although the electron impact production rate may vary during the rf cycle, its effect is time averaged due to the relatively slow rates of removal. It can be shown that the ratio of the rates can lead to a value for the steady state concentration. Thus,

$$\begin{aligned}\frac{d[P]}{dt} &= k_p - k_l \cdot [P] \\ &= 0 \text{ for steady state conditions}\end{aligned}\tag{1.4}$$

and
$$[P]_{ss} = \frac{k_p}{k_l}$$

where k_l is the first order decay constant, k_p is the production rate and $[P]$ is the concentration of the species of interest.

Many studies of the variation of steady state concentration with plasma parameter have been carried out using a variety of diagnostic techniques^{36,37,38}, and such data can produce useful information on changes in the ratio of the rates. However, to obtain a better understanding of the variation of plasma processes with plasma parameters, direct measurements of the loss rates have been made. This has been achieved by extinguishing the plasma, which has the effect of setting the production term to zero, and then following the concentration as a function of time after extinction. Thus, from equation 1.4, setting $k_p = 0$

$$\frac{d[P]}{dt} = -k_l \cdot [P]$$

and
$$[P] = [P]_{ss} \cdot \exp(-k_l \cdot t)$$

Ignition of the plasma, where the concentration starts at zero and rises up to the steady state concentration, has also been studied. Since the rise time associated with the production rate is generally much faster than the removal rate, it can be shown that the rate of rise of the concentration can also be related to the removal rate.

$$[P] = [P]_{ss} \cdot (1 - \exp(-k_l \cdot t))\tag{1.5}$$

By comparing the rates obtained by these two techniques, it is possible to examine the effect of the rf fields, and perhaps more significantly the influence of ion bombardment of the surfaces, on the removal rate. The influence of ions may also be responsible for changes in the removal after the plasma is extinguished. Gas phase reaction rates may also vary with time as the concentration of reacting species is depleted. In circumstances such as these, the removal rate during steady state plasma conditions can be taken as the initial decay rate observed. This limiting value is a reasonable approximation to the steady state removal rate, if the rate of change of the removal rate is smaller than the removal rate itself. For work in this thesis, time resolved laser induced fluorescence and time resolved actinometry have been employed to perform this plasma pulsing technique, and have produced removal rates for CF_2 , CF , oxygen and fluorine atoms, over a range of plasma conditions.

Sawin has developed a different modulation technique to investigate the kinetics of reactive species in the plasma. Instead of completely extinguishing the plasma, he applies a small modulation to the rf power and monitors LIF and emission signals from the species of interest. From this he can obtain first order loss rates for the species detected³⁹.

It should be noted that the production rate, loss rate and hence steady state concentration, may vary with position in the plasma and that a more complete understanding of the plasma processes is obtained when measurements are spatially resolved. At the pressures used, rapid diffusion rates tend to homogenize concentration and loss rates, so that only a limited investigation is required. This was found to be the case for the species monitored in this study.

1.3.1. Production Processes

Under the conditions used in processing plasmas, the major production pathway of reactive radical species is by electron impact dissociation, (or dissociative attachment), of the feedstock molecules. The low concentration of transient species in such weakly ionized plasmas, makes them a relatively

unimportant production source. The radicals may also be created as the product of gas phase and gas – surface reactions, but for most of the species of interest, the reactions are slow. A possible exception to this is the production of fluorine atoms by the reaction of oxygen atoms with CF_x radicals, although as will be seen, changes in the removal rate of fluorine have a more significant effect on its steady state concentration.



1.3.2. Removal Processes

There are several possible mechanisms for the removal of neutrals in a plasma environment, such as gas phase reaction, gas – surface reaction and, in the absence of these, loss via the pumping system, pump out. The gas phase reactions of interest can be divided into bimolecular and recombination reactions as illustrated by equations 1.9 and 1.10.



Gas Phase Reactions

Bimolecular reaction rates are generally dependent only on the concentration of the two reactant concentrations and are independent of the overall pressure. They are often dependent on temperature and such variations need to be allowed for in any kinetic models of a plasma.

Recombination reactions require that the adduct, AB^* , is collisionally stabilized by a third body, M , to ensure that the product, AB , is formed before the

adduct falls apart, back to the reactants. Thus, at low pressure, as well as depending on the concentration of the reagents, the rate is also dependent on the bath gas pressure. At very high pressure the stabilization becomes very rapid and the rate limiting step becomes the formation of the adduct, and so the rate is independent of pressure. Much investigation has been carried out into this sort of reaction, both in the forward direction as a three body recombination, and in the reverse as unimolecular decay⁴⁰. The rate of reaction at any given pressure, not just in the high or low pressure limits, can be calculated⁴¹.

The recombination reactions of interest in a CF₄ plasma are

	k @50 mTorr	k @500 mTorr	
CF + F → CF ₂	5.6 x 10 ⁻¹⁶	5.0 x 10 ⁻¹⁵	1.11
CF ₂ + F → CF ₃	5.0 x 10 ⁻¹⁴	4.2 x 10 ⁻¹³	1.12
CF ₃ + F → CF ₄	5.2 x 10 ⁻¹²	1.3 x 10 ⁻¹¹	1.13

with the rates calculated for 50 and 500 mTorr total pressure, (k(cm³molecule⁻¹s⁻¹)).

As can be seen the fastest rate is that of reaction 1.13, and this process also shows least variation with pressure. The explanation is that the energy which needs to be removed to stabilize the initially formed adduct, can be accommodated in the degrees of freedom of the complex. For reaction 1.13, the adduct, CF₄, has the highest number of degrees of vibrational freedom and is thus the most stable and long lived complex. Therefore, at a given pressure it has the highest chance of being stabilized to products. The smaller variation with pressure is indicative of approaching the high pressure limit, where rate is independent of pressure.

Overall, gas phase reactions under the low pressure conditions used in these discharges do not generally constitute the major loss processes for the species of interest. Possible exceptions to this are the recombination reaction of fluorine and CF₃ and the bimolecular reactions of oxygen atoms with CF_x radicals.

Gas – Surface Reactions

Gas – surface reactions have been shown in previous studies^{39,42} and work for this thesis to be the dominant removal process for many of the reactive species in these low pressure plasmas. The rate is usually characterized by a sticking coefficient, α ($\alpha \leq 1$)^{42,43}, which is the ratio of the number of particles which stick to a surface divided by the flux to the surface. Such coefficients have been measured for a variety of species on a variety of surfaces⁴⁴, but these tend to have been carried out under high vacuum conditions and on pure clean crystalline surfaces. There have been some recent attempts to measure the sticking coefficient^{39,42,43,45} on more realistic surfaces and work in this thesis has produced the values for fluorine and oxygen atoms, actually inside the plasma reactor. This was done by measuring the loss rates under conditions where wall reactions can be taken as the major removal mechanism.

At low pressure, the high rate of diffusion ensures that a uniform spatial concentration profile is maintained and that the removal process may be considered as homogeneous. However, at high pressure slow diffusion can allow spatial gradients to be generated, which make the effective removal rates non – uniform, and can also limit the rate of loss measured, the so called diffusion limited regime. This interaction between diffusion and wall removal has been modelled previously⁴⁶ and results from it are used in later chapters.

It should be noted that the sticking probability, hence wall reaction rate, is very dependent on the precise nature of the surface. Work in this thesis has shown that small concentrations of certain species can dramatically affect the measured loss rate, and the level of ion bombardment on the surface also appears to have an influence.

1.3.3. Models for CF₄ and CF₄ / O₂ Plasmas

Having collected experimental data on both steady state and time resolved concentrations, and determined the most probable removal processes for a given species, it is of interest to examine how the particular species influences the plasma

as a whole. This can be done by analyzing each species separately, but is best achieved using a model. For the model to produce useful information it does not need to be totally rigorous or all embracing, it merely needs to consider the particular interactions on which the concentration of the key species depend⁴⁷.

There have been a number of chemistry based models developed to explain the observations from molecular plasmas^{11,12,47,48,49}. Some of these were compiled before several of the key gas phase and electron impact processes had been properly investigated^{11,12,48}, (in particular recombinations rates for CF₂ and CF₃ with fluorine atoms⁵⁰). Plumb and Ryan⁴⁷ were the first to derive a model with a comprehensive reaction set, and they compared the calculated results with mass spectrometric results by Smolinsky and Flamm⁵¹. Their results suggested the presence of a primary dissociation channel leading to direct production of CF₂ from CF₄, which has a significant effect on the fluorine atom concentration, and were able to obtain an empirical branching ratio between this channel and the one leading to CF₃.



Their major removal mechanism was by three body recombination, and they assumed the walls to be passivated so that gas – surface reactions were negligible. Their model incorporated reactions of oxygen atoms, the most significant of which are those with CF_x radicals. These have fairly high rate constants and were shown to influence the plasma composition.

The model was based on experimental conditions of high power density, (3.5 Wcm⁻³), and high pressure, (500 mTorr). These conditions contrast those in this laboratory, where much lower power densities, (0.1 Wcm⁻³), and generally lower pressures, (50 – 500 mTorr) are used. The corresponding reduction in the overall radical concentration makes gas phase reactions less important, particularly the recombination reactions, whose rates decrease at low pressure. A reduction in

pressure also increases the diffusion rates and so can increase the significance of surface reactions.

A model has been developed in this laboratory⁵² relating to experimental results obtained on the plasma chamber described in chapter 2. The model is based on the Plumb and Ryan reaction set, but includes experimentally obtained wall sticking coefficients for CF, CF₂, F and O, for which gas – surface reactions play an important role. The model also contains reactions of negative ions which are thought to have a small but significant effect owing to their high concentrations⁵³, and it contains a further primary dissociation channel to CF, by direct electron impact on CF₄, again a consequence of experimental observation⁴².



The major weaknesses in the model concern the production terms, and in particular the variation of production rates and branching ratios as a function of plasma parameter. Attempts have been made to measure the electron density and temperature using Langmuir probe techniques, but they have not proved to be successful and so the model has to be treated with a degree of caution. Nevertheless, its development has assisted in the interpretation of the experimental results and suggested areas for further investigation, such as the removal rates of F⁻ ions. However, the experimental data has had a complimentary, if not more significant, impact on the design of the model.

1.4 Diagnostic Techniques

There is now a vast array of different experimental techniques used to investigate processing plasmas. Some of these have been developed specifically for this application whilst others are borrowed from different technologies. Many of the techniques overlap in terms of the information obtained, but this complimentary nature helps overcome the weaknesses present in all diagnostics.

Diagnostics are employed in industry to obtain direct pragmatic and

empirical observations. Optical emission is widely used as a means of detecting the end point of processing runs, by monitoring the signal from a certain species as a function of time, (for example, measuring fluorine atoms during the etching of silicon)⁵⁴. The major direction of diagnostic research however is towards the interpretation of mechanisms in the plasma, and this has resulted in the development of in – situ techniques capable of measuring reactive species, rather than analyzing stable products and trying to extrapolate. The advancement in equipment technology, such as lasers, has also widened the options available.

For the purpose of this thesis, diagnostics have been divided into three general areas of interrogation; surfaces, chemical processes and species, and physical processes and species. In line with the techniques used in this study, the diagnostics for the chemical processes are discussed in most detail.

1.4.1. Surface Diagnostics

Material processing involves the modification of a surface, either by addition or removal of some chemical species, and thus much of the diagnostic work has concentrated on analysis of these surfaces. Initially, this was confined to scanning electron microscopy and the use of surface profilers, which measured etch and deposition rates, but now techniques such as X – Ray photoelectron spectroscopy, (XPS)^{55,56}, Auger electron spectroscopy, (AES)⁵⁷, and infra red reflection spectroscopy⁵⁵ are used. They are generally operated in an ex – situ manner, owing to the technical complications and costs of incorporating these surface techniques into a plasma chamber. In spite of this, much information has been obtained on the deposition of polymers, and on the thickness and chemical composition of the layers. Some in – situ experiments have been carried out, such as the monitoring of molecular beam epitaxy and ion implantation by in – situ XPS measurements⁵⁸. The temporal evolution of a surface has been observed using ellipsometry techniques⁵⁹ and photo emission optogalvanic spectroscopy^{60,61}, since they are sensitive to any chemical changes in the surface layer.

Study of silicon surfaces during etching by fluorine atoms has been done by

McFeely *et al.*⁶² using XPS, and they were able to show the depth of perturbation of the silicon surface caused by the etching process. They found SiF_3 to be present at depths of ten monolayers from the surface, and so prompted a re-examination of some of the etching models. Similar techniques have been employed in CF_4 / O_2 systems⁵⁶, and have shown that a $\text{Si} - \text{O}_x - \text{F}_y$ layer, which forms on top of the bulk silicon, has an important effect on the etch rate of silicon.

1.4.2 Diagnostics of Chemical Processes

This section describes experimental techniques that have been used to study the concentrations and processes associated with ions and radicals. Many of these are optically based, because of the non — intrusive and state selective nature of such techniques, although mass spectroscopy has also been fairly widely implemented. The application of optical diagnostics to plasma research has been reviewed extensively^{63,64,65}.

Optical Emission

Most of the early optical diagnostics involved spectral analysis of emission from electronically excited plasma species, and the ease of operation and universality of the technique, continues its widespread use today, particularly in industrial applications. The method is non — perturbative and is carried out in — situ in real time. Typically, the emission is time averaged and spectrally resolved by a monochromator.

The first emission spectra recorded from a CF_4 / O_2 plasma was by Harshbarger *et al.*⁶⁶ who were able to assign, and hence identify, a number of different species in the plasma. The first attempts to obtain information on concentrations involved comparing the emission signal from fluorine atoms with a titration technique using Cl_2 ³⁷. It was found that as a function of the percentage of O_2 added to CF_4 , the peak in the fluorine atom emission did not correlate with the maximum in the silicon etch rate measured. One cause of this observation is in fact the major drawback in the implementation of optical emission as a diagnostic for

plasma systems, which is that the optical emission signal is proportional to the concentration of the excited state, and not ground state, species. As electron impact excitation is usually the mechanism for production of the excited state, any variation in the electron density or energy distribution, will influence the emission observed. Actinometry, developed by Coburn and Chen², can be used in an attempt to relate the emission intensity to the ground state concentration, by adding a small amount of inert gas, called the actinometer, to the processing gas mix. In the discharge, the emission from this actinometer is used as a measure of the electron excitation in the plasma, and thus normalization of the emission from the species of interest to the actinometer emission, yields information on the relative ground state concentration of the species of interest.

For actinometry to work, the excited states of both the species of interest and the actinometer should be formed by electron impact of the ground state and a constant fraction of the excited state must decay radiatively, as the process conditions are changed. Furthermore, if the electron energy distribution function changes with an experimental parameter, the electron impact excitation cross section of the inert gas needs to be similar to that of the species of interest, or at least have a similar excitation threshold³³ (eg. Ar, ($E_{th} = 13.48\text{eV}$), for F, ($E_{th} = 14.75\text{eV}$), detection). D'Agostino *et al.*⁶⁷ have extended this technique by using more than one actinometer, in an attempt to widen the range of excitation thresholds covered. It should be noted however that even if the criteria for actinometry are not obeyed, it may be possible to use actinometry over a limited parametric space⁶⁸.

Actinometry is used widely but has only been validated in a few cases by simultaneous observation of the ground state. Ibbotson *et al.*⁶⁹ compared actinometered optical emission (AOE) to absorption in a Br₂ plasma and demonstrated a good correlation, and a similar method was used on Cl atoms by Richards *et al.*⁷⁰, who showed that for a CF₃Cl plasma, AOE gives an accurate representation of the variation in the ground state concentration of atomic Cl. However, in a Cl₂ plasma large discrepancies were seen, and as previously

proposed⁷¹, following a study of the Doppler line widths of atomic emission lines, these were explained by the production of excited state Cl by electron impact dissociation of Cl₂.

Production pathways to the emitting state, independent of the ground state, have also been used to explain differences between AOE and LIF measurements for both CCl and oxygen atoms^{36,72}. Using two photon LIF of oxygen atoms and AOE, Selwyn *et al.*³⁶ showed that in O₂ / CF₄ plasmas the excited state which produces the 777.4 nm oxygen line is formed predominantly by a dissociative excitation mechanism and so does not follow the ground state concentration of oxygen atoms. However, the 844.6 nm line was shown to follow trends in the ground state qualitatively, though a dissociative excitation mechanism was also present. The validity of oxygen atom actinometry has also been examined using absorption⁷³ and electron paramagnetic spectroscopy⁷⁴ techniques. They conclude that low mean electron energies and high relative oxygen atom concentrations improve the correlation between the actinometered signal and the ground state concentration.

Application of the actinometry technique to CF₂ emission is complicated by the lack of an actinometer with a suitable threshold for excitation, ($E_{th}(\text{CF}_2) = 4.7 \text{ eV}$). However, argon, and in some cases more than one actinometer, have been used to correct the CF₂ emission. The validity of actinometry for CF₂ has been examined in this laboratory by comparison with LIF measurements⁶⁸. The results and conclusions are given in chapter 5 of this thesis and show that there are limited regions where actinometry of CF₂ can be used but great care is required. A similar technique has been employed over a limited range in CF₄ / O₂ plasmas⁷⁵.

Downstream titration techniques have been used to measure ground state F atom concentrations and have generally shown good agreement with AOE⁷⁶, but this method suffers from the disadvantage that it does not measure the ground state concentration at the same position as the emission. It has been shown however that fluorine atom emission can result from direct excitation of CF₄^{77,78} and from reactions of CF₄ with metastable helium atoms in CF₄ / He discharges⁷⁹.

As well as steady state information, optical emission has been used to study

time dependent behaviour of the plasma species. Such studies range from the application of optical emission to end point detection, with a time scale of tens of seconds, to following the variation in excitation as a function of phase of the r.f. cycle where the time scale is tens of nanoseconds. The latter has been carried out in nitrogen⁸⁰, oxygen⁸¹ and silane⁸² plasmas with 13.56 MHz applied r.f. power and in a chlorine based plasma over a range of frequencies¹⁷. Similar time scales have been probed using time resolved LIF and a comparison with ground state concentration has been made. Gottscho *et al.*⁸³ showed that the N_2^+ emission was a poor representation of the instantaneous ground state concentration, as measured by LIF in N_2 / Cl_2 low frequency plasmas.

In work for this thesis, the decay of the CF_2 radical following plasma extinction was monitored using the novel time resolved actinometry technique, and this was compared with time resolved LIF to validate the technique⁶⁸. The time resolved method was then extended to F atom decay (where LIF detection is not possible), to find estimates of the kinetics of removal of this important species on the surfaces in the plasma reactor. This technique is also being developed by Bouchoule *et al.* for studies on the kinetics of F atoms in F_2 plasmas⁸⁴.

Spatially resolved optical emission has also been achieved using both conventional optics and fibres. These have shown the influence of the spatial variation of electron impact excitation processes^{17,22,85} on the emission profile. Some spatial resolution of optical emission was carried out for this thesis.

Further information can be obtained from optical emission by careful study of the Doppler line widths. This can give information on the translational energies, and hence possibly the production pathways of the species⁸⁶. Rotational and vibrational temperatures can also be obtained from optical emission studies^{87,88} and attempts at measuring the EEDF have also been made, (see section 1.4.3).

Optical emission is a very versatile qualitative technique, which is employed extensively, but caution is required if it is to be used to infer mechanisms of the plasma processes.

Laser Induced Fluorescence

Laser induced fluorescence detects species in their ground (or metastable) state. The technique can attain high spectral, temporal and spatial resolution which allows a comprehensive examination of a particular species to be performed. The spectral resolution enables single spectral features to be probed and thus internal state distributions can be determined. The temporal and spatial characteristics of the technique make it very suitable for studying the removal processes in a plasma. The major restriction of the technique is the range of species on which it can be applied. For polyatomic species, the fluorescence quantum yield is often low and the excited states accessible from the ground state may be predissociated, (see chapter 4). Atomic species generally have high fluorescence yields but for the atoms of interest, generally the light atoms, the wavelength required to excite the first resonance transition is usually too short for existing tunable lasers. Multiphoton techniques have been employed to overcome this problem and have successfully detected a number of atoms; S⁸⁹, O⁹⁰, Cl⁹¹, N⁹⁰, H⁹². However, as explained in chapter 3 for the two photon LIF of oxygen atoms, this technique does have some complications.

CF₂ has been detected in plasmas by several groups^{42,43,75,93,94,95}. Generally, these studies have involved a parametric survey of steady state concentration, but there have been some measurements of spatial distributions⁴³ and kinetic loss rates⁹⁶. Previous studies in this laboratory have extended this to temporal and spatial variation, and absolute concentration of the CF₂ radical. For CF, there have been fewer investigations. The first detected CF was generated by a microwave plasma⁹⁷, but the signal was not clearly resolved from that of CF₂. Booth carried out an extensive study of CF LIF, probing the rotational temperature, the absolute concentration and its spatial and temporal variation⁴⁶. This work has been extended in this thesis to study predissociation of the CF radical.

LIF has been used to measure a variety of other species in plasma environments; radicals⁶⁴, products^{95,98}, ions⁸³, metastable atoms⁹⁹. These studies have included measurements of rotational and vibrational temperatures¹⁰⁰, which

have illustrated the non – equilibrium nature of a plasma.

Absolute concentrations of species can be found by LIF, although the calculations required are not trivial. They require a determination of the profile of the excitation volume in the plasma, and of the detector sensitivity and collection efficiency⁶⁵. To circumvent these calculations, which otherwise enforce a number of approximations and assumptions, comparative techniques have been developed, which calibrate the detection efficiency of the apparatus. The first of these involved Raman scattering from H₂ to calibrate the system¹⁰¹. For CF and CF₂, LIF of nitric oxide has been employed as the calibrant as it has similar excitation and fluorescence wavelengths¹⁰², and this technique is used for the work in this thesis in the ECR plasma reactor. For oxygen, a known concentration of oxygen atoms was prepared in a cell, which was optically identical to the plasma chamber, and the relative signals were compared, (see chapter 3).

LIF has often been used to measure the relative ground state concentration of a particular species as a function of plasma parameters and this is usually done by tuning the laser to a particular spectral feature, (eg. a ro–vibrational transition), and monitoring the fluorescence as the conditions are varied⁶⁵. There are however a number of caveats which need to be considered to ensure that the signal measured is a true representation of the total ground state concentration.

- i. The laser beam should not be significantly attenuated by species in the plasma, since their concentration may vary with plasma parameter.
- ii. The fluorescence should not be absorbed by species in the reactor volume, for reasons as above.
- iii. Radiative decay should be the major relaxation process for the excited state, or other processes must remain constant over the range of conditions used. This can be a complication, for example, for LIF of oxygen atoms where collisional quenching can be a significant relaxation process, even at 100 mTorr.
- iv. Corrections should be made for variation of the laser power on a shot to shot basis. For a single photon process, the intensity of the fluorescence varies linearly with laser power, (assuming no saturation effects), and so by normalizing the

fluorescence signal to the laser power, it is possible to allow for fluctuations in laser output.

v. The population of the levels of the electric ground state should not change significantly with conditions.

For CF_2 and CF in the low pressure plasmas used in this study, careful experimentation ensures that all the criteria are fulfilled, (for oxygen atoms see chapter 3). However, high levels of plasma induced emission mean that high laser pulse energies are employed to increase the fluorescence signal level. At these high intensities, the laser excitation process can significantly deplete the ground state concentration within the probing volume. Repopulation of the ground state is usually by radiative decay from the excited state but at high laser energies, the rate of excitation can be similar to the radiative decay rate, and the ground state is depleted. This can be observed by a plot of fluorescence signal against laser energy, where a sub-linear rise is seen, although such a plot also allows extrapolation back to the linear region of the dependence, (for a single photon process). This effect is known as saturation¹⁰³, and in the high intensity limit, total saturation is where the population of the ground state and excited state are only dependent on the degeneracies of the two states. However, the temporal, spectral and spatial profiles associated with a pulsed laser ensure that total saturation is not realizable. The profiles also make it possible for saturation of part of the laser beam to take place without clear experimental evidence. For CF, saturation can be a problem.

The fifth criterium also requires more consideration. For the case of CF, as the rotational temperature increases there will be a shift in the population towards higher rotational levels, but by careful selection of the transition probed, (a J value which lies above the maximum of the rotational distribution), this can be minimized. Chapter 8 illustrates a case where this effect is not negligible.

Laser induced fluorescence is a powerful technique whose characteristics are being exploited more and more in plasma studies. It does have the restriction of applicability, and is relatively costly to perform.

Absorption Spectroscopy

In principle, this is the most straight forward diagnostic for studying the ground state concentration. Using multipass and frequency modulation methods, high sensitivity is possible and quantitative data can readily be readily obtained. Atomic resonance lamps have been used on plasmas to measure the concentration of ground state atoms⁷³ and FTIR techniques have monitored stable molecular species¹⁰⁴. Tunable IR laser radiation, the tunable diode laser, has been used by Wormhoudt *et al.* and others, to detect a range of plasma formed species including CF_3 ¹⁰⁵, CF_2 ¹⁰⁶, CF ¹⁰⁷ and F ¹⁰⁸ atoms, although not all were generated in plasma environments. The ability of these laser systems to uniquely detect a wide range of species has implications for their role in future diagnostic techniques.

Laser Optogalvanic Spectroscopy

This technique involves observing the perturbation in impedance of the discharge as a laser beam is absorbed by species in the plasma. The changes can be due to photoionization or photodetachment^{53,109} processes, but can also result from more subtle effects such as excitation of an ion to change the mobility of that ion¹¹⁰. A variety of detection methods have been used including microwave interferometry and measurement of the rf current waveform¹¹¹.

The concentration of negative fluorine ions has been detected in NF_3 ¹⁰⁹ and CF_4 ⁵³ plasmas, and has shown F^- to be the major negative charge carrier present. Cl^- and BCl^- have also been monitored¹¹². The surface technique of photoemission optogalvanic spectroscopy, mentioned earlier, is also based on the change in discharge impedance but relies on the photoelectron effect to produce the extra electrons^{60,61}.

Other Optical Techniques

There are a variety of optical techniques which are capable of detecting species relevant to plasma studies, (eg. resonance enhanced multiphoton ionization^{113,114}, Raman spectroscopy and coherent anti-stokes Raman

spectroscopy¹¹⁵), and some of these have been used in plasma environments. Two other diagnostics of interest for future development of diagnostics are light scattering and four wave mixing studies. Light scattering is becoming widely used to study the formation of particles in plasmas¹¹⁶. These particles have been shown to be generated in the plasma itself and pose a serious industrial problem. Four wave mixing has been used in flame studies to obtain single shot spatial profiles of the concentration of species such as OH¹¹⁷. The directional nature of the stimulated emission enhances the sensitivity of the technique.

Amplified spontaneous emission is produced when a population inversion is generated by laser excitation of a three level system. The emission is again intense and directional and has been observed in a variety of multiphoton atomic LIF experiments, C¹¹⁸, H¹¹⁹ and O¹²⁰. However, the emission is strongly dependent on the concentration of the excited state species, and so can not readily be related to the ground state, as shown by work in this thesis.

Mass Spectroscopy

Mass spectroscopy was the first major diagnostic technique to obtain more fundamental experimental data⁵¹. However, early studies were operated in an ex — situ manner, which meant that only stable species could be reliably measured. Such observations only give indirect information on the processes in the plasma and require substantial extrapolation to obtain a knowledge of the reactive species. In an attempt to monitor reactive species directly, use has been made of a nozzle, placed inside the plasma, which can reduce the transit time for the species to travel to the analyzer. However, there is some concern as to the intrusive effect of the nozzle on the plasma. There are also some experimental difficulties in the calibration of the detector for reactive species.

One application of mass spectroscopy has been the measurement of ions from the plasma. This is usually achieved by building the orifice of the mass spectrometer into the electrode. Use of an electrostatic analyzer allows ion energy distributions to be found^{121,122}, and careful design can reduce the problems of collisions inside the

analyzer. Temporal resolution on the time scale of the rf cycle has been used to investigate the energy distribution of electrons incident on the electrode. Results showed a bimodal distribution at low pressure, indicative of secondary electrons. The sampling orifice has also been used by Pelletier *et al.*¹²³ to examine the etching products of silicon with fluorine atoms.

1.4.3. Diagnostics of Physical Processes

The physical properties of plasmas have been investigated primarily by Langmuir probe studies, although microwave, optical emission and laser based techniques have also been used.

Langmuir Probes

A description of the implementation of Langmuir probes is given elsewhere¹²⁴ and given here is a brief account of results obtained using this technique. Langmuir probes are best employed for dc, low pressure, inert gas plasmas, operated in the absence of rf and magnetic fields. Under these conditions there are no negative ions, limited contamination of the probe tip, no distortion of the trajectory of the ions / electrons within the probe sheath, and hence no perturbation of the probe characteristic. Even then it is not easy to extract information on the high energy tail of the distribution, which is the region of most interest, due to the simultaneous collection of ion current. A consistent ion current theory is required or a means of collecting electrons without ions. The latter has been achieved by Ingram and Braithwaite using an energy analyser¹²¹.

Experimental developments have included the rf biasing of the probe by Braithwaite *et al.*¹²⁵, who showed the need for such a technique to avoid the distorting effect of the rf field, which tends to predict erroneously high mean electron energies. Hopkins *et al.*¹²⁶ suggest electron bombardment to assist in maintaining a clean probe tip. There has also been much development in the probe theories and there is considerable discussion as to the application of these theories, particularly in connection with the ion current and the effect of negative ions and

fields on the characteristic^{127 - 130}. Despite the uncertainties associated with probe measurements, many experiments have been carried out in rf molecular plasmas. The rf biasing technique has been applied to Ar plasmas by Cox *et al.*¹³¹, to CCl₄ by Mandril *et al.*¹³² and to CF₄ by Welch¹³³, although the method of analysis was found to affect the densities obtained¹³¹. Probes have been used in a variety of other rf molecular plasmas^{134,135,136}, but great caution is required in the interpretation of these results.

A Langmuir probe is an intrusive diagnostic with many experimental and theoretical complications, but with care they can be used to obtain at least relative measurements of plasma density and in some cases good electron energy distributions. They are capable of spatial and temporal resolution and have been used in this mode¹³⁷.

Optical Emission Studies

As most of the emission from the plasma is a result of electron impact excitation, it is possible by careful selection of emission lines to obtain information on the electron distribution and density from analysis of the intensities of these lines. This requires that the excited state be produced by a single electron impact process on the ground state species, and not via any cascading or metastable pathway. In such a regime, comparison of the emission from two lines with different threshold energies can indicate changes in the EEDF, as a function of plasma conditions. It is this principle that was developed by D'Agostino *et al.*⁶⁷ in the use of more than one actinometer. Cox *et al.*¹³⁸ have used this technique by studying the ratio of emission from argon atoms and ions in an argon discharge, and comparing the result with rf biased probe measurements. The emission results were not put on an absolute scale, as this requires knowledge of the absolute cross sections for excitation, but good qualitative agreement was found. D'Agostino has correlated the emission from a variety of actinometers³³ in a SF₆ plasma to a full calculated EEDF, and suggested the potential of such a technique to determine these distributions. For such a method to be successful, actinometers with a wide range of

thresholds are required. The actinometers used need to be inert, and most of these species have thresholds well into the tail of the electron energy distribution, and so obtaining a full distribution has some experimental difficulties. However, the high energy thresholds of the actinometers make it an excellent probe for this region of the electron energy distribution. Time and spatially resolved optical emission has also been used to examine the excitation mechanisms in plasmas and, as described earlier, has illustrated the different regimes of plasma generation.

Other Techniques

Microwave techniques are best suited for the high density plasmas used in nuclear fusion applications. However, Vries *et al.*¹³⁹ obtained the electron density from a variety of processing plasmas at 13.56 MHz. These techniques have also been employed in the laser optogalvanic techniques.

In other work, Gottscho *et al.*³⁴ used LIF to follow the temporal variation in electric field strengths, utilizing the Stark mixing of different parity levels in BCl_3 plasmas. Similar studies have been done in N_2 plasmas⁸³. LIF of ions has also produced information on the trajectories of ions in the plasma, both in parallel plate⁸³ and electron cyclotron resonance reactors¹⁴⁰.

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Chapter Two

Experimental Apparatus

This chapter describes the experimental apparatus used in studies on a Reactive Ion Etching (RIE) chamber carried out in the Physical Chemistry Laboratory, Oxford. A further project on an electron cyclotron resonance, (ECR), reactor was carried out at Plasma Technology (UK) Ltd., Bristol and details of that system are reported in Chapter 8.

2.1 The Plasma Chamber

The reactor used was a commercial reactive ion etcher (Plasma Technology RIE 80), modified by the addition of three ports, to hold quartz windows which transmit the laser beam, the laser induced fluorescence and the optical emission, (figure 2.1). The cylindrical chamber (diameter 280 mm) was constructed from borosilicate glass and formed a vacuum seal with the upper, grounded, electrode and the anodized aluminium base plate.

The driven electrode, 170 mm in diameter and 55 mm from the grounded electrode, was fitted with a "dark space shield" mesh to restrict the plasma from extending down the pump outlet. The aluminium electrodes were water cooled and typically maintained at 15°C by flowing tap water.

The chamber was mounted on a steel table, capable of moving it 100 mm vertically without any displacement in the horizontal plane. The mechanism was driven by a large stepper motor (McLennon 34HS) and controlled by computer, and it allowed repositioning of the table with an accuracy of 0.1 mm. For spatial studies of species in the plasma the table was scanned up, thus reducing the distance between the optical axis of collecting optics and where appropriate laser beam, and the powered electrode surface. The window arrangement limited the viewing region between the electrodes to a distance of 0 – 20 mm above the driven electrode.

The power was supplied by a solid state r.f. power supply (Advanced Energy RFX 600, 13.56MHz, 600W Max). This was connected to an impedance matching

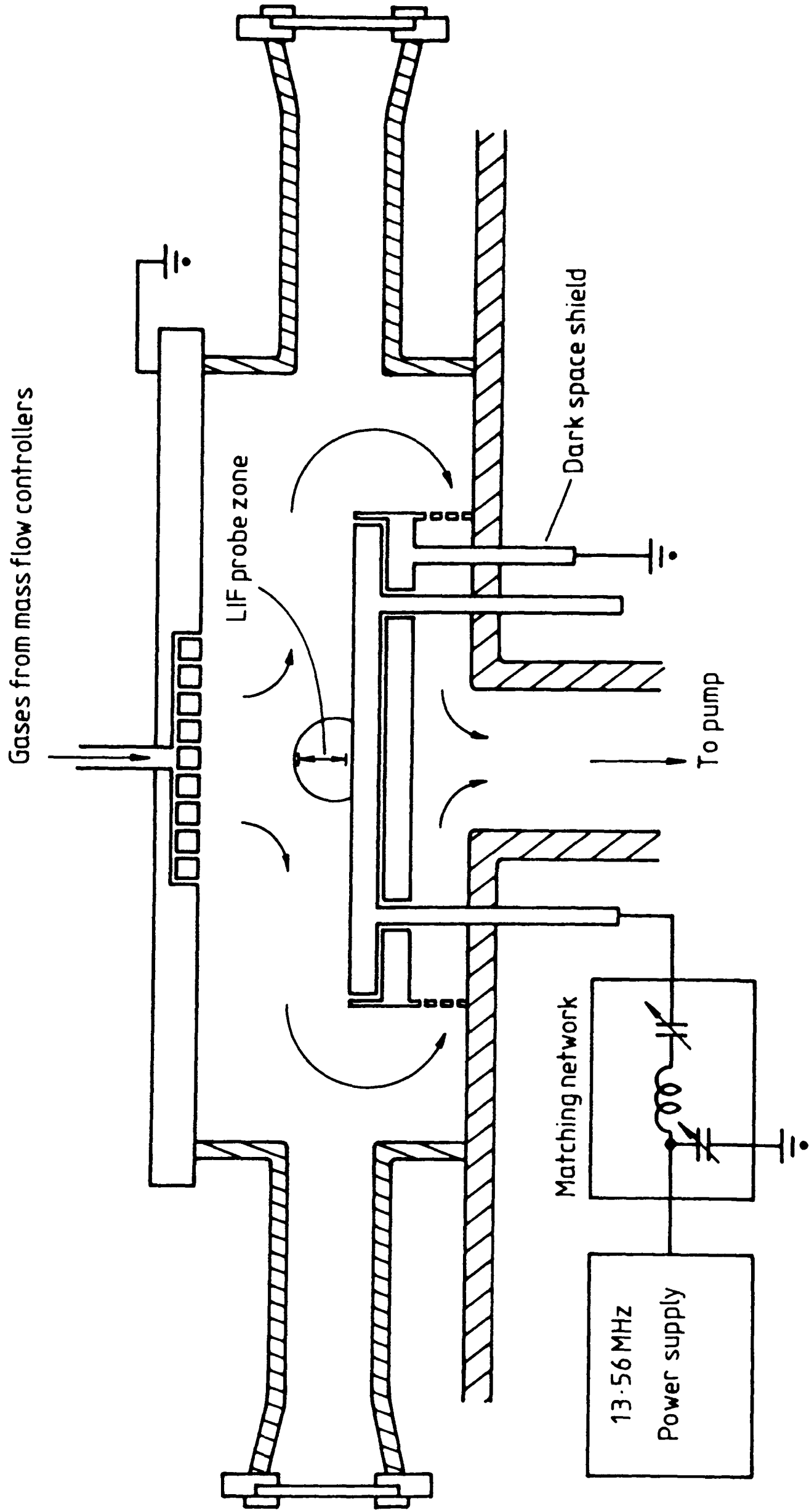


Figure 2.1 Schematic cross section of the Plasma Technology RIE 80 plasma chamber used in this study, indicating the electrics and optics of the system. (Hatched areas are insulating surfaces.)

network, which was used to minimize the reflected r.f. power by matching the output impedance of the power supply to the combined impedance of the matching unit and the plasma, (figure 2.1). The network contained a blocking capacitor restricting any damaging d.c. current to the power supply, but allowing high d.c. voltages to develop between the plasma and the driven electrode.

The reflected power, which was maintained at levels lower than 15% of the forward power, was measured by an on line power meter (Bird 4311 50 Ω) and by a power meter in the power supply. The power meter measurements strictly relate to the sum of the power dissipated in the plasma and the matching unit, but in the absence of the necessary probes to monitor the precise r.f. current and voltage waveforms on the electrodes, these values were used.

The power supply could be operated in pulsed mode and had a rise time of 5 μ s. This facility was utilized both in the time resolved studies of the radical kinetics and the steady state measurements. In the latter the plasma was extinguished, typically for 300 μ s, during which time the laser was fired and the fluorescence collected, this reducing problems caused by the high level of plasma induced emission. The short time period was chosen so that the composition of the ground state species present in the plasma remained unchanged, whilst the concentration of emitting electronically excited states was much reduced.

The gas handling equipment comprised three mass flow controllers (Tylan FC 260 total flow 20, 50 and 100 sccm (standard cm³) of N₂), which fed gas into a small mixing volume before it entered the chamber via a "shower head" in the upper electrode. The chamber was pumped by a Roots pump with a mechanical booster (Edwards E2M40 & EH250), via a 50 mm diameter aperture under the driven electrode and 70 mm diameter corrugated flexible tubing. The tubing enabled relative movement between the pump and the chamber, which was necessary for the spatial variation studies, and also isolated the chamber from vibrations from the pump. The precise flow patterns inside the chamber were not determined, but the residence time of species in the chamber was calculated approximately to be 350 ms under conditions of 50 mTorr and 42 sccm.

The operating pressure was varied using a throttle valve and was measured by a capacitance manometer (MKS 220A, 0 – 1 Torr). The base pressure was better than 0.5 mTorr and the leak rate of the system was generally better than 3 mTorr / min., equivalent to 0.4% of the total flow used for most experiments, which was 42 sccm. The gases used were BOC Electra Grade CF₄ (99.99%), CHF₃ (99.99%), O₂ (99.97%), Ar (99.999%) & Ne (99.999%), BOC CP grade NO (99.8%) and Fluorochem C₂F₄ (99.9%). All the gas mixtures used included 2.1 sccm of argon but the percentages given in this thesis refer only to the O₂ and CF₄ components.

2.2 Laser System

An excimer pumped dye laser system was used (Lambda Physik EMG 201 MSC and FL 2002) to generate the wavelengths required for the LIF of CF, CF₂, NO and O atoms, as given in Table 2.1. The XeCl excimer laser produced output at 308 nm at repetition rates up to 50 Hz with good shot to shot energy stability, and pumped the dye laser which, using a variety of dyes, can produce laser output across the whole visible spectrum.

The output was tuned by a thermostatically stabilized diffraction grating, which was scanned and controlled by a stepper motor (Berger Lahr RDM 50) with a resolution of 1/1190 nm for the 5th diffraction order. The dyes used in this study were LC4700 (Coumarin 120) and LC4400 (Coumarin 47), both in methanol. The visible output from these dyes was frequency doubled using a barium – β – borate (BBO) crystal to produce ultra-violet radiation in the required region. The crystal, also thermostatically stabilized, was angle tuned to provide conditions for phase matching of the fundamental and doubled beams¹, necessary for frequency doubling to occur. This was achieved using a high resolution stepper motor (Berger Lahr RDM 564/50), whose motion was correlated with the movement of the grating to ensure optimum output of ultra-violet radiation as the wavelength is scanned. The ultra-violet beam was strongly horizontally polarized and where necessary this was checked using a calcite Glan – Taylor polarizer.

Species	Excitation Band and Wavelength		Fluorescence Band and Wavelength	
CF ₂ (A – X)	(11,0)	234nm	(11,4)	248.5nm
CF (A – X)	(0,0)	232.9nm	(0,1)	240.1nm
	(1,0)	223.9nm	(1,1)	230.6nm
	(2,0)	215.9nm	(2,3)	235.2nm
NO (A – X)	(0,1)	236.6nm	Various	
	(0,0)	226.6nm	Various	
	(1,0)	215.1nm	Various	
O (3p ³ P – 2p ³ P)	³ P ₂ – ³ P	225.67nm	844.6nm	
	³ P ₁ – ³ P	226.07nm	844.6nm	
	³ P ₀ – ³ P	226.24nm	844.6nm	

Table 2.1

The bandwidth of the laser was measured by a monitor etalon to be 0.35 cm⁻¹ for the fundamental beam, ($\approx$ 0.6 cm⁻¹ in the ultra-violet). In the LIF of O atoms, to resolve the spin orbit states of the upper electronic level, higher resolution was required, and so an intracavity etalon was placed into the tuning block of the dye laser. The etalon has an air gap of 5 mm producing a free spectral range $\bar{\nu}_{\text{fsr}}$, of 1cm⁻¹. The resolution of the etalon is determined by $\bar{\nu}_{\text{fsr}}$ and the finesse, F, which is a measure of the reflectivity of the etalon windows,

$$\text{Resolution} = \bar{\nu}_{\text{fsr}} / F$$

where $F = \frac{\pi \cdot r}{(1-r^2) \cdot \sqrt{2}}$ and r = reflectivity ($0 \leq r \leq 1$), thus as $r \rightarrow 1$, $F \rightarrow \infty$, and resolution $\rightarrow 0$. The intracavity etalon used had a finesse of 25 – 30 though it was slightly wavelength dependent. At 452 nm the resolution of the laser was of the order of 0.04 cm⁻¹.

An etalon can be angle tuned, but the motion needs to be carefully correlated with grating and doubler crystal movement in order to maintain optimum output. The output was found to be very sensitive to the alignment of the etalon so that the stepping mechanism and the mount for the etalon needed to be very precise.

Etalons can also be pressure tuned, since a change in pressure varies the refractive index of the medium and hence the wavelength. Changing the pressure of gas inside the whole tuning block caused the grating to be tuned synchronously with the etalon mode, so that only the doubling crystal motion needs to be correlated. It also eliminated any motion of the etalon itself and so in this work pressure tuning was used.

The major limit on pressure tuning was the small range available; a pressure change of 1 atmosphere of Ar produced only a 15cm^{-1} (0.08 nm) variation in the ultra-violet output. This constraint required detailed knowledge of the positions of the spectral features sought, and also knowledge of the offset in wavelength caused by the presence of the etalon inside the laser cavity. In this regard the NO ($A^2\Sigma - X^2\Pi$) transition was used to assist in locating the three spin orbit transitions of atomic oxygen.

Spectra were taken by flowing research grade Ar into the evacuated tuning block. This meant that the data points were taken whilst the pressure was changing, but owing to the low flows used and the low dependence of wavenumber, $\bar{\nu}$, on pressure, the wavenumber typically only varied by 0.001 cm^{-1} during acquisition. The tuning block has a volume of about 1.3 litres and with a flow of 10 sccm of Ar, a full scan from 10 – 760 Torr typically took about 90 minutes. However, scanning over a single oxygen peak only required a range of 100 Torr.

2.3 Detection and Data Acquisition

There have been a number of different experimental designs used in this study, for the detection and acquisition of data for both laser induced and plasma induced emission. These generally involve the use of quartz lenses and MgF_2 coated AR mirrors to collect, focus and direct the emission, the use of monochromators and filters to select the emission spectrally and the use of photomultipliers to detect the light transmitted by the spectral discriminators. A general schematic diagram of these designs, including the control systems, is shown in figure 2.2.. In every case all the optics were positioned on one table to reduce problems of alignment of both the

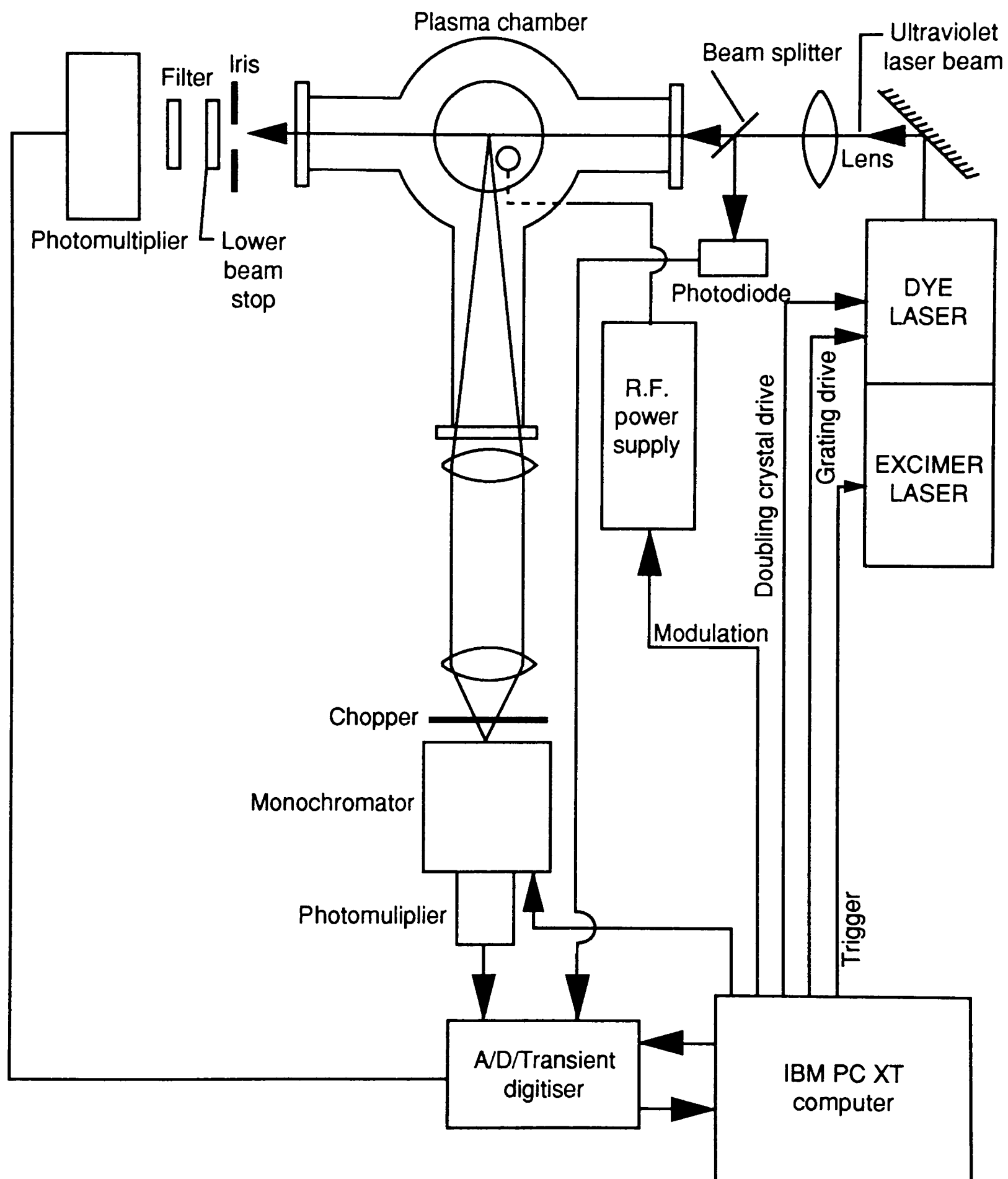


Figure 2.2 Schematic diagram of the equipment used for the detection of radical species by LIF, ASE and AOE, illustrating the detection optics and data collecting and processing systems.

laser and the collecting optics.

The experiments were all controlled and the data collected on an IBM PCXT, fitted with a Tecmar Labmaster board, which was capable of digital and analogue input and output. The outputs were used to drive stepper motors to move the laser grating, the doubling crystal, the monochromator gratings and the plasma chamber table. The inputs were used for time resolved and time independent measurements; time resolved, via a transient digitiser (Datalab DL912, dual channel, temporal resolution 50ns, 1M Ω impedance, 8 bit resolution), and time independent, via slow analogue – digital (A/D) converters ($\pm$ 10V, 12 bit). Use of a pulsed laser meant that all the LIF data was collected using the transient digitiser, but for the optical emission studies both systems were used. The signals were stored, averaged and analyzed on the computer.

The precise timing required in the experiments was set using a timer chip (AM9513) incorporated on the Tecmar board. This allowed programming of five TTL pulse outputs, triggered internally or externally, which were used to control the pulsing of the plasma, the firing of the laser and the triggering for data collection with microsecond resolution.

2.3.1 Optical Emission

The plasma induced emission was spectrally resolved using a 0.5 m monochromator, (Spex 1870 f/6.9, 1200 grooves/mm, blazed at 500 nm, dispersion 1.6 nm/mm, limiting resolution of 0.02 nm), and detected using a photomultiplier, (Hamamatsu R298), which has good sensitivity from 200 – 900 nm. The photomultiplier tube was terminated by 10M Ω for steady state measurements and by 3.3 – 33 k Ω for time resolved studies, in order to maximize the signal whilst ensuring that the response time of the electronics was smaller than the time scale of the changes in the optical emission being observed. The detection sensitivity of the Spex instrument was measured as a function of wavelength using calibrated standard lamps, although in most cases the data shown are uncorrected.

The emission from the plasma was imaged onto the monochromator slits using two lenses. For the majority of the experiments the lenses were positioned so as to collect light from a large double cone volume inside the chamber, and so any spatial variation present was averaged out. Some spatial resolution of the emission was carried out. In these experiments two sets of slits were positioned such that the light collected was from a thin horizontal disc shaped volume inside the plasma, and thus by moving the chamber (as described in section 2.1) spatial information was obtained. Two orthogonal mirrors were used to rotate the image by 90° in order to align the image onto the vertical slits of the monochromator, which vastly increased the sensitivity.

In the time independent steady state measurements, the signals were collected using the A/D converters. The monochromator was scanned over the feature of interest and the resulting spectra were analyzed and the peaks integrated using the computer. The transient digitiser was used for the time resolved optical emission experiments, for which the monochromator was also scanned, but here a time trace was stored at each wavelength instead of a single value as in the steady state case. The result was a two dimensional array of signal against wavelength and time, an example of which can be seen in figure 2.3.

It was found that by simply measuring the peak of the spectral line and subtracting a background level, the values observed generally behaved identically to the integral technique. This was particularly true for atomic lines where the line shape of the features were determined by the instrument resolution and not by any variation of the plasma conditions. Thus to economize on time and computer memory the peak method was often used, most usually for the time resolved work.

2.3.2 LIF and ASE

An Edinburgh Instruments monochromator 121 S15 (f/4, dispersion 5.3 nm/mm, blazed at 250 nm, resolution of 1.35 nm for 250 μm slits), was used to resolve spectrally the fluorescence collected perpendicular to the laser beam from CF, CF₂ and NO, and an EMI 9813QKB photomultiplier was used to detect it. The

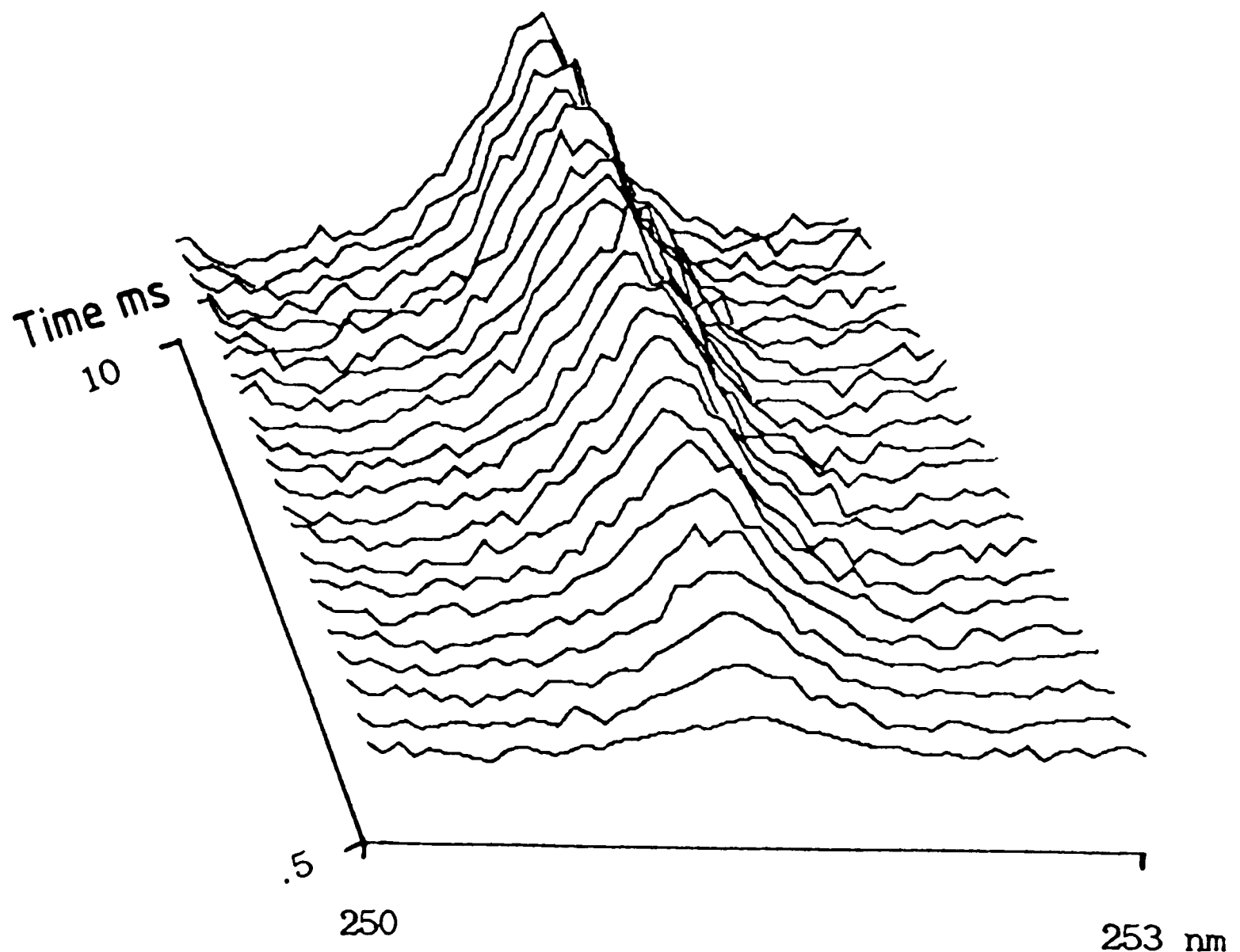


Figure 2.3 Example of the two dimensional arrays recorded for the time resolved optical emission studies; CF_2 $A(0,5,0) - X(0,0,0)$ transition taken from a 50 mTorr 100 W CF_4 plasma.

photomultiplier tube was terminated by a $3.3\text{k}\Omega$ resistor for all experiments, except for the radiative lifetime studies, in which a 50Ω resistor was used which provided a temporal response of about 5ns for a single photon event. For these lifetime studies a fast storage scope and a fast gated sampler (Stanford Research Systems SR 255, 1 ns gate), were used to acquire the data and, in the case of the sampler, to transfer it to the computer for further analysis.

The monochromator differentiated the specific fluorescence wavelength from the broad band plasma induced emission and the fluorescence signal was also temporally discriminated by gating the signal using the transient digitiser. This allowed collection of the signal synchronous with the laser firing, to ensure that the measured signal was due to the laser induced effect. This method was further improved using the fast switching technique described in section 2.1. Two lenses were used to collect and focus the fluorescence onto the monochromator slit and in this case the position of the laser beam defines the region being probed.

A reflection from a quartz plate directed onto a photodiode (Vactec VTB

6061UV) was used to measure the relative laser energy on a shot to shot basis. The absolute scale was found by calibration against readings from a pyroelectric joule meter (Gentec ED100A). Some experiments involved the measurement of signals as a function of laser energy. Laser attenuation was achieved by partially blocking the excimer pump beam to the dye laser amplifier. This allowed attenuation of the laser over a couple of decades without altering the profile of the beam.

For LIF of oxygen atoms further adaptation was required due to the high level of plasma induced emission at the fluorescence wavelength of 845 nm, and low levels of fluorescence associated with two photon LIF. A lens (fl.300 mm) was used to focus the laser beam at the centre of the chamber in order to increase the energy density and hence the fluorescence observed. Also, a mechanical chopper (Scitec, 0 – 10 Hz) was synchronized with the laser pulse and the plasma modulation so that the photocathode was blocked from the plasma emission when the plasma was ignited and when the plasma was extinguished, the chopper was opened, the laser was fired and the fluorescence was collected. This enabled high gain to be used on the photomultiplier tube without the plasma emission saturating the device. The chopper was also used to study the CF (2,0) band, due to the low levels of fluorescence observed.

The fluorescence from oxygen atoms at 845 nm was detected by the Hamamatsu tube or an RCA C31034 red sensitive photomultiplier and was initially resolved by the Spex monochromator. In later experiments the monochromator was replaced by a Schott cut-off filter, RG 850, using the reduction in sensitivity of the photomultiplier at higher wavelengths to act as a high wavelength cut-off. The filter was used in combination with some slits, typically set at 500 μ m, to allow the fluorescence to be collected whilst minimizing the level of plasma induced emission.

Amplified Spontaneous Emission (ASE) from oxygen atoms was observed in this study. ASE is anisotropic and propagates along the axis of the exciting laser beam. To observe the ASE a monochromator (Edinburgh Instruments), later replaced by a cut-off filter (RG 780), combined with a perspex laser beam stop and a red sensitive photomultiplier, were placed in line with the laser beam, (figure 2.2).

Even when using the filter the level of ASE was higher than the intensity of plasma induced emission, although it was possible to use an iris to cut down the PIE without reducing the ASE. In these studies the polarization of the ASE and fluorescence became of interest and gelatin polarizers were used to determine the degree of polarization. This was done in conjunction with the filter based detection systems so that any variation in response of the monochromator with polarization was avoided. In the experiments where ASE and fluorescence were measured simultaneously, both red sensitive photomultipliers were used together with the cut off filters described above. The presence of ASE was undesired in many of the experiments and so a long focal length lens was used to maintain high levels of fluorescence whilst reducing the amount of ASE.

2.4 The Flow Cell Apparatus

Determination of the absolute concentration of oxygen atoms in kinetic studies is often achieved by a titration technique designed by Kaufman² and improved by Reeves *et al.*³. This titration technique is not possible within a plasma environment and so in this study a comparative method was used. A flow cell, in which titrations are possible was set up, such that the optical arrangement was identical to that of the plasma chamber, the laser and collecting optics were not moved at all. The laser induced fluorescence signal from oxygen atoms in the plasma was then compared to the signal from a titrated concentration of oxygen atoms in the flow cell, keeping the signal levels and laser energies as similar as possible.

To ensure that the optics were the same, LIF from a known concentration of nitric oxide was used as a monitor of the collection efficiency for both arrangements. The NO fluorescence was detected by the Edinburgh Instruments monochromator set up, using the reflection from a quartz flat positioned in the collection pathway, to reflect the fluorescence towards the monochromator slits, (as shown in figure 2.4). It was necessary to restrict further both the height and the width of the slits in front of the detection systems to obtain the required effect.

The titration technique involves the reaction of NO₂ with the oxygen atoms,

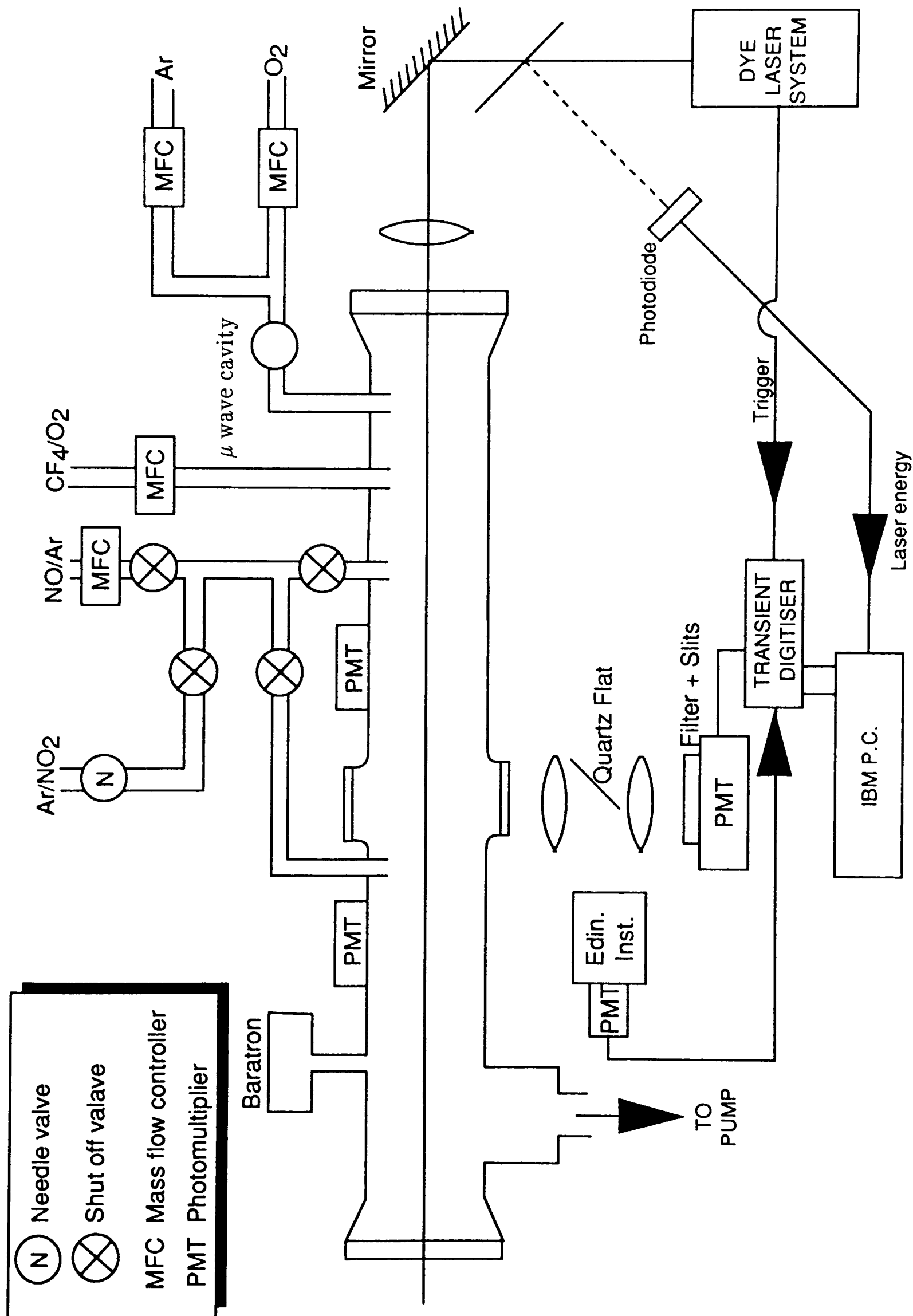


Figure 2.4 Schematic diagram of the flow cell apparatus used in the determination of the oxygen atom concentration.

which leads ultimately to the production of excited NO_2 , emission from which was monitored by the photomultiplier tubes, (RCA 1P28). Details of the technique are given in Appendix 1. The flow cell was also used to measure the quenching rate of the $3p\ ^3\text{P}$ level of atomic oxygen by molecular oxygen and CF_4 . This was done by comparing LIF and titration measurements in the presence and absence of these gases.

Chapter Two References

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2. F.Kaufman, *Prog.React.Kinet.*, 1 1 (1961)
3. R.R.Reeves, G.Mandella, P.J.HartecK, *J.Chem.Phys.* 32 632 (1960)

Chapter Three

Laser Induced Fluorescence Studies of Oxygen atoms

3.1 Introduction

Oxygen is used widely in processing plasmas and plays an important role in the chemistry of such systems. The removal of organic photoresists by oxygen based plasmas, often combined with small concentrations of CF_4 or SF_6 , is one of the oldest dry etching processes used in the semiconductor industry¹. Small percentages of O_2 are added to fluorine based plasmas to enhance the F atom concentration and thus increase silicon etch rates². In these plasma environments oxygen is present in a variety of forms and states, many of which have been detected directly^{3,4,5,6,7}, for example, oxygen atoms in the ^3P ground state and various excited states, O^- ions, O_2 in the $^3\Sigma_g$ ground state, and excited states, including the metastable $^1\Delta_g$ state.

The energetics and spectroscopy of molecular oxygen have been widely studied and some comprehensive reviews have been published^{8,9}, (see figure 3.1, which shows some of the low lying states of molecular oxygen). Of particular interest is the $^1\Delta_g$ state, usually referred to as 'singlet oxygen', which is important in biological chemistry¹⁰ and atmospheric chemistry³. In plasmas, its long radiative lifetime (4000s), and slow gas phase and gas – surface kinetics^{3,11}, means it can be present in high concentrations; in d.c. discharges, it has been measured at levels of 10% of the initial O_2 feedstock concentration⁶. For this study, the $\text{B}^3\Sigma_u^-$ and $\text{A}^3\Sigma_u^+$ states are also of interest, since they can be populated by absorption of one 226 nm photon by the electronic ground state. The systems are known as the Schumann–Runge and Herzberg I Bands respectively and are of particular interest because of the possibility of photodissociation through such transitions, as discussed in section 3.3. The interaction of molecular oxygen with electrons has also been fairly widely studied.⁸ Oxygen has a dissociation energy of 5.1eV, which taken with typical electron energy distributions found in these plasmas, results in relatively high levels of dissociation of the parent molecule, and thus high concentrations of oxygen atoms. Previous studies have observed 1 – 5% dissociation of O_2 in d.c.

discharges⁶ and up to 15% in conventional rf discharges¹². Levels as high as 30% have been reported in the highly dissociating distributed electron cyclotron resonance plasmas¹³, but the results obtained for this thesis give values of 1 – 12%.

The electronic configuration of the ground state oxygen atom is $1s^2 2s^2 2p^4$ which leads to a 3P ground state term. The triplet level is split by spin orbit coupling, producing three states, 3P_2 , 3P_1 and 3P_0 , with 3P_2 being lowest in energy. Other low lying energy levels and electron configurations of atomic oxygen are shown in figure 3.2. The major states of interest in this work are the triplet and quintet states, because of their involvement in both the optical emission and LIF techniques used. The majority of studies in the plasma etching field on oxygen atoms have used optical emission from both the $3p^3P_{2,1,0} \rightarrow 3s^3S_1$ transition at 844.6 nm and the $3p^5P_{3,2,1} \rightarrow 3s^5S_2$ transition at 777.3 nm. The upper states of these two transitions are populated by both excitation of ground state oxygen atoms and dissociative excitation of molecular O_2 , which makes interpretation of the optical emission data more difficult. Cross sections and thresholds for these processes are however known and are discussed further in chapter 5. Laser induced fluorescence of oxygen atoms uses two photons at 226 nm to excite atoms from the ground state to the $3p^3P_{2,1,0}$ levels, and as explained later in this chapter, this excited state may relax by a variety of processes including spontaneous fluorescence to the $3s^3S_1$ state at 844.6 nm.

3.2 Laser Induced Fluorescence of Oxygen Atoms

Atoms are generally the most reactive and abundant species inside rf discharges, but direct in-situ measurement of their ground state concentration has been rare. Actinometric optical emission techniques as described in chapter 1 have enabled some monitoring of species, but there are many problems and dangers associated with this method, particularly where the emission can result from electron excitation of a species other than the atomic ground state. Absorption techniques using resonance lamps have also been used¹³, but differences in the line shape of the lamp emission and absorbing atoms can sometimes result in erroneous

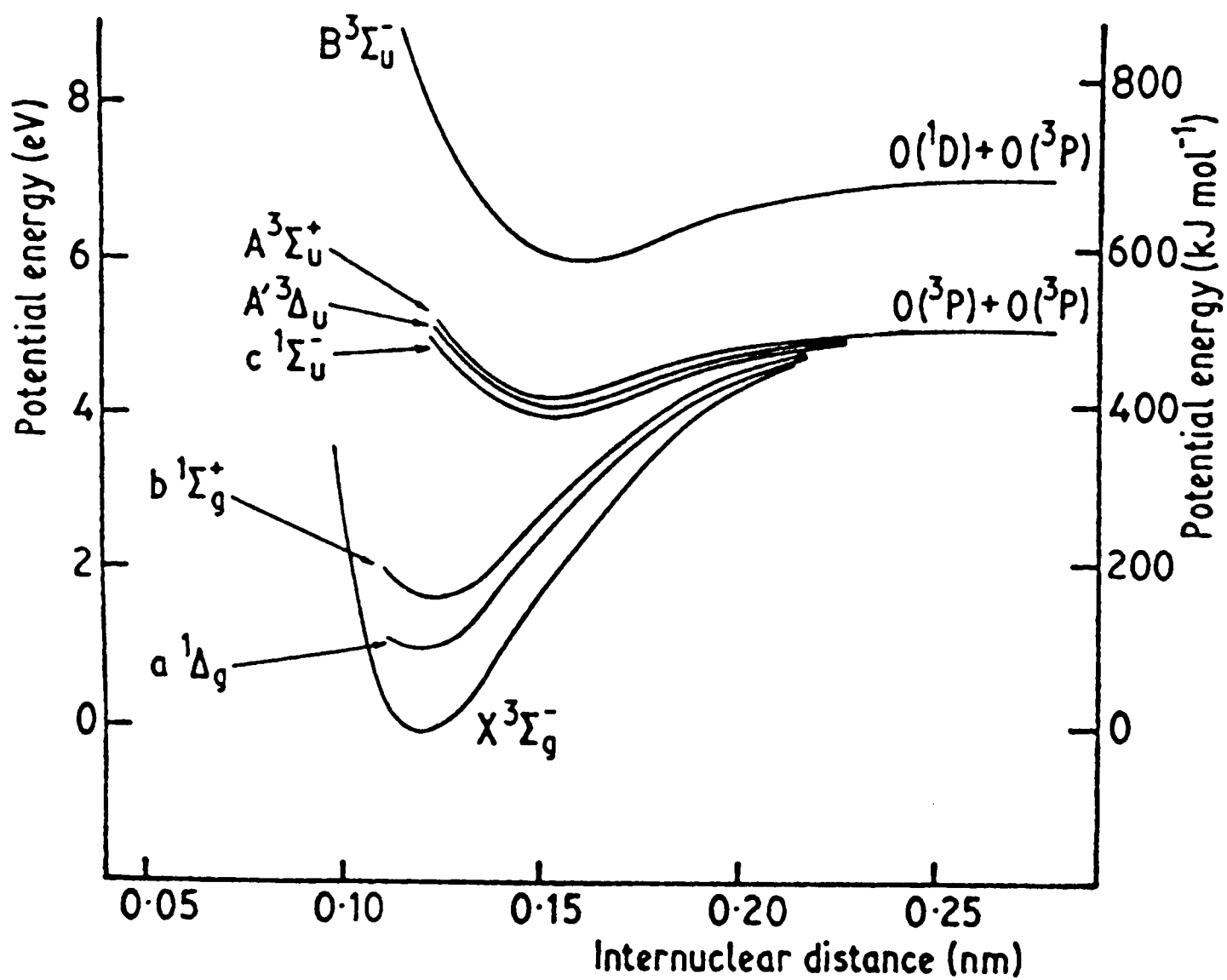


Figure 3.1 Some low lying states of molecular oxygen.

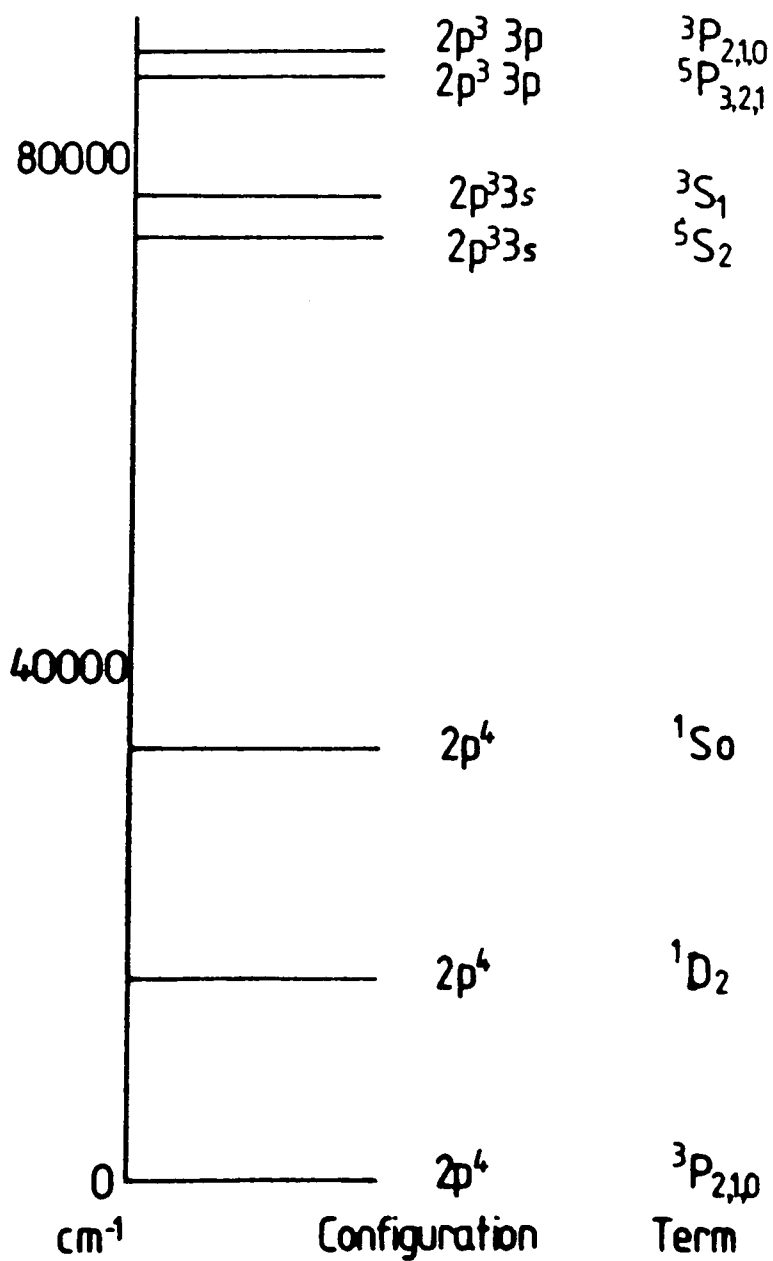


Figure 3.2 Energy levels and electron configuration of atomic oxygen.

results and great care is required. Electron paramagnetic resonance investigations have also been carried out on fluorine and oxygen atoms¹², although the measurements cannot be made inside the active region of the plasma.

Generally, LIF represents an optical diagnostic which does directly probe the ground state without the problems of interpretation. The problems lie in the experimental considerations. Many of the species of interest are atoms from the first two rows of the periodic table, "light atoms", which tend to have energy diagrams similar in magnitude to that shown in figure 3.2. It can be seen that for oxygen atoms the lowest energy allowed optical transition, $3s^3S - 2p^3P$, requires an energy of 76800 cm^{-1} , equivalent to a wavelength of 130 nm, and most of the light atoms require photons at similar short, vacuum ultra-violet, wavelengths. At present there are no convenient tunable lasers in this wavelength range and so multiphoton excitation methods have been developed, which bring the wavelengths required back into the ultraviolet / visible region. This general technique has been applied to a number of light atoms though not necessarily for plasma applications, for example, Cl¹⁴, N, O¹⁵, H, D¹⁶, C¹⁷, S¹⁸.

For oxygen atoms the lowest allowed two photon transition is from the ground state to the $3p^3P$ level, an energy separation of 88600 cm^{-1} , requiring two photons at 226 nm, which can be readily produced from a frequency doubled dye laser system. The fluorescence is to the 3S_1 state and is monitored at 844.6 nm, which illustrates another advantage of the two photon method, that the fluorescence is not radiation trapped, a potential problem associated with fluorescence from the 3S_1 state. The cross sections for the excitation processes are however small, considerably less efficient than most allowed single photon processes, and thus high laser intensities are required to obtain measurable signal levels. The consequence of this is the presence of secondary laser induced effects, such as photoionization and amplified spontaneous emission, which influence the level of the fluorescence yield and hence complicate the interpretation of the fluorescence data. Details of these competing effects are given in sections 3.3 and 3.4.

Two photon LIF of oxygen was first carried out in a flow cell in 1981 by

Bischel *et al.*¹⁵ and was first observed in a plasma environment by Di Mauro *et al.*⁵ It has however not been widely used in plasmas owing to the intense plasma induced emission at 844.6 nm and the high laser energies required. Of particular interest to the present work are the results of Selwyn *et al.*, who compared LIF studies with optical emission measurements to probe the validity of actinometry for oxygen atom emission¹⁹, and also looked at the spatial distribution of oxygen atoms in the presence of loading surfaces such as polyimide resist and carbon films²⁰. Visser has also used LIF of oxygen in an attempt to characterize the mechanism of resist etching by O₂ based plasmas²¹.

By comparison, combustion studies have utilized the two photon technique for both oxygen and hydrogen atoms^{22,23}. In these systems the oxygen concentration is generally higher than in a plasma and there is a much reduced level of background emission at 844.6 nm. The option of optogalvanic detection, using 2 + 1 multiphoton ionization has also been used²⁴.

3.2.1 Theory of Two Photon LIF of Oxygen

The excitation rate of a two photon process between two states can be expressed as¹⁵

$$W (s^{-1}) = \frac{\alpha \cdot I_L^2}{h\nu}$$

where α is the two photon absorption cross section. For a transition between the ground state, with angular momentum J_g , to the excited state, J_e , this cross section can be given as¹⁵

$$\alpha = \frac{(2\pi)^3}{hc} \cdot \nu_1 \cdot |P_{eg}|^2 \cdot g(2\nu_1)$$

and

$$P_{eg} = \sum_i \frac{\langle J_e | r | J_i \rangle \langle J_i | r | J_g \rangle}{\Delta E_i}$$

where ν_1 is the laser frequency, $g(2\nu_1)$ is the two photon normalized absorption line

shape, ΔE_i is the energy difference between the photon energy and that of the state i and the sum is over all states i , accessible by a one photon transition from g and e .

In the case of oxygen, since the two photon transition is between two 3P levels, suitable intermediate states can be 3D or 3S , but because of the energy difference denominator, ΔE_i , and the oscillator strengths²⁵, the majority of the contribution will be through the $3s^3S_1$ state. This approximation simplifies the calculation of the cross section and in particular the relative components of the spin orbit fine structure. A full analysis, summing over all accessible states has been done²⁶, and showed that the 3S_1 state component accounts for 97% of the total cross section. Applying the single intermediate state approximation produces a single matrix element which can be separated into radial and angular parts. The radial integral relates to the absolute value of the cross section, whilst the angular integral affects the relative spin orbit components. The latter involves calculating matrix elements, summed over the required J and m_j values of the lower, intermediate and upper levels concerned. The intensities of the spin orbit transitions can then be related, since they depend on the population of the ground spin orbit state, $N(J_g)$, and the cross section component, $\alpha(J_g, J_e)$. Thus, the intensity for each transition $J_e - J_g$

$$I(J_g, J_e) \propto \alpha(J_g, J_e) \cdot N(J_g)$$

However, the spin orbit splittings are such that under typical operating conditions, the different ground state J values are resolvable, but those of the upper state are not, so

$$I(J_g) \propto N(J_g) \cdot \sum \alpha(J_g, J_e)$$

The relative components of each of the spin orbit cross sections have been calculated using both the approximate three state method¹⁵ and the full analysis over all relevant states²⁶, and the results are given in table 3.1. There are differences in the two sets of results but the single intermediate state approximation does predict the same two photon selection rules ($\Delta J = 0, \pm 1, \pm 2$ but $J = 0 \rightarrow J = 1$) and give the same value for the sum over the upper spin orbit states.

J_g	J_e	One State Intermediate	Full Calculation
0	0	333	542
	1	0	0
	2	667	458
1	0	0	0
	1	500	656
	2	500	344
2	0	133	92
	1	300	206
	2	567	702

Table 3.1
Relative values of $\alpha(J_g,J_e)^{15,26}$.

3.2.2 Experimental Observations of Oxygen

A full spectrum of the three ground spin orbit states taken in an 85% O₂, 50 mTorr, 100 W rf plasma is shown in figure 3.3. The spin orbit splittings are detailed in table 3.2²⁵.

	States	Separation
2p	$^3P_1 - ^3P_2$	158.5 cm ⁻¹
	$^3P_0 - ^3P_2$	226.5 cm ⁻¹
	$^3P_0 - ^3P_1$	68.0 cm ⁻¹
3p	$^3P_2 - ^3P_1$	0.54 cm ⁻¹
	$^3P_0 - ^3P_2$	0.16 cm ⁻¹
	$^3P_0 - ^3P_1$	0.70 cm ⁻¹

Table 3.2

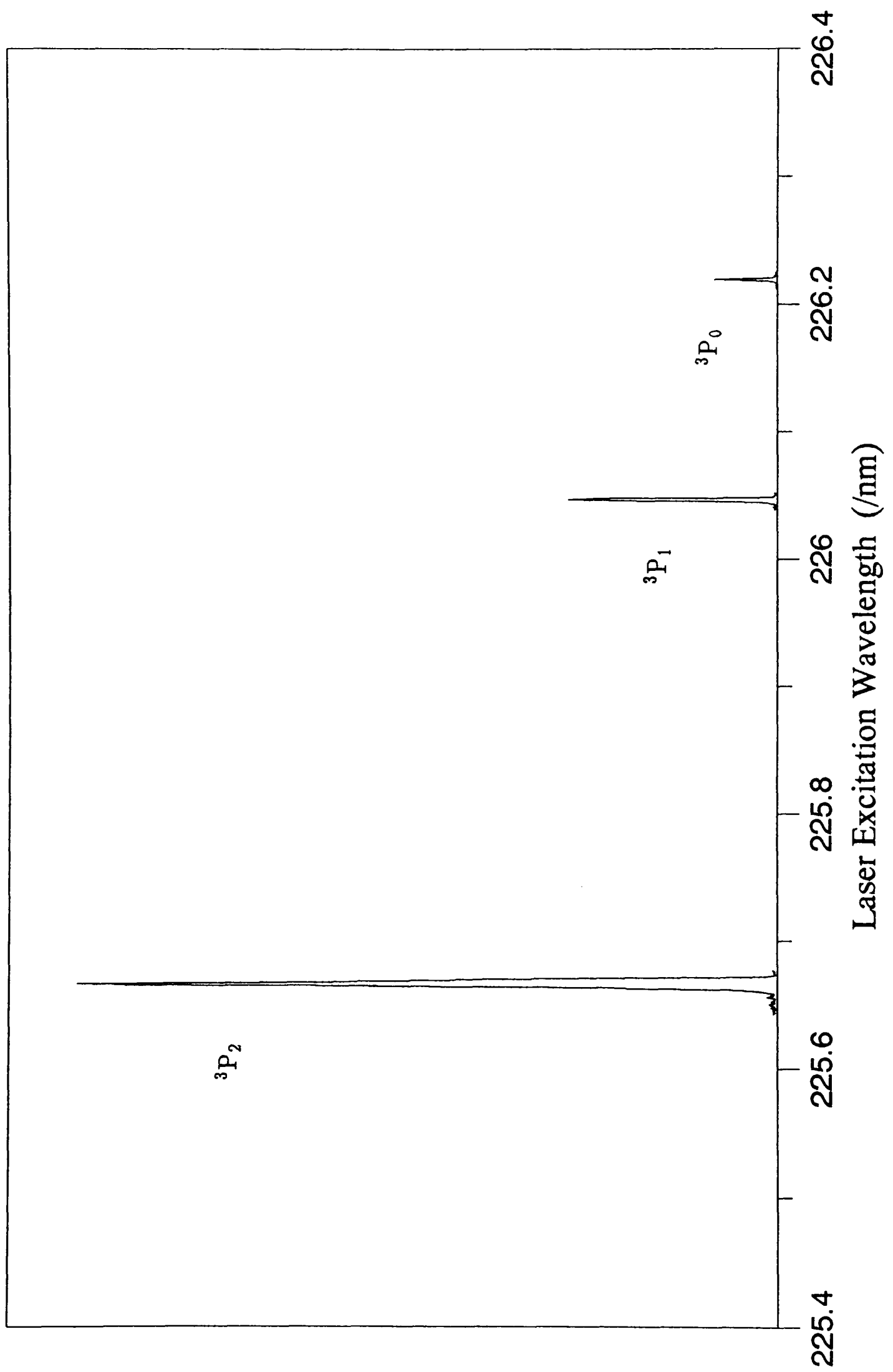


Figure 3.3 Two photon LIF spectrum of oxygen atoms measured in an 85 %, 50 mTorr, 100 W rf plasma.

In the previous studies on two photon LIF, it has only been possible to resolve the spin orbit states of the ground state, but not those of the upper state. The dye laser system used in this work has a linewidth in the ultra-violet of 0.6 cm^{-1} , and so is also not able to resolve them. However, using an intracavity etalon, the linewidth of the laser is theoretically reduced to about 0.06 cm^{-1} . This was tested by taking a LIF excitation spectrum of part of the NO ($A(v' = 0) - X(v'' = 0)$) band. Figure 3.4 illustrates the NO spectrum taken with and without the intracavity etalon and the increased resolution can be seen. For the spectrum taken with the etalon, the resolution obtained for a single rotational line is 0.13 cm^{-1} . The Doppler width for NO at room temperature is 0.1 cm^{-1} , and so assuming a Gaussian distribution for the laser linewidth, this linewidth can be extracted using the deconvolution formula¹⁵ —

$$\Delta\nu_1^2 = \Delta\nu_{\text{exp}}^2 - \Delta\nu_d^2$$

and thus,

$$\Delta\nu_1 = 0.08 \text{ cm}^{-1}$$

where $\Delta\nu_1$, $\Delta\nu_{\text{exp}}$ and $\Delta\nu_d$ are the laser, measured and Doppler linewidths respectively.

The Doppler width of oxygen atoms at room temperature is 0.27 cm^{-1} , and so in spite of the narrow laser linewidth, sub-Doppler techniques are required to resolve the $3p^3P_2$ and $3p^3P_0$ states, (see section 3.4.1). The etalon scanned spectra for the spin orbit transitions are given in figure 3.5 and they show that the $3p^3P_{2,0}$ and the $3p^3P_1$ states have been resolved. Also shown are the theoretical expected positions and strengths of the transitions, based on the full calculation by Pindzola²⁶. The absence of the $3p^3P_1 \leftarrow 2p^3P_0$ transition is apparent and generally there is good agreement with the theoretical predictions discussed above.

One motivation for the etalon studies was the hope that the increased spectral energy density of the laser output, when the etalon was present, would lead to an enhanced LIF signal from oxygen. Unfortunately, the etalon caused a reduction in the total output energy of the laser and also resolved the upper spin

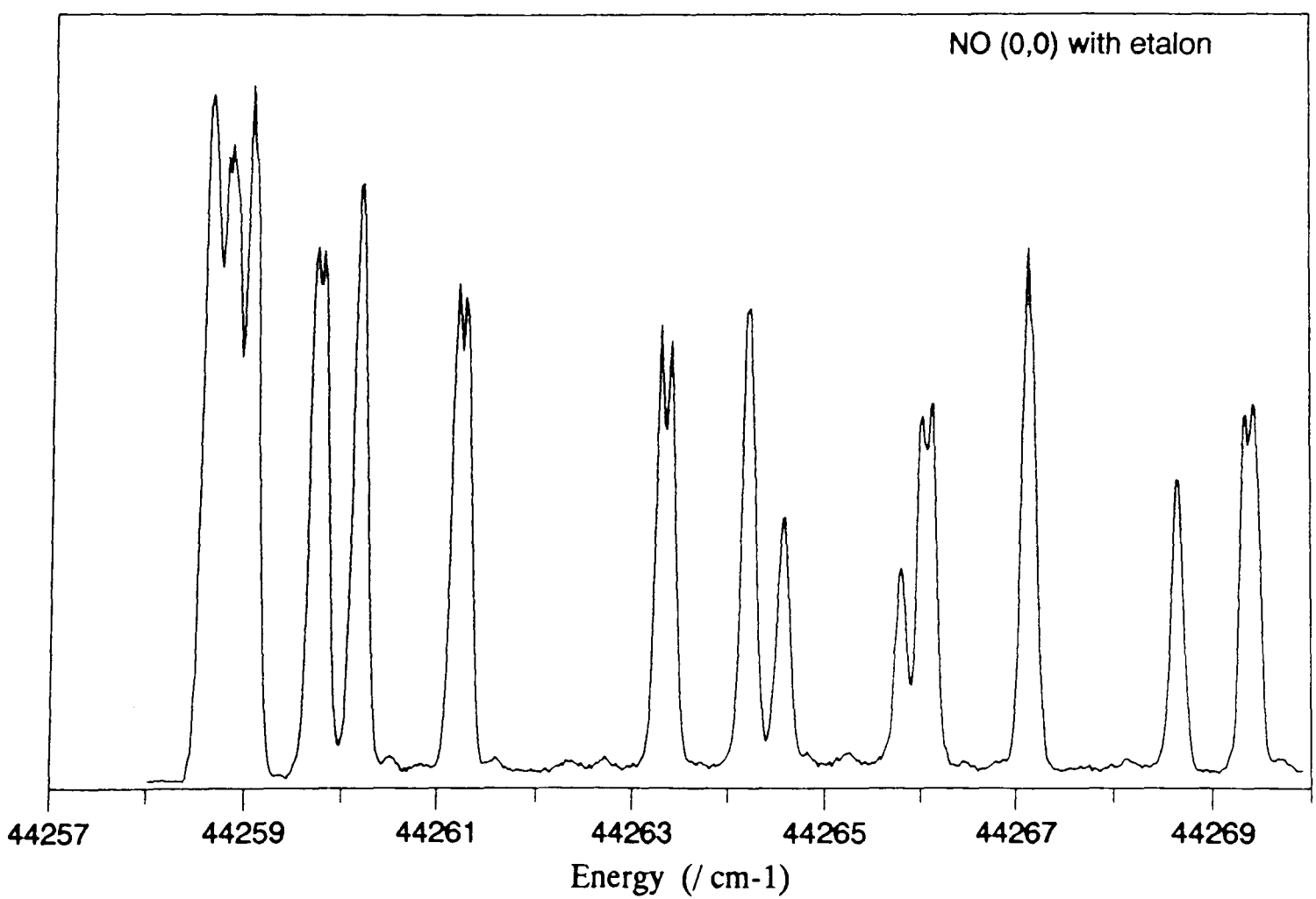
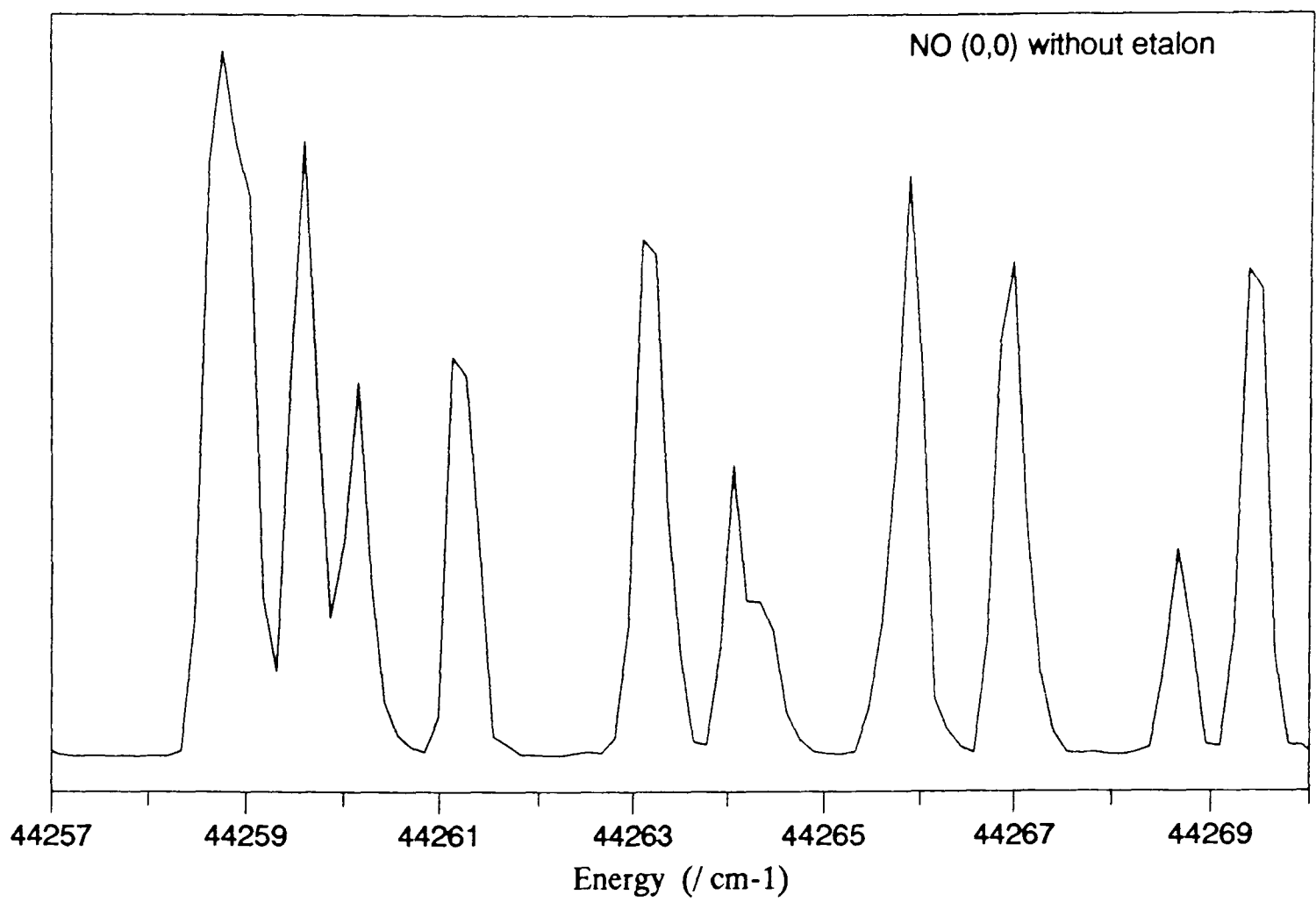


Figure 3.4 LIF excitation spectra of the $Q_{11} + P_{21}$ head from the NO $A(\nu = 0) - X(\nu = 0)$ transition, taken with and without the intracavity etalon.

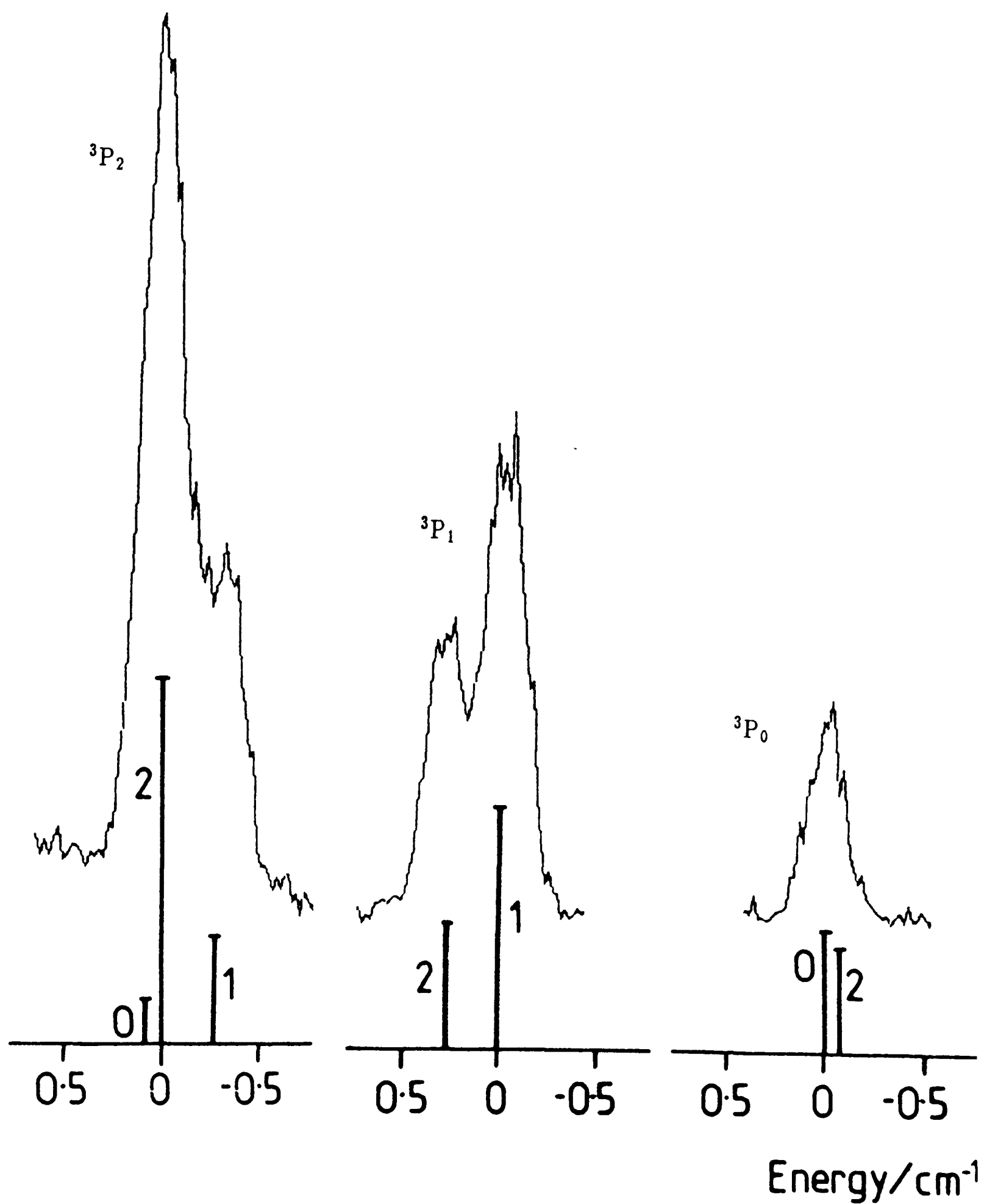


Figure 3.5 Etalon scanned spectra of the transitions from the three spin orbit ground states, together with the theoretical positions and strengths as calculated by Pindzola²⁶.

orbit states, both of which tended to reduce the signal observed. This, combined with the experimental complications associated with the etalon operation, meant that most studies on oxygen were performed without the etalon.

The energy separations between the ground spin orbit states are such that at room temperature all three of the states are populated. The intensities of the transition can be used to calculate the relative populations, and if a Boltzmann distribution is assumed, to obtain a temperature for the oxygen atoms. This requires knowledge of the line strengths and relative energies of the states²⁵. In general, at thermal equilibrium

the intensity measured	$I_{J''}$	$\propto \frac{S_{J''} \cdot N_{J''}}{g_{J''}}$
where	$N_{J''}$	$\propto g'' \cdot \exp(-E_{J''}/kT)$
thus we obtain	$I_{J''}$	$\propto S_{J''} \cdot \exp(-E_{J''}/kT)$

where E is the energy of the state, S is the line strength, N is the population, g is the degeneracy of the lower state, k is the Boltzmann constant and T is the temperature, (I and S are summed over all upper spin orbit states).

The relative intensity ratios are given in table 3.3 together with the calculated temperatures, for a variety of plasma conditions. It can be seen that the temperatures are very sensitive to the intensity ratios, but they are comparable with CF rotational temperatures measured under similar conditions. It should be noted that these measurements were taken under conditions of low laser energy because, as shown in section 3.4, the presence of ASE can affect the relative intensities of the spin orbit transitions.

Gas Composition	Plasma Power	Plasma Pressure	$^3P_2: ^3P_1: ^3P_0$ Intensities	Temp.
85% O ₂ 15% CF ₄	100 W	50 mTorr	1:0.28:0.08	305±10K
85% O ₂ 15% CF ₄	50 W	200 mTorr	1: 0.27	294±10K
85% O ₂ 15% CF ₄	200 W	200 mTorr	1: 0.31	344±10K
100% O ₂	100 W	50 mTorr	1: 0.29	317±10K

Table 3.3

3.3 Competing Processes

As mentioned earlier, low excitation cross sections result in the need for high laser energy intensities. These intensities are sufficient in the case of oxygen atoms to produce a range of laser energy dependent processes which compete with spontaneous fluorescence. There are also competing mechanisms which are not laser induced such as collisional quenching, which can result in complete relaxation of the excited state to the $2p^3P$ ground state²⁷ or in intersystem crossing to lower electronic states such as the $3p^5P_{3,2,1}$ states²³. A summary of the pathways available to the laser excited $3p^3P$ oxygen atom is given in figure 3.6.

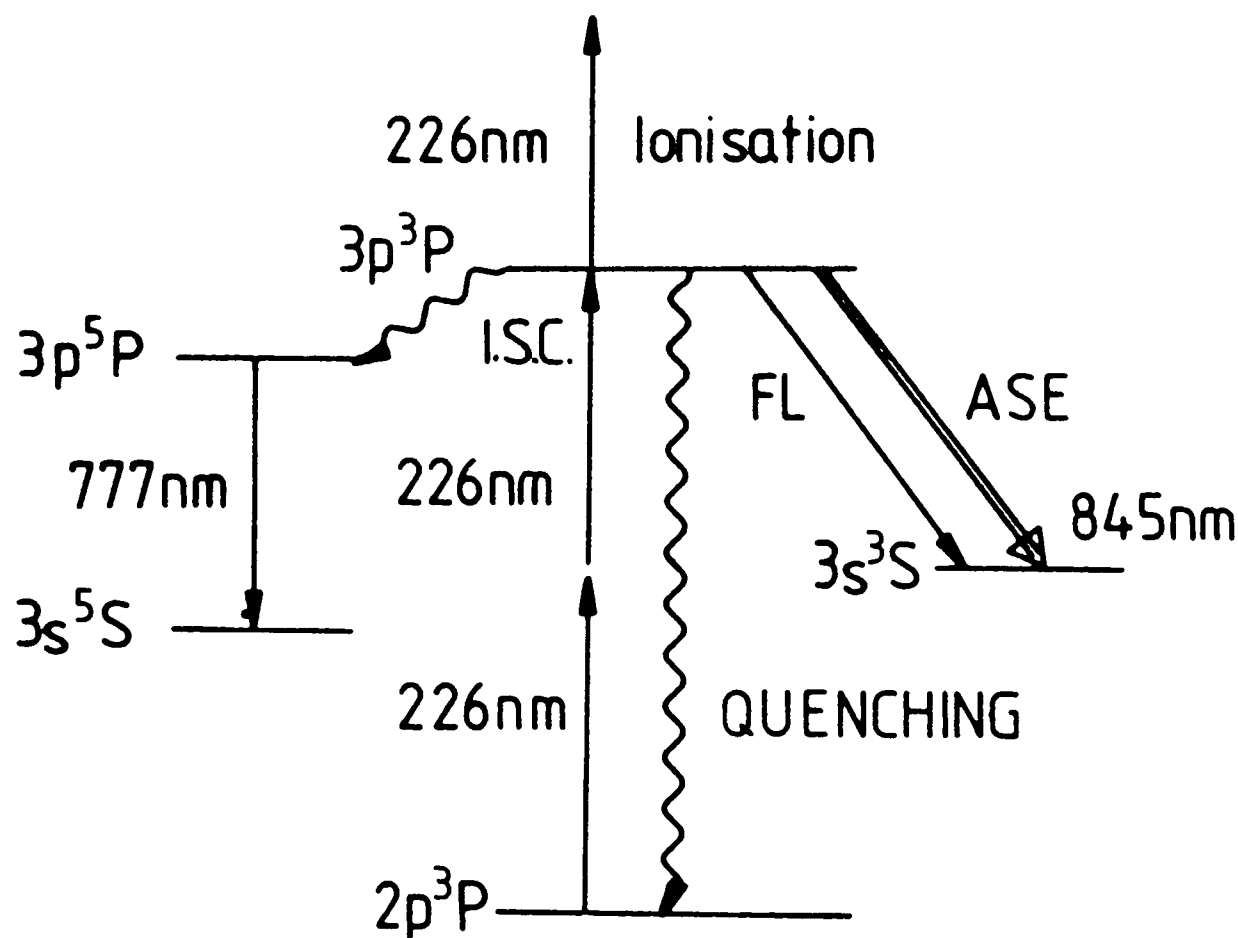


Figure 3.6 Processes involved in the two photon LIF of oxygen atoms.

All the processes competing with spontaneous fluorescence complicate the use of LIF for the measurement of ground state oxygen atoms. For the purpose of plasma diagnostics, it would be preferable for the spontaneous fluorescence to be the single or at least the major relaxation process for the $3p^3P$ level, since the signal then obtained would be directly proportional to the ground state concentration, as the probing conditions are changed. Most of the competing processes however, can be investigated further.

Intersystem crossing (ISC) to the 5P level can be studied by observing the subsequent emission of 777.3 nm radiation, (see figure 3.6). At 500 mTorr, the highest pressure used in this work, such radiation was observed but it was found to constitute less than 2% of the decay pathway for the $3p^3P$ level. The amount observed was found to be highest in a pure O_2 plasma, and increased with pressure (~5% at 1 Torr of pure O_2), but for most of the conditions used in this study it was negligible. Previous combustion studies involving the LIF of oxygen have noted this phenomena^{23,28} and at the higher pressures used, the relative importance of such a pathway is enhanced. In one study involving an atmospheric flame²³, there was three times as much emission at 777.3 nm as compared to that at 844.6 nm. ISC by collision with molecular oxygen is spin allowed and so is a relatively fast process.

Overall quenching of the $3p^3P$ level is a very rapid process with molecular oxygen, ($k_q = 6.3 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$)²⁷, due to an attractive potential leading to formation of an O_3 complex produced during the quenching mechanism. The rate is such that the concentration of molecular oxygen present under typical conditions studied in this work, was high enough to affect the fluorescence yield, and so a calibration factor was required. Since most of the studies on atomic oxygen were in CF_4 / O_2 plasmas, the quenching rate of CF_4 was also needed. The rates for a variety of gases have been measured²⁷ but not the CF_4 value, and so an attempt was made in this work to repeat the measurement with molecular oxygen, and to obtain a value for CF_4 . This was carried out in the flow cell equipment described in chapter 2. Details are given in section 3.5.

The remaining pathways are affected by the laser energy and so can best be

studied by considering the effect of these competing mechanisms on the dependence of the fluorescence signal with laser energy. The variation of measured fluorescence with laser energy is shown in figure 3.7, plotted in a log – log format. The gradient of such graphs give a direct indication of the power dependence between, in this case, the fluorescence signal and the laser energy. At laser energies below $30 \mu\text{J} / \text{pulse}$, the slope of the fluorescence is 1.7 ± 0.1 falling at higher laser energies to around 0.9. The expected behaviour for two photon laser induced process is a slope of 2, but photoionization from the excited state ($3p^3P$) and / or partial saturation of the two photon transition would tend to reduce this value. The observed fall in the dependence at energies above $100 \mu\text{J} / \text{pulse}$ may be due to these effects, since their influence increases with laser energy, but it may also be due to depletion of the excited state by amplified spontaneous emission, (ASE).

This phenomenon, which is discussed in more detail in section 3.4, was observed in this work and its variation with laser energy is also shown in figure 3.7. The magnitude of ASE is very sensitive to the excitation volume produced by the laser, and particularly to the concentration of oxygen atoms pumped to the excited state. This correlates with the behaviour demonstrated in figure 3.7, which also shows the strong correlation between the onset of ASE and the fall off region in the fluorescence behaviour.

Precise rates associated with the laser induced processes are difficult to calculate owing to the ill defined spatial, spectral and temporal profiles of the laser beam, but knowledge of the cross section for excitation^{29,30}, ($\alpha = 5.5 \times 10^{-28} \text{ cm}^4\text{W}^{-1}$), and for photoionization, ($\sigma_i = 5.3 \times 10^{-19} \text{ cm}^2$)³⁰, together with the Einstein A coefficients and quenching rates allow a simple numerical model to be devised to interpret the dependences observed.

If the profiles are all assumed to be step functions and the laser linewidth is greater than that of the two photon transition, (as is the case in this work), then for a laser energy, (E_l), of $0.1 \text{ mJ} / \text{pulse}$, of 20 ns duration, (τ_l), focused down to an area, (A), of 10^{-4} cm^2 (based on the diffraction limited size of the focused beam) and

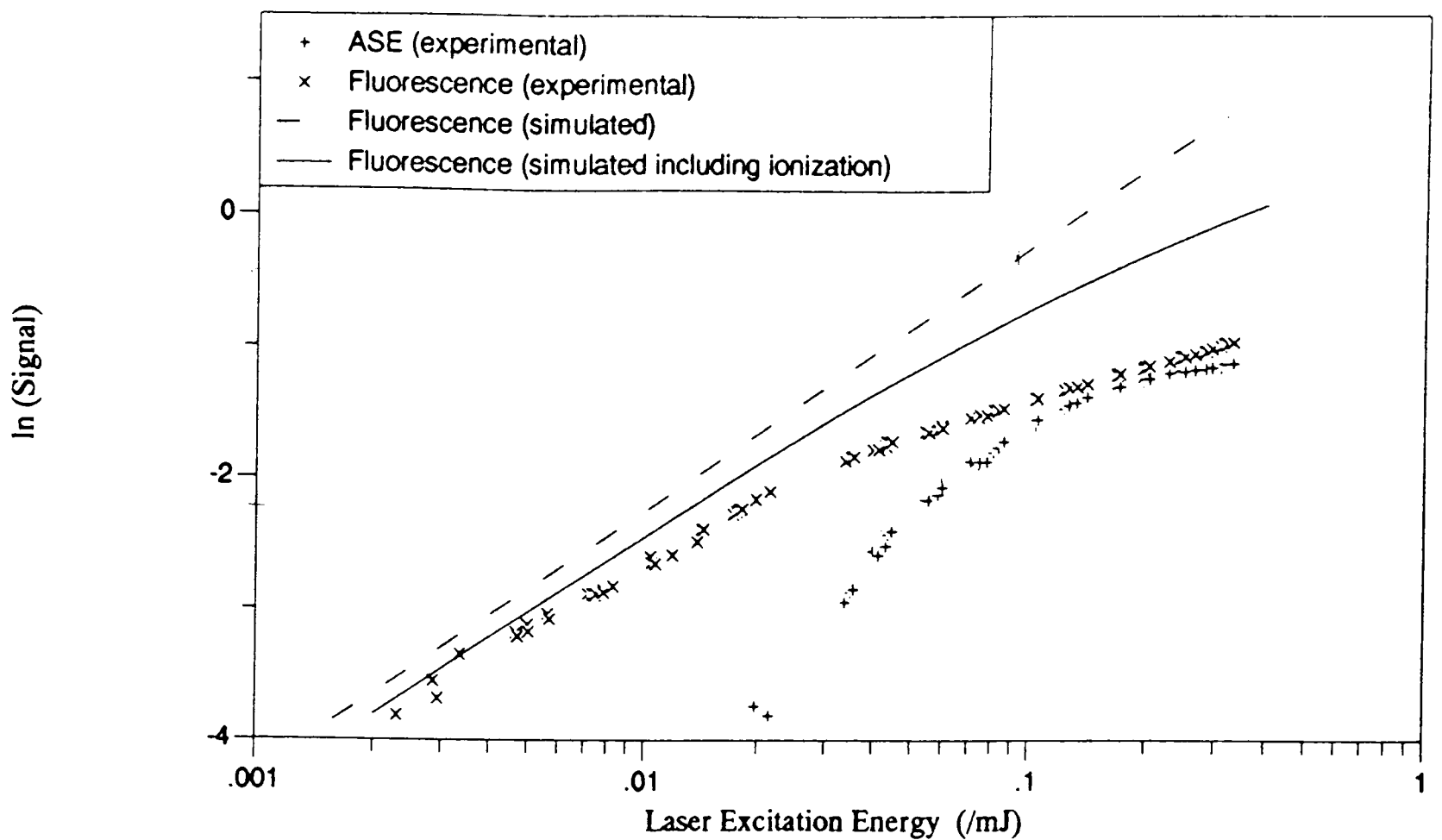


Figure 3.7 Variation of the spontaneous fluorescence and ASE from oxygen atoms as a function of laser energy (in an 85% O₂, 500 mTorr 100 W plasma), together with simulations of the two photon process, with and without ionization, (see text).

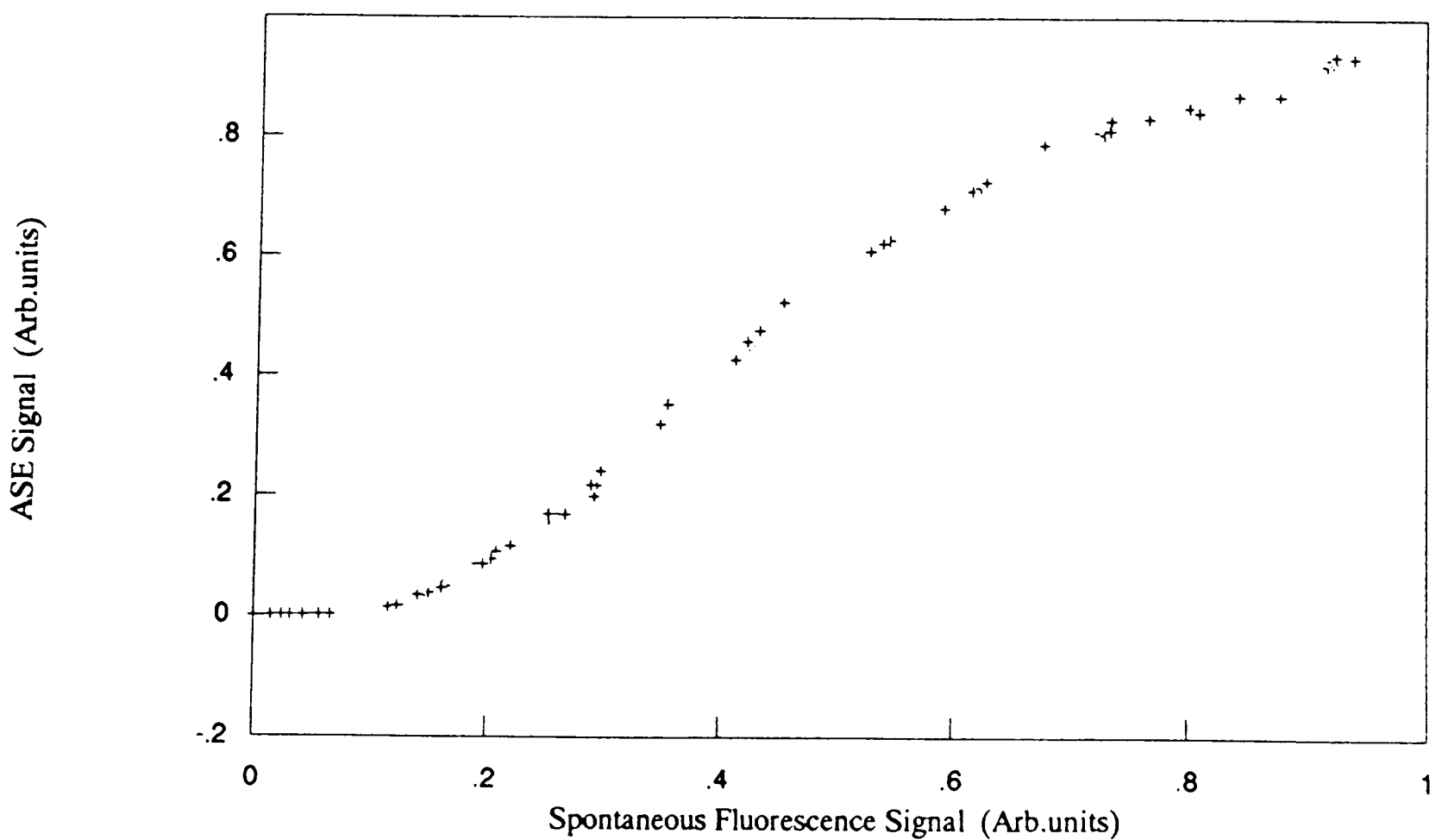


Figure 3.8 Variation of ASE with spontaneous fluorescence as a function of laser energy in an 85% O₂, 500 mTorr 100 W plasma.

tuned to the $3p\ ^3P_{2,1,0} \leftarrow 2p\ ^3P_2$ transition at 226 nm :

$$\begin{aligned} \text{the photon flux,} \quad N_p &= \frac{E_1}{A \cdot \tau_1 \cdot h\nu} \\ &= 10^{-4} / (8.8 \times 10^{-19} \times 20 \times 10^{-9} \times 10^{-4}) \\ &= \underline{5.7 \times 10^{25} \text{ photons cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{the laser power density,} \quad I_L &= \frac{E_1}{\tau_1 \cdot A} \\ &= 10^{-4} / (20 \times 10^{-9} \times 10^{-4}) \\ &= \underline{5.0 \times 10^7 \text{ W cm}^{-2}} \end{aligned}$$

and the rate of two photon excitation¹⁵,

$$\begin{aligned} W_{21}, &= \frac{\alpha \cdot I_L^2}{h\nu} \\ &= (5.5 \times 10^{-28} \times 25 \times 10^{14}) / 8.8 \times 10^{-19} \\ &= \underline{1.4 \times 10^6 \text{ s}^{-1}} \end{aligned}$$

where $h\nu$ is the energy of a 226 nm photon.

Saturation involves the depletion of the ground state by rapid laser induced excitation, and occurs when the rate of excitation is less than the rate of replenishment of the ground state. It is a process which only takes place within the excitation volume formed by the laser beam, and during or shortly after the laser pulse, and so replenishment of the ground state by diffusion is too slow.

Quenching can lead to repopulation of the ground state, with a rate of $1.02 \times 10^7 \text{ s}^{-1}$ for 0.5 torr of O_2 , but this relates to the rate of removal from the $3p^3P$ level and there are a variety of metastable oxygen atom states, (5S , 1S & 1D), which may act as temporary sinks for the relaxing atoms. Such a case is the ISC phenomenon discussed above, which produces oxygen atoms in the 5S state. This would effectively slow the rate of repopulation of the ground state concentration by this mechanism.

Fluorescence from the excited state results in population of the 3S_1 state

which itself can radiatively decay to the ground state. Even allowing for the three spin orbit states of the $2p^3P$ level, the Einstein coefficient for radiative decay from $3s^3S_1$ to $2p^3P_2$, ($2.4 \times 10^8 \text{ s}^{-1}$), is faster than that for the $3p^3P_{2,1,0} \rightarrow 3s^3S_1$ transition, ($2.78 \times 10^7 \text{ s}^{-1}$)²⁵, so the latter is rate determining for this pathway. This is over 100 times faster than the excitation rate and so saturation is unlikely to be responsible for the energy dependence observed. Amplified spontaneous emission also repopulates the ground state via the 3S_1 level and, as with quenching, will increase the repopulation rate and decrease the probability of saturation.

The photoionization rate can be calculated using the cross section, σ_i , and the photon flux. Thus,

$$\begin{aligned} k_{\text{ion}} &= 5.7 \times 10^{25} \times 5.3 \times 10^{-19} \\ &= \underline{3 \times 10^7 \text{ s}^{-1}} \end{aligned}$$

This value is of the same order of magnitude as the fluorescence rate and thus would be expected to effect the measured fluorescence signal. The rate rises linearly with laser flux and has the effect of reducing the square dependence of fluorescence towards the limit of a linear dependence at high laser energy.

This simple model suggests that photoionization of oxygen atoms, and not saturation, may be the cause of the reduction in power dependence of fluorescence on laser energy below the theoretical value of 2. With the cross sections and conditions mentioned above, figure 3.7 shows the result of the calculations for the theoretical variation of fluorescence with laser energy, with and without the presence of photoionization. The calculation assumes the presence of no ASE and is plotted on a log – log graph for comparison with the experimental data. The results show that the fluorescence dependence can best be explained by competition of photoionization with fluorescence, causing a reduction in the gradient, over the lower range of laser energy, with ASE becoming an even greater draw on the excited state at high laser energies.

As mentioned above, the laser pulse has non-uniform temporal, spatial and spectral profiles, all of which cause enhancement of the laser induced effects at the peaks of these profiles, but which will be less significant in the wings. This phenomenon produces the need for care when normalizing data with respect to the laser energy, and is best avoided by keeping the laser energy constant during an experimental run. In terms of using LIF as a measure of the ground state concentration, the photoionization process is only a problem when the laser energy varies significantly, since its rate is linearly dependent on the laser energy and the $3p^3P$ state concentration. This ensures that the magnitude of its effect on the fluorescence yield is independent of the $3p^3P$, and hence ground state, concentration. On the contrary, ASE has a non-linear dependence on the upper state concentration and so its effect on fluorescence varies as a function of ground state concentration. Thus, in all experiments where the ground state concentration was being probed, an attempt was made to maintain a constant laser energy, (to within 10%).

The photodissociation of molecular oxygen is also a possible source of error in the use of LIF for oxygen atom measurements, since one photon absorption of the ultra - violet radiation can result in the localized production of two oxygen atoms and will perturb measurement of the true plasma produced concentration. The dissociation limit for O_2 is 5.1 eV (or 242 nm) and so absorption of photon energies greater than this can result in dissociation. The Herzberg I band, $A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$, produces a continuum in the absorption spectrum in the 170 - 240 nm region and has been extensively studied⁸. It is not an allowed transition and despite its low value, there is now good agreement for the cross section, $(\sigma_d = 3 \times 10^{-24} \text{ cm}^2)^{31,32}$. The Schumann - Runge bands ($> 175 \text{ nm}$) and continuum ($< 175 \text{ nm}$) involve an allowed transition to the $B^3\Sigma_u^-$ state. This state can predissociate to produce $O^3P + O^3P$ instead of the $O^3P + O^1D$ states with which it correlates³². The cross section and Franck-Condon factors for the Schumann - Runge transitions have also been measured over a range of upper and lower vibrational levels. The energy

separation between the two electronic states is 6.12 eV and so the electronic ground state needs to be at least in the $\nu'' = 3$ vibrational level for a 226 nm photon to reach the $^3\Sigma_u^-$ state.

The photochemical production of oxygen atoms by 226 nm radiation has been observed in combustion^{32b} and plasma studies¹⁹. In the former, the measured spatial concentration profiles in a flame, were found to be dependent on the laser energy used. This was interpreted as being due to single photon photochemical formation of atomic oxygen from molecular oxygen, followed by two photon LIF, all taking place within the laser pulse. The researchers were able to show that the photodissociation was via the (0,3) and (2,4) Schumann – Runge bands, (these coincided with the $3p^3P - ^3P_2$ transition wavelength), and to resolve some of the rotational structure of the transition. This was done in an atmospheric pressure flame at vibrational temperatures of 3000 K, and using a focused laser beam with energies of 2 – 5 mJ. In a 72 Torr flame, no such photochemical effects were seen.

In the plasma studies, the photodissociation of molecular oxygen was used as a means of calibrating the concentration of the oxygen atoms¹⁹. This was done by comparing the LIF signal from a plasma system to that from a concentration of oxygen atoms, which were produced by photodissociation of molecular oxygen, using the same laser beam. This technique was also attempted in this study using the flow cell apparatus, but lower laser energies resulted in no observed signal, even at pressures in excess of 300 Torr. This result indicates that vibrationally cold O_2 was not a source of oxygen atoms in this work. Vibrational temperatures of over 1000 K have been measured in plasmas and so it is possible that the higher vibrational levels of the electronic ground state are populated. However in this study, the laser energy was less than 0.5 mJ and the concentration of molecular oxygen less than 1 Torr, and so comparison with the combustion studies suggest that photodissociation is also not a significant production pathway for atomic oxygen. Therefore, as far as the work in this thesis is concerned, photochemical production of oxygen atoms does not affect the measurements made by two photon laser induced fluorescence.

3.4 Amplified Spontaneous Emission

The high laser intensities required in the multiphoton excitation of atomic and molecular species can create a transient inversion of the excited state with respect to a lower lying intermediate state. This can result in the development of amplified spontaneous emission (ASE), which then propagates in the direction of the excitation beam. Detailed theoretical studies of this phenomenon have been carried out³³, and the conclusions are discussed here. The first concerns the dependence of the emission intensity on the concentration of the excited state. It has been predicted, and found (see below), that the intensity has three regions. The first region is where the excited state density is not sufficient for ASE to occur, (below threshold). Above this is the second region, in which high gain is attained, such that the emission intensity increases exponentially with excited state concentration. Finally at very high concentration, there is a saturation region, where the limiting process becomes the rate of production of the excited state, and so the emission becomes proportional to the excited state concentration, a dependence similar to that for LIF. These regions are seen in figure 3.7, where the laser intensity is used as a means of changing the excited state concentration.

The geometry of the excitation region is also an important factor in the levels of ASE measured. ASE propagates in the direction which has the longest path length of excited state species, which is why it is observed as a beam co-linear with the exciting laser path. The dependence of ASE intensity on pathlength has been studied and its effects can be seen by varying the focal length of the focusing lens used. The volume from which ASE radiates is not necessarily the same as that which leads to fluorescence, particularly in view of the non – uniform profiles of the laser. Thus, ASE may influence the excited state concentration in the central core of the zone excited by the laser, but not in the surrounding region.

Experimentally, ASE has been observed as a result of the laser excitation of a variety of species³⁴; including H³⁵ and O²⁸. For oxygen atoms, the previous observation was in flame studies, where its influence on the spontaneous fluorescence signals was studied. A more comprehensive study has been carried out

on ASE from hydrogen, which revealed the anisotropic, beam like, nature of the emission and the dependence of ASE on laser energy. There was also evidence that the polarization of the emission followed that of the exciting laser beam. A comparison between the behaviour of spontaneous fluorescence and ASE signals was also carried out, as a function of atomic concentration.

3.4.1 Dependence of ASE on Concentration

In the present study the ASE was readily detected, with an intensity far greater than that of the plasma induced background emission, and was found to be co-linear with the exciting laser beam. Use of an iris showed it to be propagating within the dimensions of the laser beam. Previous studies³⁵ on hydrogen have illustrated the bidirectional nature of this emission, but only the forward direction was examined in this work. The ASE is at 844.6 nm and corresponds to the same transition as the spontaneous fluorescence process, (figure 3.6). The high sensitivity of the intensity of ASE to the concentration of the $3p^3P$ level was mentioned in connection with figure 3.7, and is illustrated further in figure 3.8, where ASE is plotted against the simultaneously measured fluorescence signal, the latter being proportional to the excited state. The result correlates well with the general form predicted by theoretical modelling of ASE³³, (discussed above).

The dependence also explains the observed differences and similarities between fluorescence and ASE as a function of ground state concentration, (figure 3.9). The concentration is varied by altering the rf. power, and for the 500 mTorr data there is reasonable agreement between fluorescence and ASE, whilst in the 50 mTorr case the correlation is poor. At the lower pressure, the concentration of oxygen atoms is reduced and this, combined with slightly lower laser energy used for the 50 mTorr scan, means that the ASE is in the exponential regime and hence there is poor correlation between ASE and fluorescence. In the 500 mTorr experiments, the ground state, and thus excited state concentration, is higher so that ASE is near the saturation region. This results in similar responses for fluorescence and ASE. The non-linear dependence of the ASE on the concentration

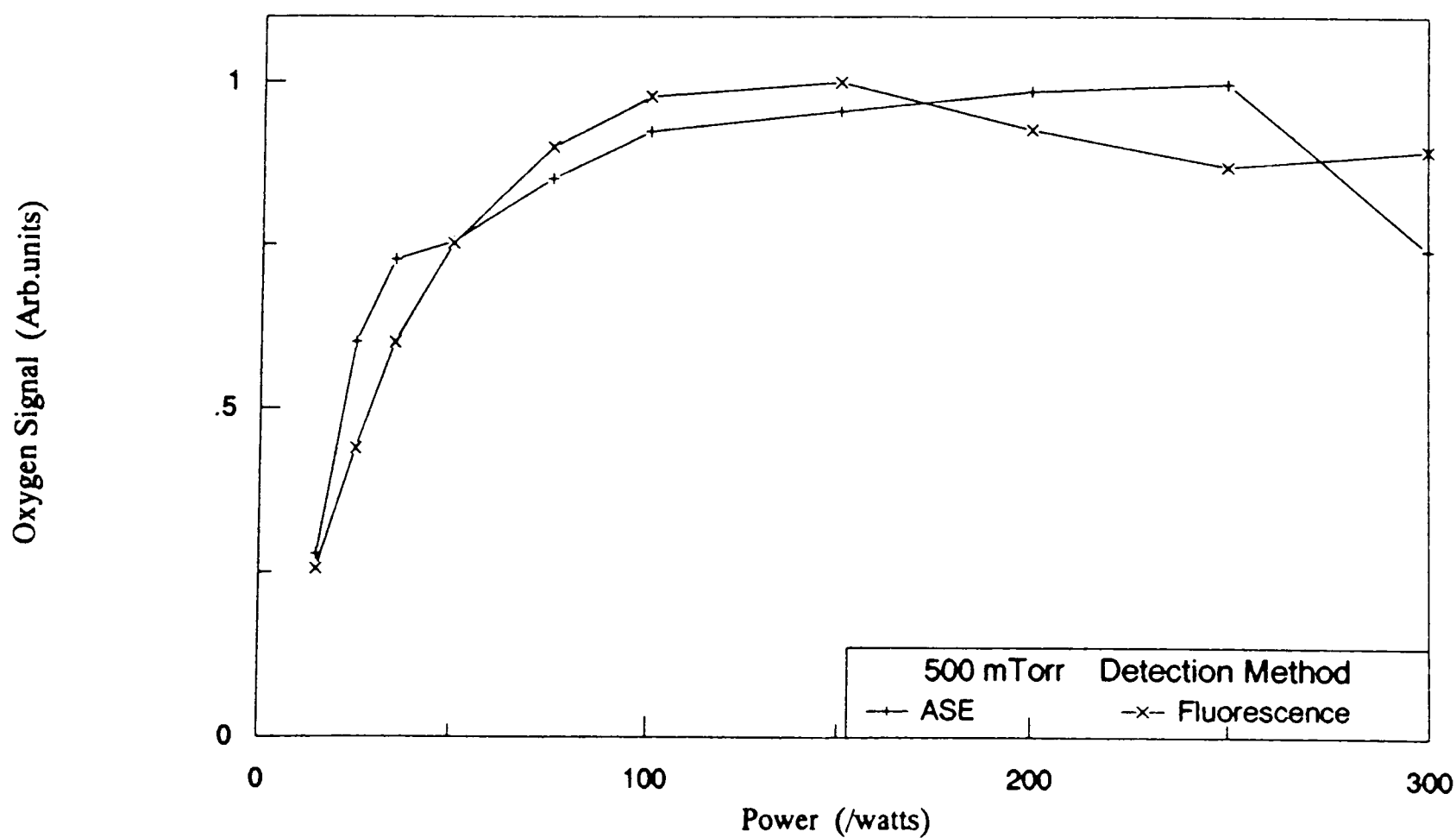
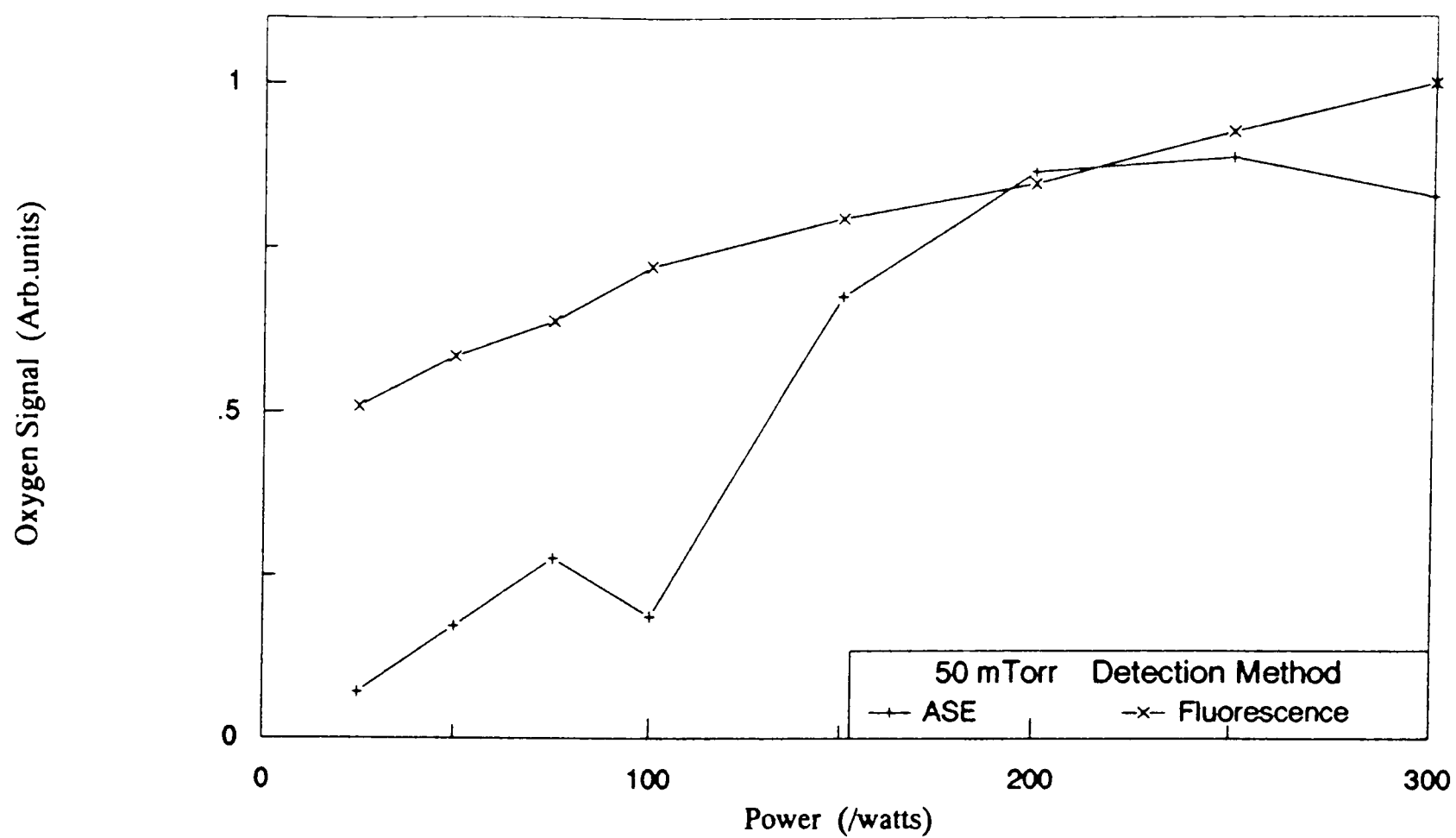


Figure 3.9 Comparison of the spontaneous fluorescence and ASE measured as a function of rf power, at 50 mTorr and 500 mTorr in a 85% O₂ plasma.

of oxygen atoms was often observed and (sadly) acts as a major restriction against using ASE as a diagnostic technique.

The dependence manifests itself in other experimental observations, in particular the excitation linewidths and kinetics of oxygen atoms. The excitation spectra obtained using ASE as the detection method are given for the three spin orbit ground states in figure 3.10, together with those gained using spontaneous fluorescence for detection. In the ASE case, the observed linewidths are dramatically reduced leading to resolution of the upper spin orbit states. The linewidths observed are far narrower than the Doppler width for room temperature oxygen atoms, as described in section 3.2. An explanation for this behaviour is as follows. In the wings of each spin orbit transition, the concentration of atoms being excited by the laser is small relative to that in the centre. Due to the exponential dependence of ASE on concentration, ASE from atoms excited by the peak of the transition is amplified to a greater extent than from those in the wings. The result is a relative enhancement of the peak of the transition and hence narrowing of the line shape. ASE can thus obtain sub-Doppler spectra of the spin orbit transitions, but great care would be required to relate the intensities measured to populations or line strengths.

Figure 3.11 shows the decay curve for oxygen atoms measured by both ASE and fluorescence. Enhancement of ASE at higher concentration of oxygen atoms, (that is at early times after plasma extinction), is again observed and this prevents the use of ASE for kinetic measurements.

3.4.2 Effect of ASE on Fluorescence Yields

The ASE mechanism involves the rapid stimulated depletion of the laser excited $3p^3P$ levels, and as discussed in section 3.3, such a process will affect the measured spontaneous fluorescence signal. This effect explains the otherwise confusing observation that the oxygen decay rates depended on the the spin orbit state probed. In figure 3.12, decay curves for the three spin orbit ground states are shown. The laser energy and plasma conditions were kept constant for all three decays, but as can be seen there are significant differences between them at early

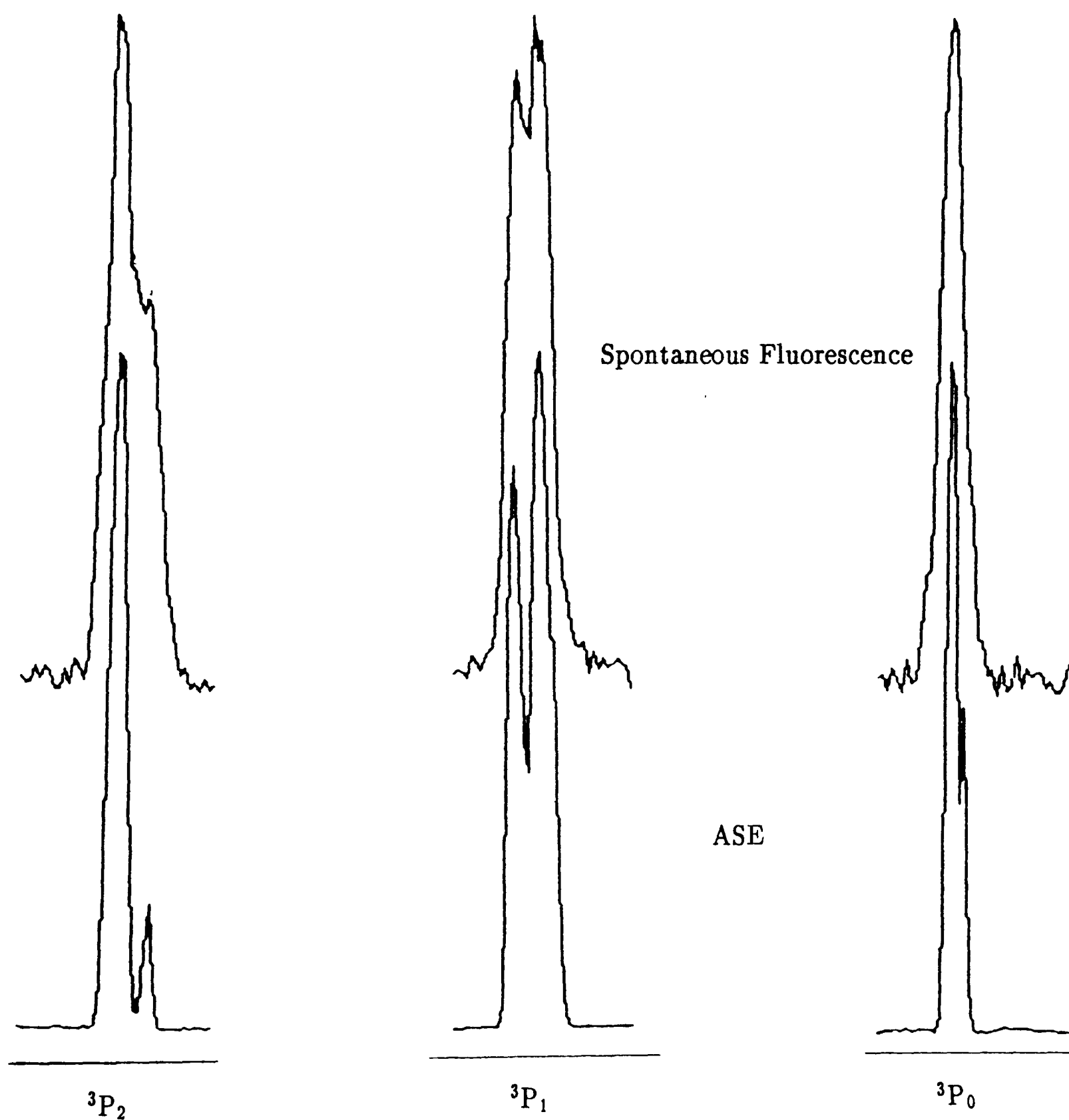


Figure 3.10 Comparison of the spectra of transitions from the three spin orbit ground states using ASE and spontaneous fluorescence as the detection method.

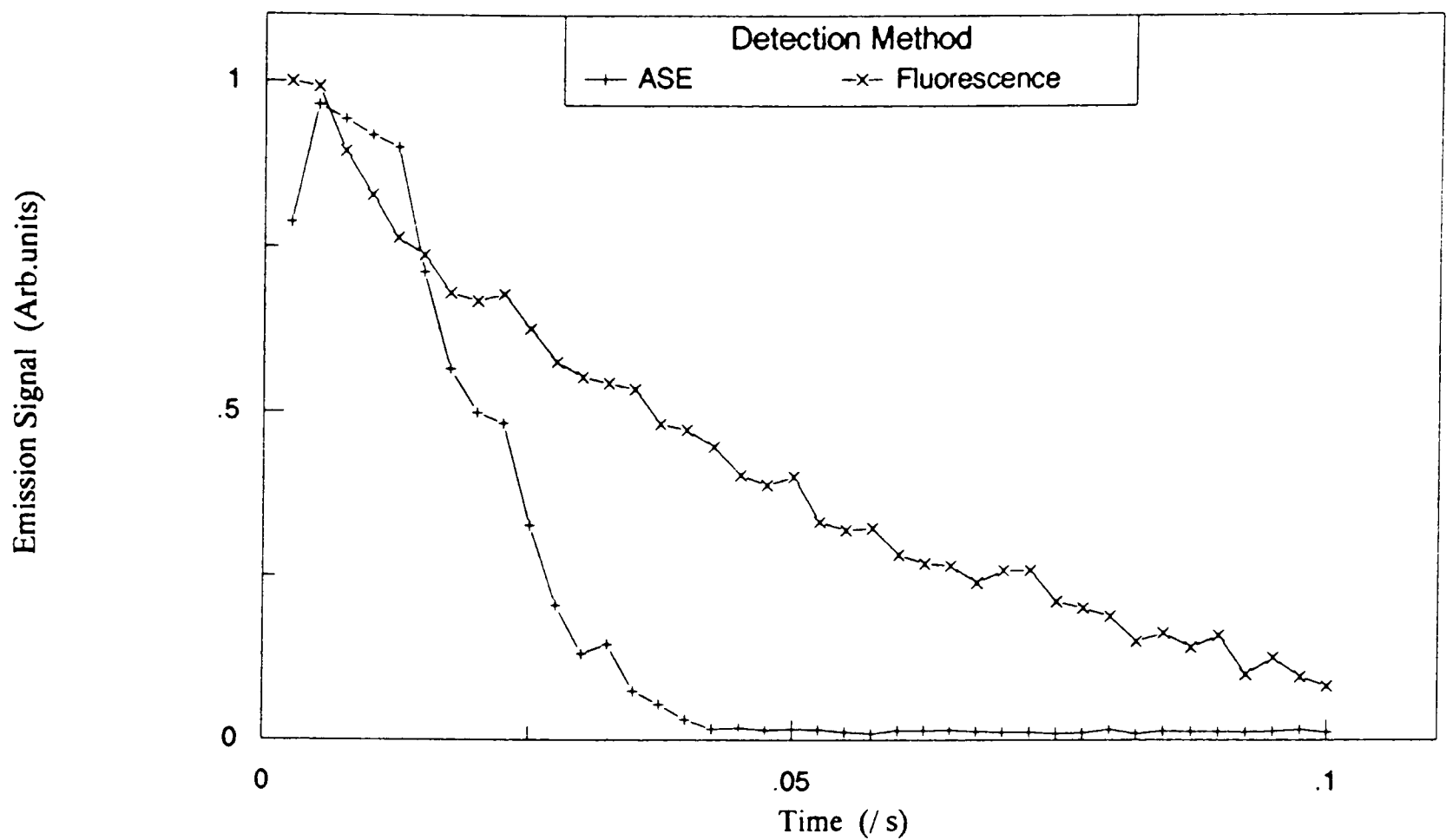


Figure 3.11 Temporal variation of oxygen atoms detected by ASE and spontaneous fluorescence after plasma extinction in a 85% O₂, 1 Torr, 200 W plasma.

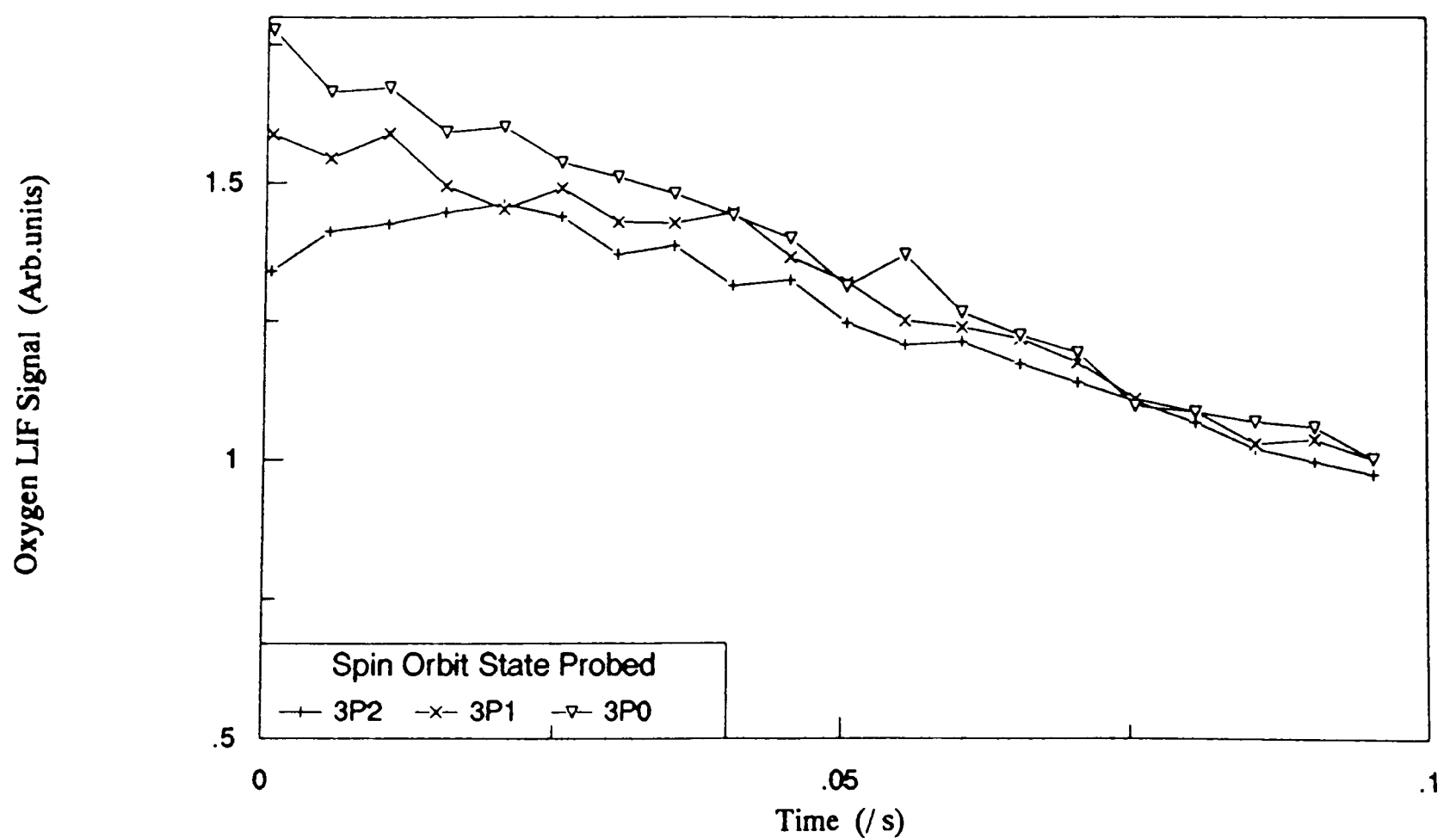


Figure 3.12 Observed decay curves for the three spin orbit ground states of oxygen taken after plasma extinction in a 90% O₂, 1 Torr, 200 W plasma.

times. In particular the relative signal level of the $^3\text{P}_2$ curve and to some extent the $^3\text{P}_1$ curve, is reduced compared to that of the $^3\text{P}_0$ trace.

This observation was first thought to be due to cooling of the oxygen atoms after the plasma was extinguished, leading to cascading of the upper two spin orbit states into the $^3\text{P}_2$ state. However, the absence of the expected rapid drop in the $^3\text{P}_0$ concentration at early times, and the observation of ASE during the $^3\text{P}_2$, (and to a lesser extent $^3\text{P}_1$), scans leads to another explanation. At early times, ASE depletes the $3\text{p}^3\text{P}$ levels for excitation of the $^3\text{P}_2$ transition, which, as seen in figure 3.11, is when the ASE is most intense. The depletion is highest for the $^3\text{P}_2$ transition because of the high relative concentration of atoms in this spin orbit state.

This explanation was tested by following the loss rate of oxygen atoms measured using the $^3\text{P}_2$ and the $^3\text{P}_1$ transitions, at a variety of laser energies. In each case the fluorescence and ASE were monitored and the results are shown in figures 3.13 and 3.14. Figure 3.13 shows that by reducing the laser energy used, the $^3\text{P}_2$ decay curve can produce the same loss rate as the $^3\text{P}_1$ trace. This variation of decay rate with laser energy is also seen in figure 3.14, with the lowest rate corresponding to the higher levels of ASE, and can be attributed to the ASE mechanism causing depletion of the $3\text{p}^3\text{P}$ state, and hence lower than expected signals at early times. This has major implications as far as the use of laser induced fluorescence for the determination of loss rates of atomic oxygen, and clearly illustrates the need to carry out these measurements under conditions of no ASE.

ASE can also effect the spin orbit temperature measurements. When ASE is present, the $^3\text{P}_2$ transition is again most reduced in intensity, which results in the apparent measurement of higher temperatures, with values of 1000 K and above. Previous LIF studies have also measured the oxygen atom temperature to be between 500 K and 1000 K¹⁹, and it is possible that these values were a result of this misleading ASE effect.

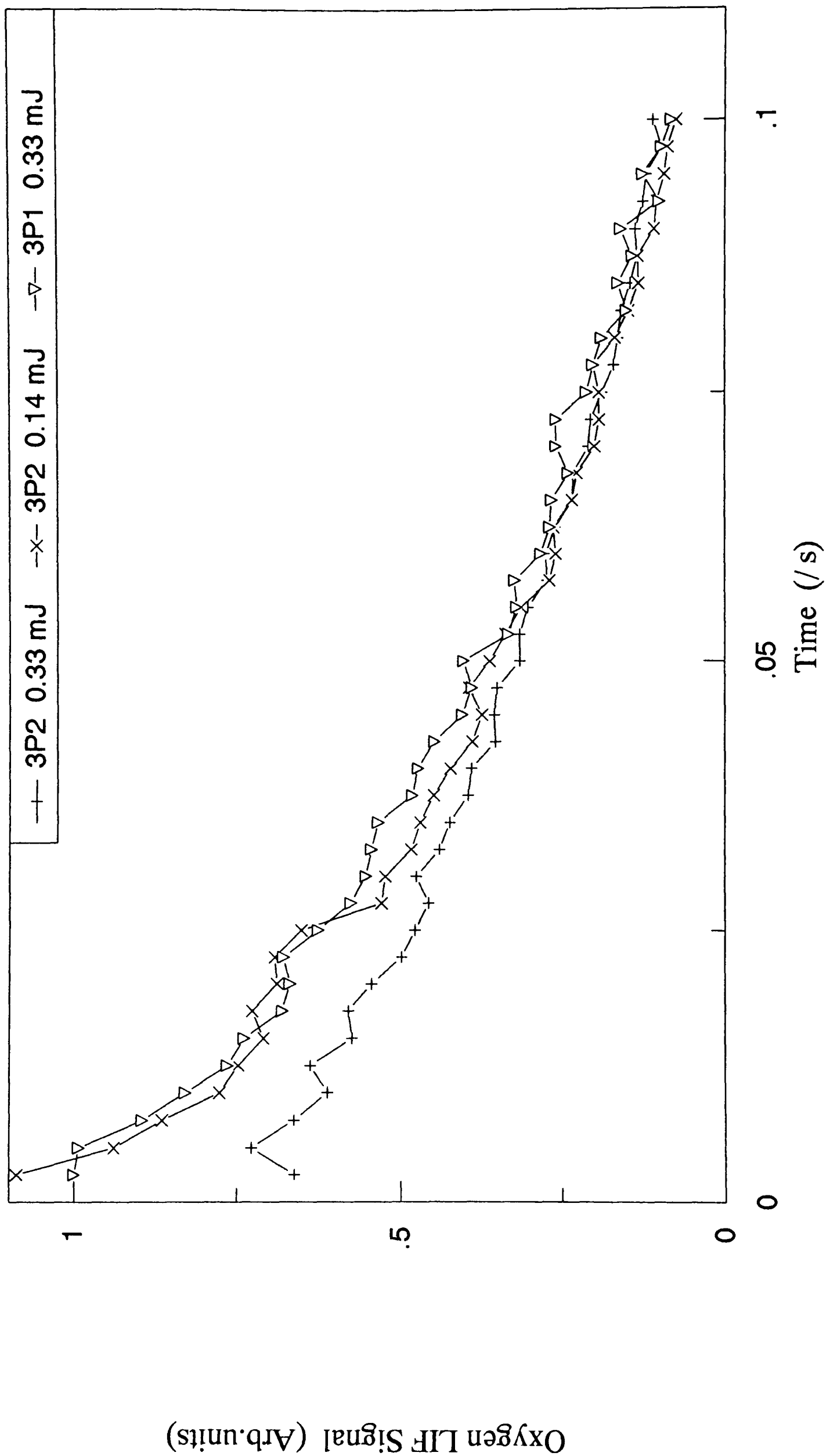


Figure 3.13 Normalized decay curves for two spin orbit ground states of oxygen in an 85% O₂, 1 Torr, 200 W plasma, showing the effect of laser energy.

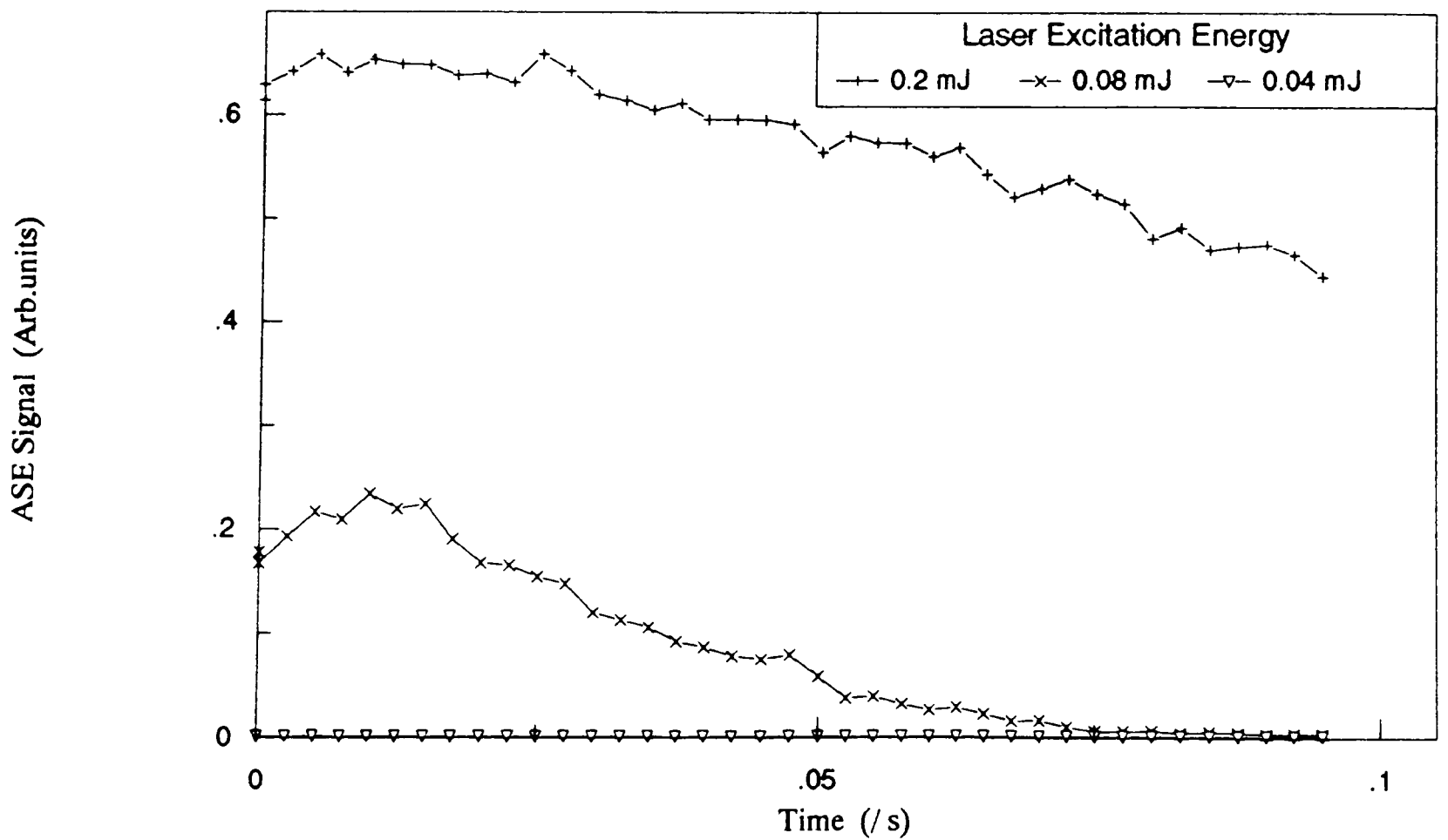
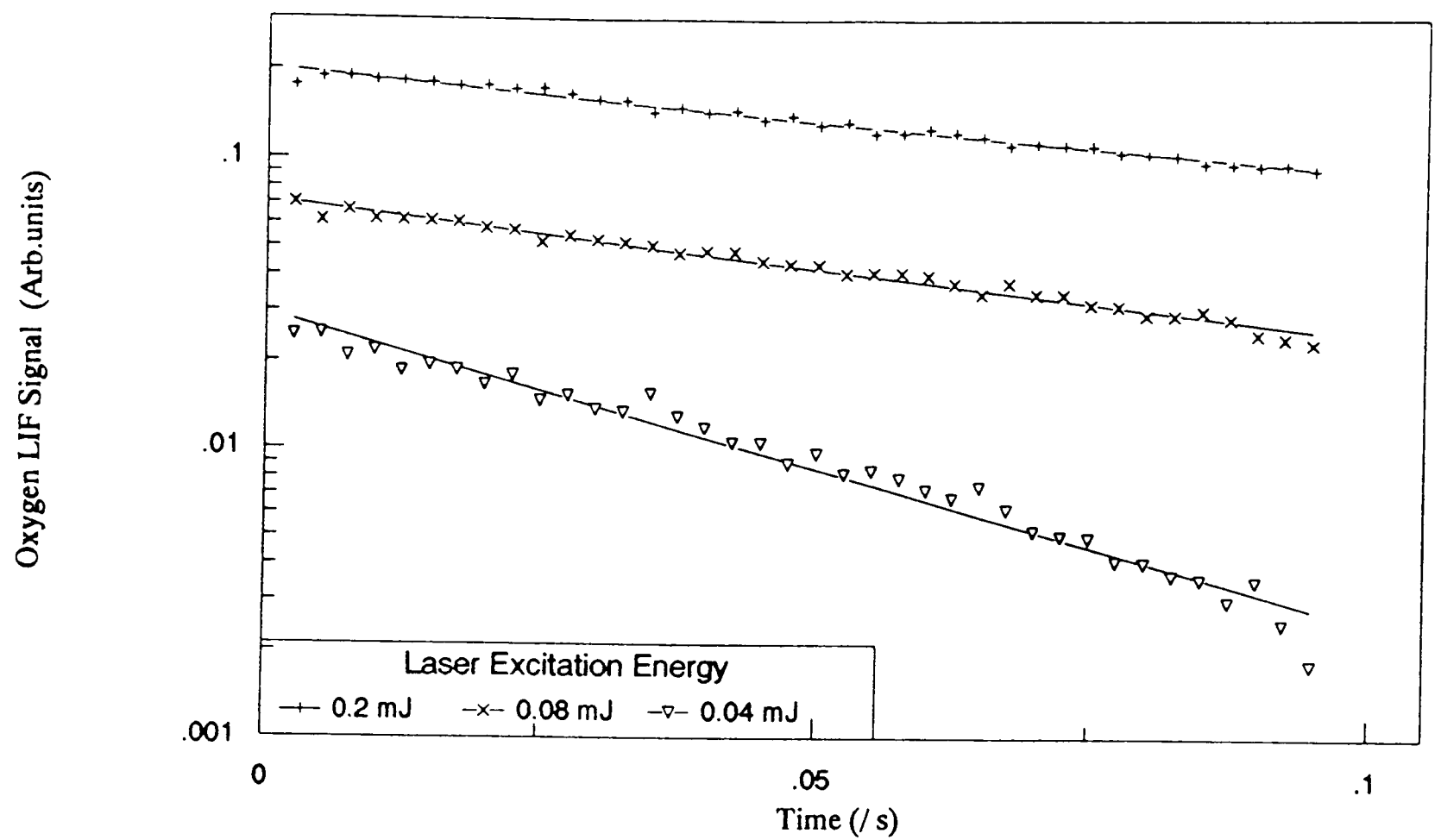


Figure 3.14 Decay curves for oxygen detected by fluorescence and ASE after laser excitation of the $^3\text{P}_2$ ground state at three laser energies, (90% O_2 , 1 Torr 200 W).

3.4.3 Polarization Effects

The polarization of the ASE and spontaneous fluorescence was measured relative to the polarization of the exciting laser radiation. The laser radiation was predominantly horizontally polarized, but a calcite polarizer was positioned as the last optical component before the laser entered the plasma chamber, to ensure that only horizontally polarized laser radiation was present. The ASE and fluorescence were measured using the filter systems to remove the complications of the sensitivity of monochromator gratings to polarized light, and gel polarizers were used to pass the required polarization of the emission.

The spontaneous fluorescence was found to be unpolarized for all three spin orbit ground states as expected³⁶, under conditions of both 100 mTorr and 1 Torr, whilst the ASE was polarized, although the results obtained were unclear. The resolution of some of the upper spin orbit states allowed individual spin orbit transitions to be probed and initial results showed predominantly horizontal polarized ASE for transitions from the $2p^3P_2$ state, whilst for the 3P_1 and 3P_0 states approximately equal levels of ASE were observed with the polarizer passing vertically and horizontally polarized radiation. However, it was noted that in these latter cases, the sum of the two components, vertical and horizontal, was greater than the signal obtained when no polarizer was present. This can only be explained if the polarization lies between the horizontal and vertical orientations of the polarizer and led to some experiments where the gel polarizer was placed on a rotating mount, and the ASE signal was measured as a function of the angle of the polarization passed.

A selection of the results are shown in figure 3.15. As can be seen the emission is polarized, but the polarization vector does not always correlate with that of the laser beam. In some cases, the polarization vector appears to have been rotated by angles of between 0° and 45° . This behaviour was not always observed as can be seen from the figure, and although it was frequently seen, no parametric variations of the laser or plasma were found to correlate with the presence of this effect. The rotation effect was observed for all resolvable spin orbit transitions,

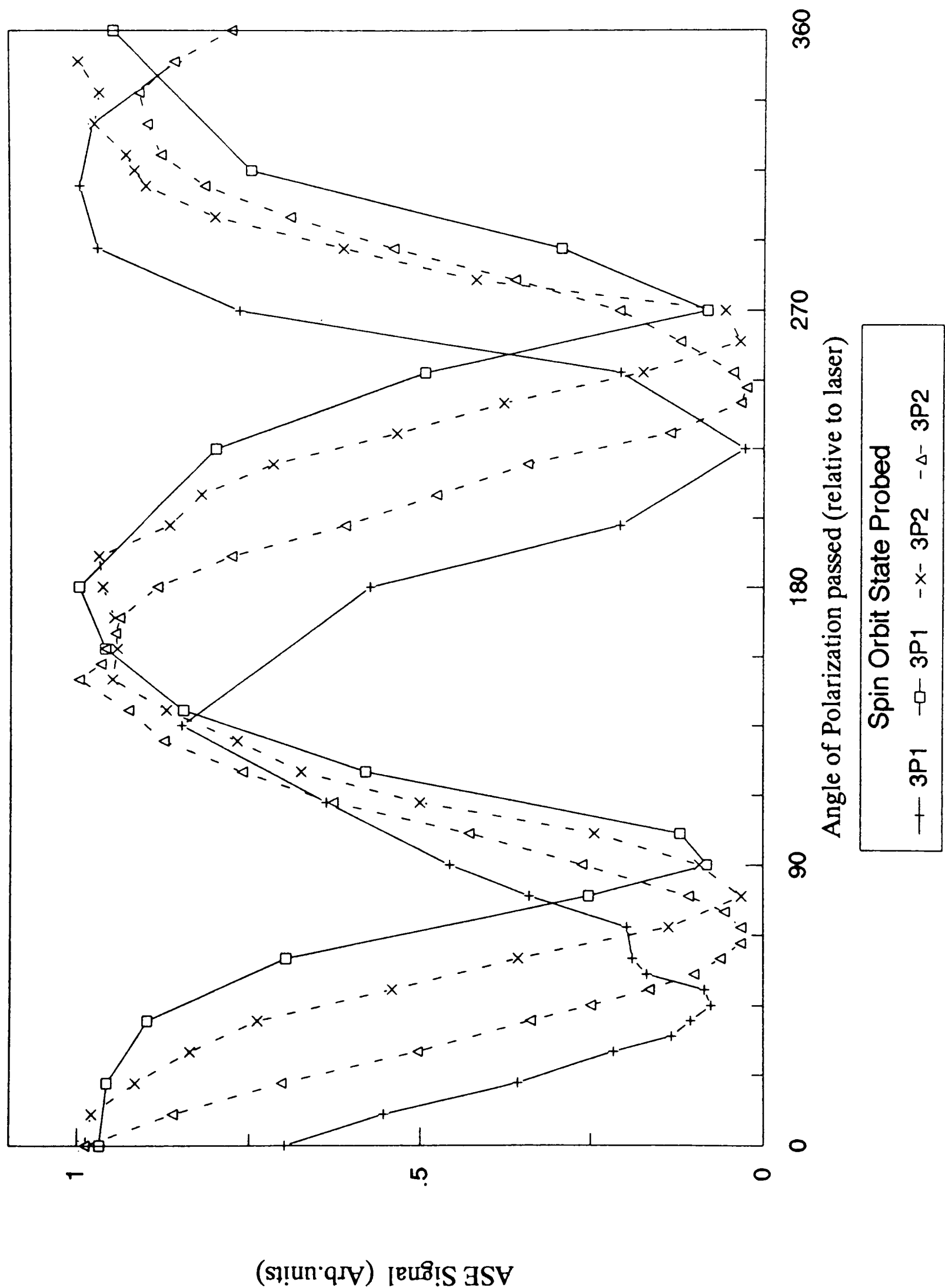


Figure 3.15 Variation of ASE signal with angle of polarization passed, relative to the polarization of the laser beam, indicating in some cases, an apparent rotation.

although they also demonstrated the more explicable horizontal polarization.

Of particular interest is that the rotation was always found to be in one direction and thus suggests some sort of "handedness". Magnetic fields are known to rotate the polarization of radiation with the rotation depending on the direction of the field³⁷. This effect, known as Faraday rotation, is used in tokamak plasmas to measure the magnetic fields present^{37a}. The angle of rotation is generally small, even for large magnetic fields^{37b}, and since no fields of such magnitude are expected to be present in parallel plate rf plasma chambers, this effect is unlikely to account for the rotations seen in this study. Experiments however, were carried out to compare the rotation effect whilst the plasma was ignited to that 5ms after the plasma was extinguished, to see if the electric rf fields influenced the phenomenon. The results are given in figure 3.16 and show no variation in the rotation as a function of time after plasma extinction, which suggests that the rf fields were not responsible.

Limited studies on the polarization of ASE were carried out on the flow cell apparatus and revealed no rotation of the emission. The non – reproducibility of the observations in the rf system suggest that the behaviour is an artifact of the experiment. Effects such as thermally induced birefringence however cannot account for the large angles of rotation measured, and no experimental explanation has been found. Further experiments are clearly required to explain these observations.

3.4.4 Other Observations

A direct comparison between the magnitude of ASE and spontaneous fluorescence was carried out using the same detection system, and the magnitude of ASE signal was found to be 10^3 times greater than the fluorescence signal detected perpendicular to the laser beam. If the limited solid angle of collection is allowed for and an isotropic distribution of the fluorescence is assumed, the sum of the fluorescence intensity over all space was calculated to be about a quarter of that of the ASE. However, the excitation zones responsible for the respective emissions were

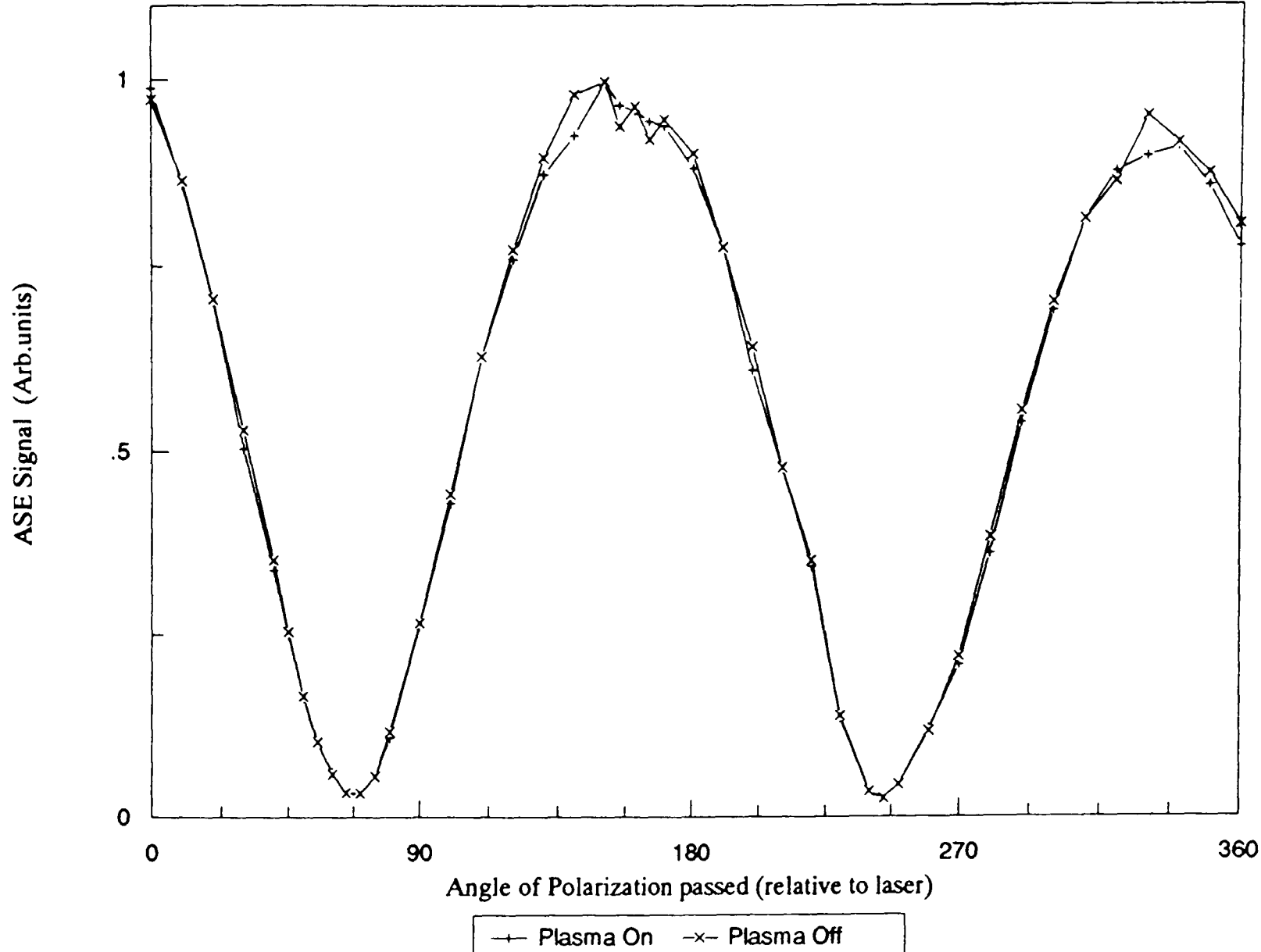


Figure 3.16 Comparison of the variation of ASE signal with angle of polarization passed, during and 5 ms after a plasma pulse, ($^3\text{P}_2$ spin orbit state probed).

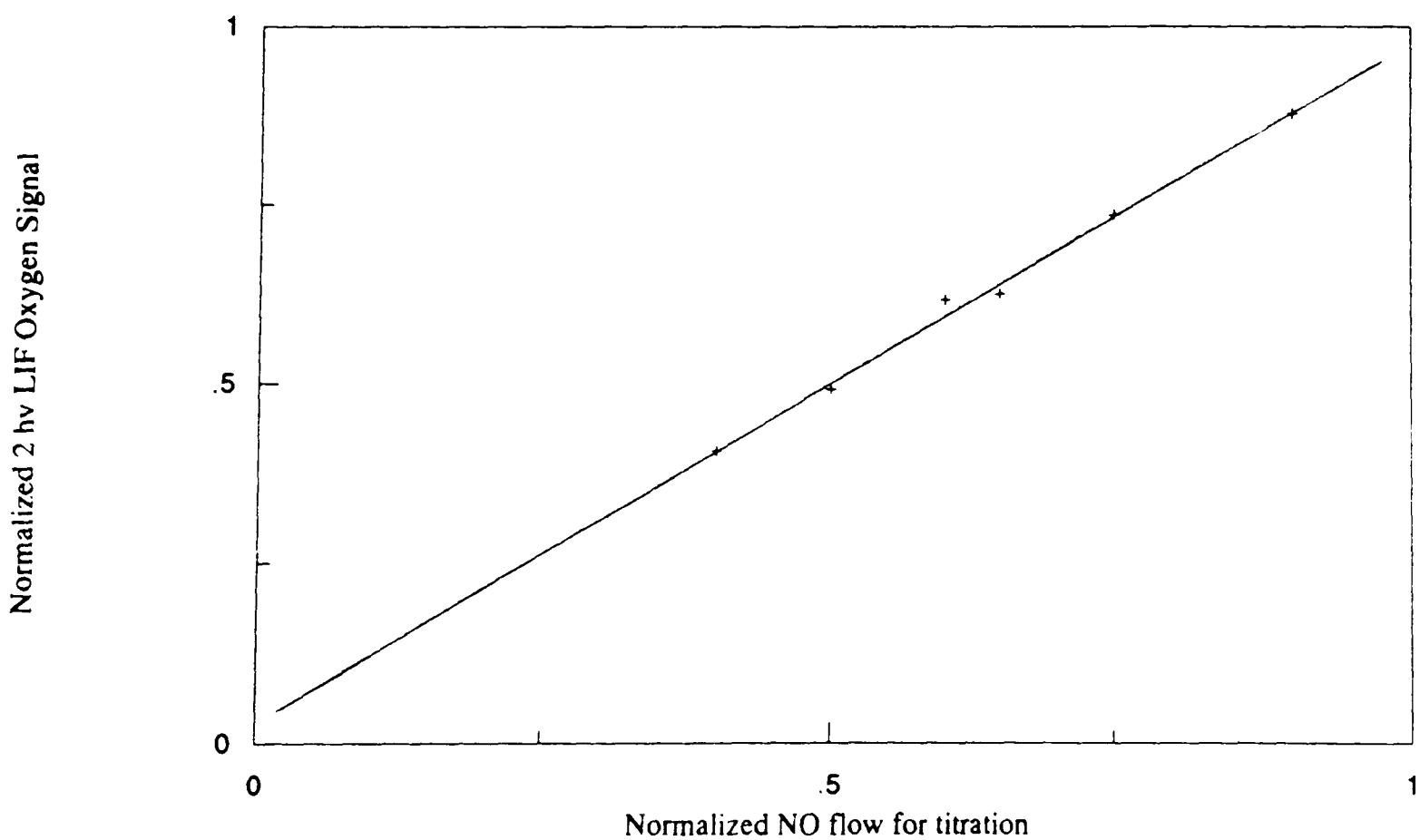


Figure 3.17 Variation of two photon LIF signal with titration measurements of oxygen in the flow cell, using O_2 flow through the microwave discharge to vary the oxygen atom concentration.

different. Due to the size of the collection window ($\phi = 36$ mm), the observed fluorescence emanated from a short length of the laser excitation volume inside the plasma, whereas the ASE signal resulted from emitting atoms throughout the length of the plasma chamber. The laser was focused at the centre of the chamber and so the effect of the excitation region near the walls was lower than that from the centre, but the laser beam passed along a pathlength of at least 300 mm through the oxygen atoms, and as mentioned above the pathlength has been shown to be an important parameter in the magnitude of ASE³³. Also the ASE may not radiate from the whole of the laser excited region, but may be confined to an inner core, where the laser intensity is highest.

An attempt was made to measure the rate associated with ASE, but the time profile of the ASE was indistinguishable from that of the laser pulse itself. This implies ASE has a time scale shorter than 20 ns, but alternative equipment is required for verification.

ASE has been found to exhibit a number of interesting phenomena. The directional and intense nature of the emission would make it a very suitable optical diagnostic, particularly in a plasma environment where high signal levels are required to overcome the background plasma induced emission. However, the sharp and non-linear dependence of ASE on concentration restricts its use considerably as a quantitative diagnostic technique, but it nevertheless has an important use in the location of the transitions.

3.5 Absolute Oxygen Atom Concentration

The need to measure the absolute concentration of radicals in the plasma has been mentioned and this is particularly true for oxygen atoms because of their importance both as an etchant and as a reactive gas phase species. By measuring this concentration, it was hoped to gain a greater understanding of the chemistry and physics of the plasma, not only for oxygen atoms, but also for species such as CF_2 , CF and fluorine atoms which are directly affected by the oxygen

concentration.

There have been a few previous attempts to measure the absolute concentration of oxygen atoms in a variety of plasma environments. Two of these have been downstream techniques, one using electron paramagnetic resonance¹² and the other involving NO₂ titration³⁸. These require knowledge of the kinetics of the atoms, particularly the heterogeneous recombination rates, to extrapolate the measurements back to the concentration inside the plasma region. Selwyn *et al.*¹⁹ used the two photon LIF and photodissociation technique discussed in section 3.3 as a calibration method, but for this it is necessary to make a number of assumptions about the laser beam profiles. Absorption at 130 nm using a resonance lamp has been used in a distributed electron cyclotron resonance plasma¹³ and although calculations were done to allow for the line shape problems associated with these absorption experiments, this problem was not investigated experimentally.

3.5.1 Absolute Concentration Measurements

This work used the two photon laser induced fluorescence technique, and to circumvent the problems associated with obtaining absolute concentration measurements from LIF, such as sensitivity of the detection system and assumptions about the laser beam profile, a comparative experiment was devised. In the experiment, the signal from a known concentration of oxygen atoms generated in a flow cell by a microwave discharge, was compared to that from the plasma. The LIF spectrum of oxygen was first measured in the plasma chamber, which was replaced by the flow cell apparatus, without modification or movement of the laser beam and collection optics. The LIF spectrum of oxygen was then taken in the flow cell and the oxygen concentration was determined by the NO / NO₂ air–afterglow technique.

Laser induced fluorescence signals for part of the NO ($A(v' = 0) - X(v'' = 0)$ band were taken using a known concentration of NO, in both the experimental set-ups and were compared to ensure that the optics were not affected by the exchange or the chamber geometries. The windows through which the

fluorescence was collected were different in the two cases. For the plasma chamber, the window had a diameter of 36 mm and was positioned 280 mm from the laser beam path, (f/7.8), and the flow cell window had a diameter of 20 mm placed 60 mm from the beam, but the limiting aperture for each system was the first, collecting lens, which had a diameter of 30 mm and was 300 mm from the beam, (f/10). The f. number method is however strictly applicable for a point source, and in these experiments there was an extended source and an extended collecting slit. Therefore it was necessary to limit the collecting aperture to ensure that the images from both set-ups were the same. This was done and the NO LIF signals from the two systems were found to agree to within 16%.

In view of the hazards associated with the variation of fluorescence signal with laser energy, the oxygen (and NO) signals were taken using the same laser power and also with similar atomic concentrations, and conditions were such that no ASE was present. The conditions used were :

Plasma Chamber	50mTorr, 100W, 85% O ₂ / 15% CF ₄
----------------	---

Flow Cell	420mTorr, 0.85% O ₂ / 99.15% Ar
-----------	--

These were chosen so that there would be no quenching of the 3p³P level.

For a correct comparison, all three spin orbit states had to be scanned in both the pieces of apparatus. The distributions were found to be slightly different, with a spin orbit temperature in the plasma chamber of 305 K and that in the flow cell of 470 K. This difference in populations was considered in the final calculations of concentration.

Details of the mechanism and kinetics of the titration technique are given in Appendix 1, but the general concept is quantitative removal of oxygen atoms by NO₂ molecules, which ultimately results in emission of radiation, the so called "air-afterglow", and it is this which is used to monitor the end point of the titration. There were two titration points in the cell, as shown in figure 2.4, and in order to

determine the concentration at the LIF observation zone an interpolation was necessary. This was investigated experimentally by varying the oxygen atom concentration and comparing the titration results at both points. The oxygen atom loss was seen to exhibit first order loss kinetics over the range of concentrations tested, which is consistent with a wall removal mechanism. With this information it is possible to calculate the concentration of oxygen atoms in the observation region.

As well as the titration measurements, the LIF signal was monitored as a function of oxygen atom concentration, (varied by O₂ flow through the microwave discharge), in an attempt to certify that the LIF and titration techniques, under the conditions used, showed a linear relationship. A plot of LIF signal against oxygen concentration, as measured by titration, is given in figure 3.17, and shows an excellent correlation indicating that the LIF signal is proportional to the ground state oxygen atom concentration under these conditions.

The relative intensities of fluorescence measured in these absolute concentration studies are summarized in table 3.4.

	Flow Cell	Plasma Chamber
NO LIF signal	0.84 ± 0.04	1.0 ± 0.04
Oxygen LIF signal	1.06 ± 0.05	1.0 ± 0.06

Table 3.4

The concentration of oxygen atoms in the flow cell, measured by titration and interpolated for the LIF observation zone, is $9.33 \pm 0.45 \times 10^{13}$ molecules cm⁻³. Allowing for the difference in nitric oxide and oxygen LIF signals, this gives a concentration for a 50 mTorr, 100 W, 85% O₂ / 15% CF₄ plasma as

$$\underline{7.40 \pm 1.4 \times 10^{13} \text{ molecules cm}^{-3}}$$

This is equivalent to a 5.4% conversion from molecular oxygen, which is comparable with percentages obtained from similar plasma systems.

3.5.2 Quenching of 3p ³P by O₂ and CF₄

The flow cell apparatus was also used in an attempt to determine the quenching rate coefficients for O₂ and CF₄ on the 3p³P state of oxygen. The idea was to measure the LIF signal in the absence of any quenching and to compare it with the signal when quenching was present. Any observed reduction in signal could then be related to the competing processes of quenching and radiative decay, and from the known rate of the latter, that of the former could be obtained.

This was done by flowing molecular oxygen and CF₄ through an extra line connected to the flow cell and entering upstream of the discharge input. However, addition of these gases affected the discharge as well as the total pressure and flow rate, which influenced both the production and loss rates for oxygen atoms in the cell, and thus altered the concentration of oxygen atoms in the LIF observation zone. To account for the changes in concentration, oxygen atom titrations were carried out which enabled a ratio of the LIF signal to the ground state concentration to be obtained, which were then used to determine the quenching coefficients. However, the coefficient was found to be very sensitive to the signal:concentration ratio and the results obtained indicated large variation between runs, which illustrated the need for a more direct measurement of the quenching rate, such as monitoring the radiative lifetime as a function of pressure of the quenching species. This technique was used in a previous study by Bittner *et al.*²⁷ to measure the quenching rate coefficient for oxygen and hydrogen atoms by rare gas and several molecular collision partners. For oxygen atoms, they obtained a rate of $6.3 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ with molecular oxygen, $2.1 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ with argon and values between $4.3 - 6.6 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ for molecular species, such as CO₂ and CH₄.

Comparison with the values obtained in this work suggest that molecular oxygen has a slightly higher quenching rate coefficient than CF₄. The data also showed that for the plasmas used in this study, with pressures in the 50 – 500 mTorr range, the LIF process was affected by quenching of the 3p³P state and that a correction factor was required. These factors were calculated using values of $6.3 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ for the rate constant with molecular oxygen and $4.0 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$

for the rate with CF_4 , and have been used to correct all the parametric oxygen atom data taken by laser induced fluorescence. It should be noted that at the highest pressures used in this work, 500 mTorr, the quenching rate in pure oxygen is $1.02 \times 10^7 \text{ s}^{-1}$ and thus accounts for 27% of the total decay processes from the upper state. An error in the evaluation of the CF_4 quenching rate constant will thus not significantly affect the trends in the parametric data.

It can be seen that two photon laser induced fluorescence of oxygen atoms is a complicated system and great care is required when interpreting results taken using such a technique. However, using low laser energies so that ASE is not present and calibrating or calculating the quenching rate can provide a qualitative and quantitative tool for this important radical species in gas phase plasmas. As well as the absolute measurement of oxygen atoms described in this chapter, this technique has been used to determine the relative concentration and loss rates of oxygen atoms as a function of plasma conditions and spatial position, at all times ensuring minimal variation in the laser energy and excitation zone.

Chapter Three References

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Chapter Four

Spectroscopy of CF

The CF radical has been known for 40 years and was first observed by Andrews and Barrow¹, who made a rotational analysis of a variety of vibrational bands for the A–X and B–X electronic transitions. It has been studied by a number of groups both experimentally and theoretically, generally to obtain knowledge of the structure and form of the radical. More recently CF has been identified as an important species in fluorocarbon plasmas and has been detected by optical emission², laser induced fluorescence³ and I.R. laser diode spectroscopy⁴. In these latter studies, the steady state concentration, internal state distributions and kinetics of CF were of interest.

For the work in this thesis, laser induced fluorescence was used to investigate the incompletely defined predissociation of the A state of CF, for $\nu' \geq 2$, which involved the observation of laser induced emission from the $\nu' = 2$ level and an attempt to determine the magnitude and mechanism of the predissociation rate. This was necessary to examine the suitability of laser induced fluorescence as a diagnostic for CF in processing plasmas, and in particular to ensure that the concentrations and internal state distributions obtained from other vibrational bands were valid³.

4.1 A – X Transition of CF

The electronic configuration of the CF radical in its ground state is

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^1$$

The unpaired electron in the antibonding 2π orbital leads to a $^2\Pi$ state with orbital angular momentum about the internuclear axis of 1. This can couple with the electron spin to produce two spin orbit components, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, the lower of which is the $^2\Pi_{1/2}$ and is assigned by convention as the F1 state, with the $^2\Pi_{3/2}$ state as F2. The orbital angular momentum is strongly coupled by an electrostatic field to the internuclear axis, and the spin orbit coupling pins the electron spin to this axis too.

The angular momentum associated with nuclear rotation, N , forms a resultant total angular momentum, J , with the total electronic angular momentum, Ω . These two angular momenta interact, splitting each J level into Lambda doublets. This splitting increases with J and relates to the distinction between the π orbital lying in or out of the plane of rotation of the molecule and pertains to a phenomenon known as electron slip. Each doublet has differing parity and a degeneracy of $2J + 1$. These observations are consistent with the ground state being an example of Hund's Case (a).

The A state is produced by excitation of the unpaired electron to the 6σ Rydberg orbital to produce a $^2\Sigma^+$ Rydberg state. The only electronic angular momentum is the spin which is not tied to the internuclear axis, characteristic of Hund's Case (b). It adds and weakly interacts to the nuclear framework angular momentum, N . Strictly for Hund's Case (b), N first adds to the electronic orbital angular momentum, Λ , to produce K , but since Λ is zero N and K are the same. Thus, $J = K + \frac{1}{2}$ (F1 state) and $J = K - \frac{1}{2}$ (F2 state).

For transitions of the type Hund's Case (b) to (a), the selection rules are $\Delta J = 0, \pm 1$, producing 12 branches, P_{ij} , R_{ij} and Q_{ij} , where i and j represent the F type of the upper and lower state respectively. This should lead to 12 observed transitions but the spectrum is somewhat simplified due to the negligible spin splitting, and hence near degeneracy of the levels with like N (but different J), in the upper state. This reduces the number of discernible branches to 8; P_{11} , $Q_{11} + P_{21}$, $R_{11} + Q_{21}$, R_{21} , $P_{22} + Q_{12}$, $Q_{22} + R_{12}$, R_{22} and P_{12} . These are illustrated schematically in figure 4.1. The spin splitting in the upper state was resolved for the isoelectronic nitric oxide molecule, during intracavity etalon studies on oxygen atoms and can be seen in figure 3.4.

At high J , there is a transition from Hund's Case (a) to (b) for the $^2\Pi$ ground state, due to the uncoupling of the electron spin from the internuclear axis. This occurs at fairly low J for the CF radical due to the relatively weak spin orbit coupling associated with light atoms. The intermediate nature of the $^2\Pi$ state results in weakening of the branches for which $\Delta K = \pm 2$ (P_{12} and R_{21}), as they

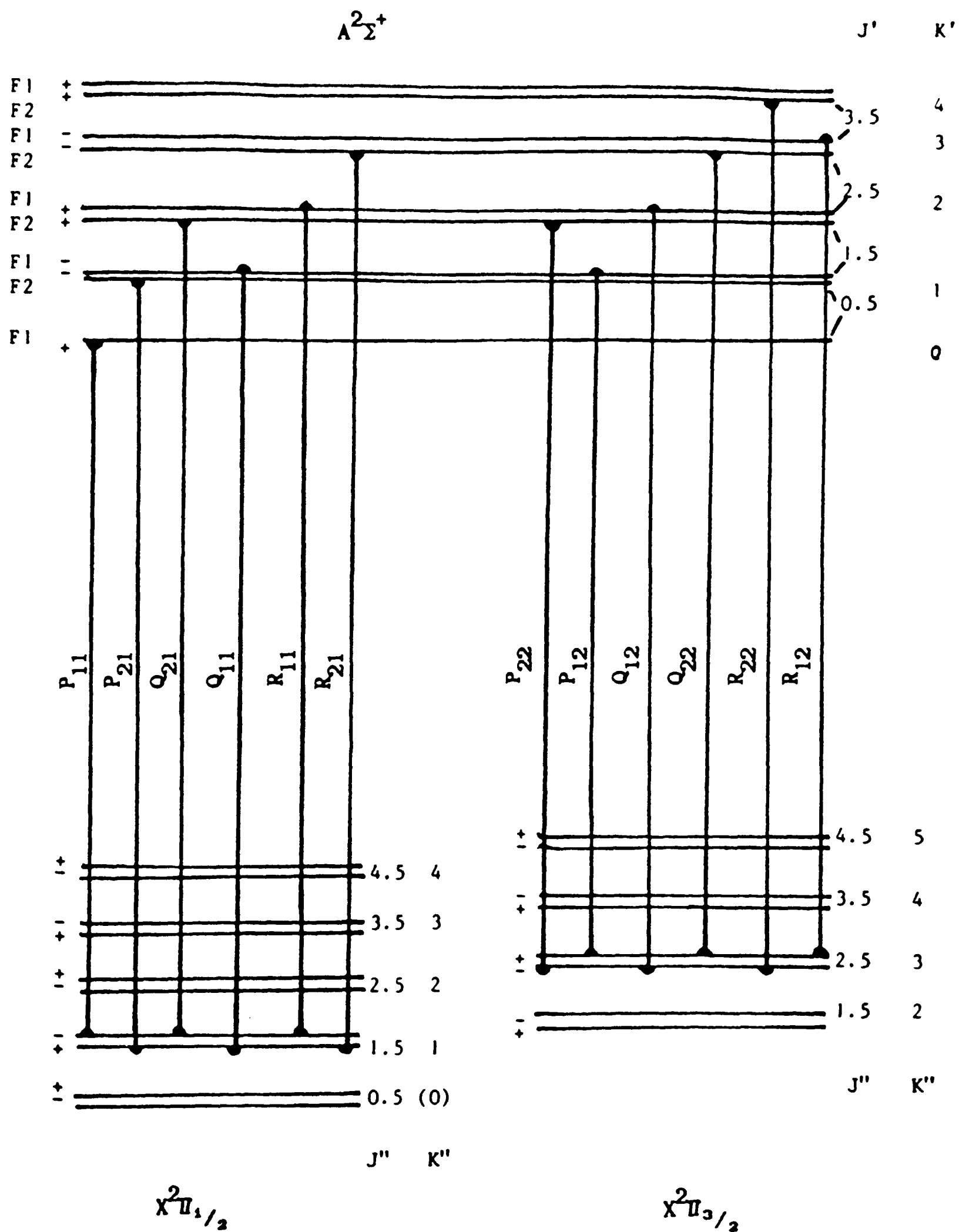


Figure 4.1 Schematic energy level diagram for the CF $A^2\Sigma^+$ – $X^2\Pi$ system, illustrating the observed transitions.

contravene a selection rule for a Case (b) – Case (b) transition, ($\Delta K = 0, \pm 1$). Earls has developed line strength formulae to account for such behaviour⁵.

Experimentally, the A – X system has been studied by a number of workers. After the initial observation by Andrews and Barrow, Porter *et al.*⁶ published a comprehensive analysis of the $(1, \nu'')$ and $(0, \nu'')$ bands and derived the molecular constants of both states. Minor adjustments to these values have subsequently been made, particularly to the ground state, due to a variety of experimental studies, such as electron resonance spectroscopy⁷, laser magnetic resonance⁸, microwave studies⁹ and laser diode spectroscopy⁴. Brown *et al.*¹⁰ published a global fit of the data for the $^2\Pi$ state and it is these constants that are used in the simulations described later in this chapter.

The A state has been shown to be a Rydberg state¹¹, and the internuclear distance and vibrational frequency ($r_e = 1.14 \text{ \AA}$, $\omega_e = 1780 \text{ cm}^{-1}$), which are respectively smaller and higher than the equivalent values for the ground state, ($r_e = 1.27 \text{ \AA}$, $\omega_e = 1308 \text{ cm}^{-1}$), are consistent with this assignment. The near negligible spin splitting is also expected for a Rydberg state.

4.2 Predissociation

In a number of spectroscopic studies, the position and strength of some bands and lines are not as predicted. This is often due to the presence of a perturbation of the energy levels of the species caused by the interaction of two or more overlapping states. The degree of this perturbation depends on the proximity in energy of the states and on a matrix element relating to the wavefunctions and symmetry properties of the states involved. The interaction allows transitions between the states and therefore, if a bound state is perturbed by a dissociative one, the result can be dissociation of the molecule at an energy below the true dissociation of the bound state. This process is known as predissociation.

4.2.1 Predissociation : General Theory

A molecule in a particular (ν, J) state, lying below its dissociation limit, can predissociate into its component atoms by interaction of the (ν, J) state with the continuum "levels" associated with a repulsive state. This is shown in figure 4.2 for a curve crossing case, although avoided crossings, (adiabatic predissociation) may also occur. In terms of energy, predissociation can occur for all bound states which lie above the lowest dissociation limit. Predissociation is however fairly rare for diatomics, which is due to the need for overlapping states that interact strongly. Since predissociation is a form of perturbation, the degree of interaction is related to the perturbation matrix element, with the associated selection rules for which the element is non-vanishing. These rules, which are similar to their optical counterparts, were derived by Kronig¹².

- i. $\Delta J = 0$
- ii. $\Delta S = 0$
- iii. $\Delta \Lambda = 0, \pm 1$
- iv. the states must have the same reflection symmetry

For predissociation, rules (i.) and (iv.) assume that J and the symmetry properties can be defined for a continuous range of levels. This can be done¹³ and the result is that rule (i.) is generally realizable, but the symmetry selection rule does restrict a number of interactions, (such as $\Sigma^- - \Sigma^+$). The spin selection rule is found not to be rigorous, analogous to radiative transitions observed, for example, for heavy molecules. For the third rule, Mulliken¹⁴ called transitions where $\Delta \Lambda = 0$ as homogeneous, as it involves a perturbation between states of the same type, and where $\Delta \Lambda = \pm 1$ as heterogeneous. In the case of $\Delta S \neq 0$, homogeneous refers to $\Delta \Omega = 0$, and heterogeneous to $\Delta \Omega = \pm 1$.

Mulliken¹⁵ also identified several classes of predissociation, using the location of the curve crossing, (energy E_c and internuclear separation R_c), relative to the dissociation energy of the repulsive state, (D_0), and the equilibrium separation of the predissociated state, (R_e), (see figure 4.2). The classification is made up of a

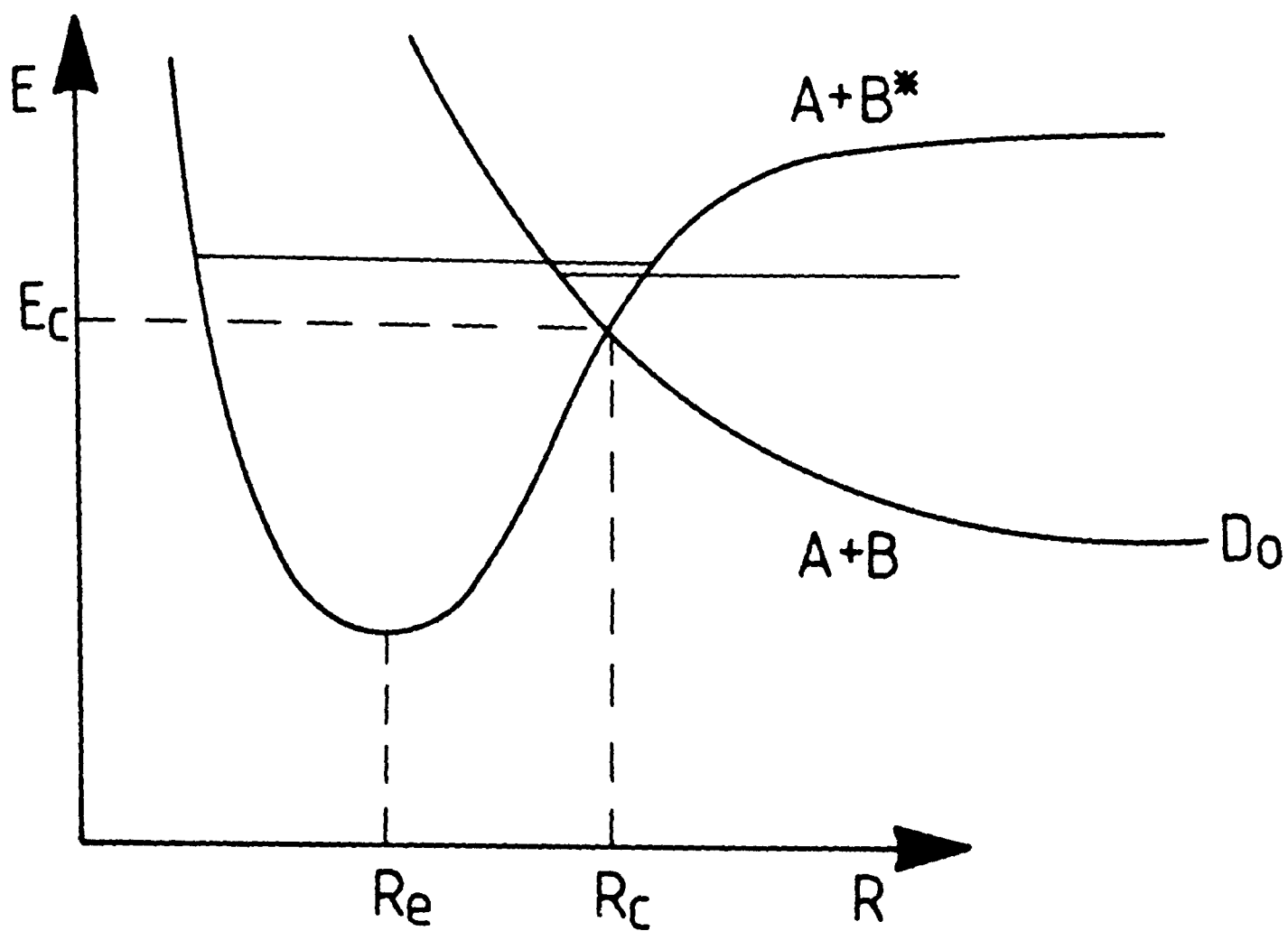


Figure 4.2 Example of interacting levels caused by the crossing of two potential energy curves, intersecting at E_c and R_c .

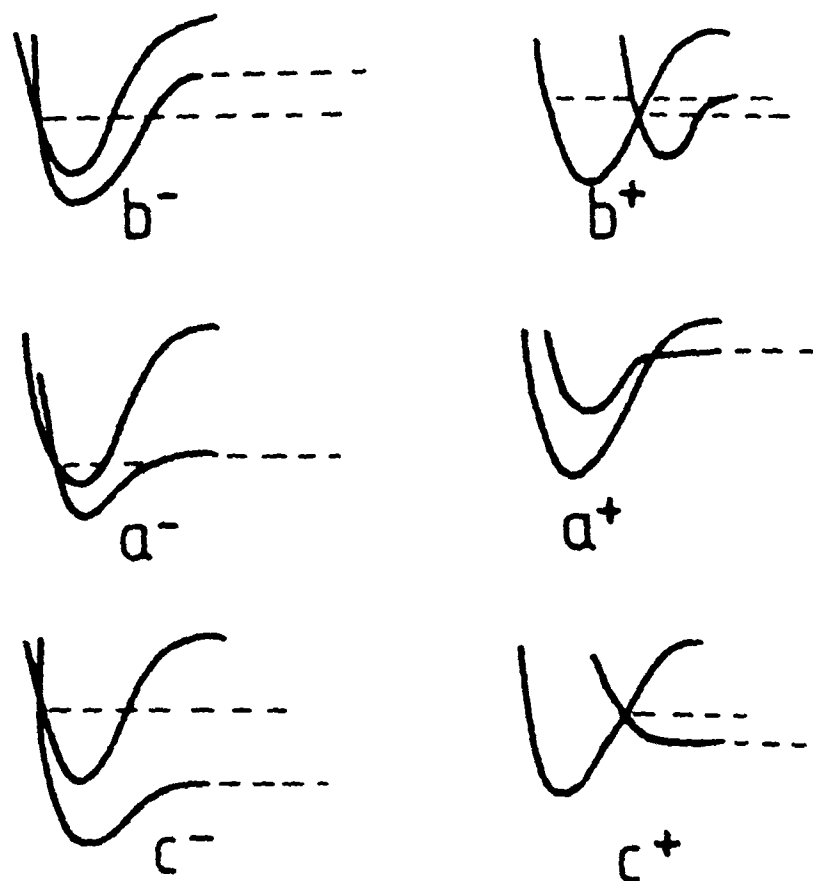


Figure 4.3 Representations of Mulliken's¹⁵ classes of predissociation.

letter and a superscript, where case a,b and c correspond to $E_c = D_0$, $< D_0$ and $> D_0$ respectively and $-$, i , $+$ and o refer to $R_c < R_e$, $= R_e$, $> R_e$ and non-crossing curves. Some of the cases are shown schematically in figure 4.3.

The rate of predissociation depends on the strength of the interaction which can be calculated using the perturbation, or predissociation, matrix element. This matrix element will contain a term relating the overlap of the wavefunction for the repulsive state with that for the bound state. For an outer limb crossing, (see cases a^+ , b^+ and c^+ in figure 4.3), this term shows oscillatory behaviour as the overlap integral varies as a function of ν and J . Large fluctuations in the predissociation rate are seen with ν , and with J for species with large rotational constants such as hydrides. The J dependence with heavier molecules such as O_2 is small. The rates of oscillation can be shown to depend on the difference in the slopes of the two interacting potentials, at the crossing point. Thus, for an inner limb crossing (see cases a^- , b^- and c^- in figure 4.3), the steeper but more equal gradients of the potentials result in reduced oscillatory variation and so the rate of predissociation is less dependent on ν or J .

The effect of rotational motion can also be considered in terms of the centrifugal energy associated with such motion. Conservation of angular momentum requires that a centrifugal term, $\frac{\hbar^2}{2 \cdot \mu \cdot R^2} \cdot (J(J + 1))$, be added to the ordinary electronic potential curve, to produce so called effective potential curves, (R is the internuclear distance and μ is the reduced mass). Such a set of curves are illustrated in figure 4.4. The equilibrium energy of the bound state, now including a term $\frac{\hbar^2}{2 \cdot \mu \cdot R_e^2} \cdot (J(J + 1))$, needs to be greater than the highest part of the effective potential curve for the continuum state for $R > R_c$, if predissociation is to take place. For outer limb crossings, R_c is always greater than R_e and so the rotational energy of the bound state will increase more rapidly than the maximum height of the dissociating curve. Thus, above a critical ν, J limit, predissociation is possible for all ν, J values. The lower limit on ν, J can in some cases lie below the classical limit if tunnelling through the barrier is significant.

For a case b^- predissociation where $E_c < D_0$, since the maximum in the

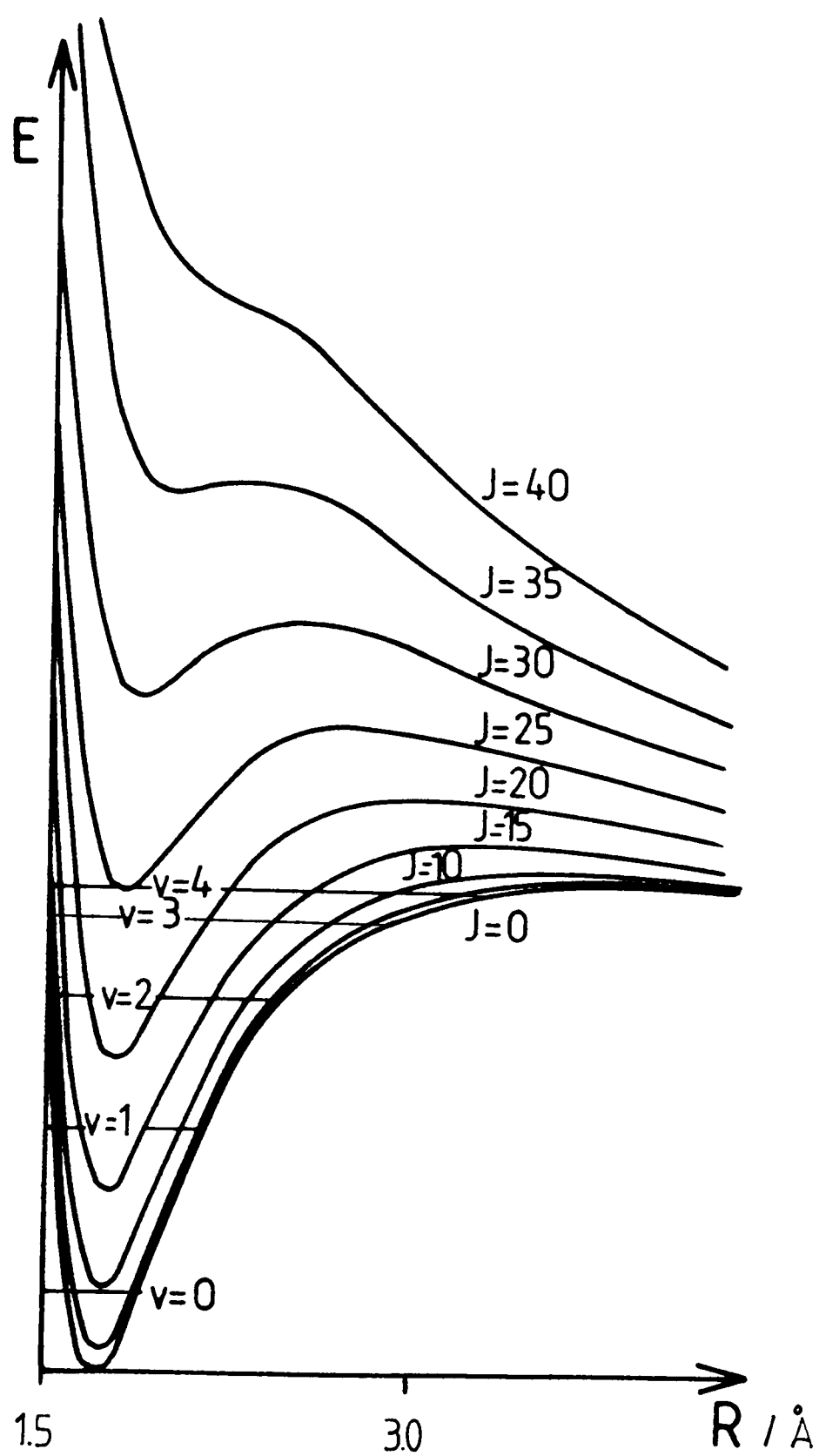


Figure 4.4 Effective potential energy curves of HgH in the ground state.¹⁶

Vibrational levels shown refer to $J = 0$

effective potential will occur for $R > R_e$, then a similar argument holds. However for case a^- or c^- predissociations, where $E_c \geq D_0$, the relevant maximum is now at R_c , and the energy at this point will increase with J faster than the rotational energy of the bound state. Thus, predissociation will only occur below certain critical J values and these values will increase with increasing ν . Figure 4.5 attempts to illustrate this effect. This also means that isoenergetic levels in different vibrational states will not predissociate at the same rate, since the lower ν , higher J level will have a higher barrier, and hence weaker overlap, with the dissociating state.

The full details of the ν, J dependence and the selection rules of predissociation depend on the full predissociation matrix element, and hence on the mode of interaction. This manifests itself in the form of the operator used in the element. The coupling operator can be based on electrostatic, spin orbit or rotational interactions. An electrostatic interaction tends to be important for homogeneous predissociation between states of the same multiplicity, and particularly for light molecules. The spin orbit interaction is the most frequent cause of a perturbation, especially between states of different spin. The effect is greater for heavy systems. Rotational predissociation, often referred to as gyroscopic predissociation to avoid confusion with another type of predissociation (predissociation by rotation¹⁶), only connects states of the same multiplicity and varies in magnitude with rotational constant, thus is more important for light molecules.

4.2.2 Predissociation : Experimental Investigation

Experimentally, predissociation can be studied because of the competition between the radiative pathway and the predissociative, non – radiative pathway. The effect can be observed by a variety of means in both absorption and emission, depending on which of the states is predissociated. Taking the situation where the upper state is predissociated, the magnitude and apparent radiative lifetime of emission from the upper state, and the line widths of the absorption spectrum can

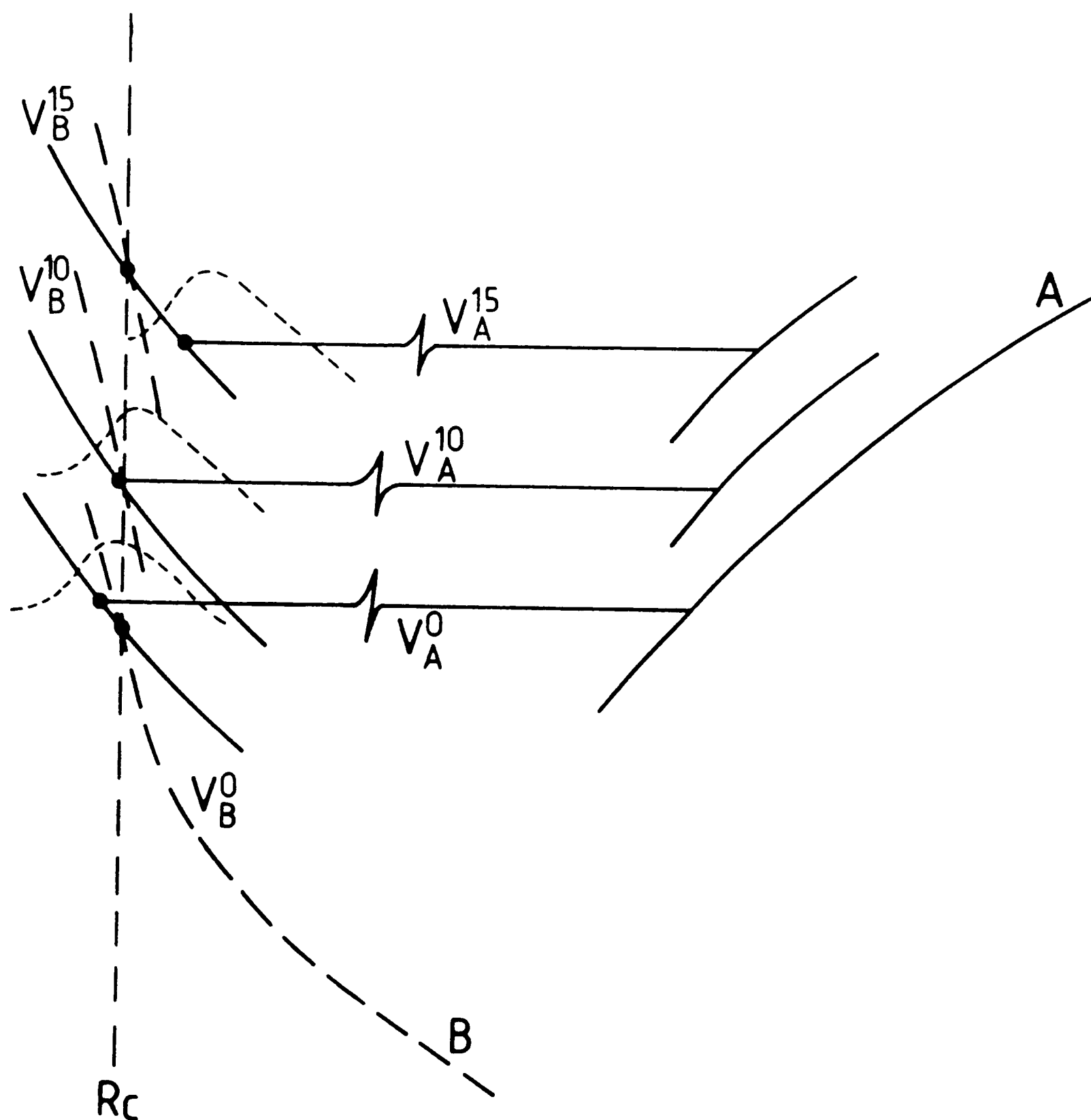


Figure 4.5 Schematic diagram to show the J dependence of a class c^- predissociation, where A is the bound and B the dissociative state. Part of the effective potential curves for three J values are shown for both states, A (—) and B (---), for a given vibrational level, v . Also shown is the energy of the bound state for each J level, together with the relevant part of the vibrational wavefunction. The wavefunction of the B state is a distorted translational wave, and so it can be seen that as J increases the overlap between the vibrational wavefunction decreases, hence the predissociation rate is expected to fall.

be examined to gain information on the predissociation rate.

The competition between radiative and non – radiative processes can be considered using a simple kinetic scheme, where after excitation, the rate of loss of the excited state is given by :

$$\frac{dN}{dt} = -(k_r \cdot N + k_{nr} \cdot N)$$

where k_r and k_{nr} are the radiative and non – radiative loss rates respectively and N is the concentration of the excited state.

The solution is

$$\begin{aligned} N(t) &= N_0 \cdot \exp(-(k_r + k_{nr})t) \\ &\equiv N_0 \cdot \exp(-t/\tau) \end{aligned}$$

where
$$1/\tau = k_r + k_{nr} = 1/\tau_r + 1/\tau_{nr}$$

and τ is the measured radiative lifetime.

Thus, a direct measurement of the lifetime of the predissociation state, together with knowledge of the true radiative lifetime can yield the rate of predissociation. This simple model assumes that the excitation pulse is short compared to the measured lifetime, although it is possible to deconvolute lifetimes in some cases where this is not the case, and assumes that there are no other de-excitation mechanisms, such as collisional quenching. Also, care is required when finding the true radiative lifetime of the state. This is usually done by measuring the lifetime of a non – predissociation level in the same electronic state, but the true lifetime often has a small dependence on ν and J and so a series of values are required to extrapolate to the ν, J level of interest.

The kinetic scheme for determining the predissociation rate can also be applied to the fluorescence quantum yield. Hence fluorescence yield,

$$\begin{aligned} \phi_{fl} &= \frac{k_r}{k_r + k_{nr}} \\ &= \tau / \tau_r \end{aligned}$$

Thus, if the fluorescence signal obtained can be compared with that expected from the system in the absence of any non – radiative process, then the rate of predissociation can be calculated.

The rates of predissociation that can be measured by these techniques depend

on the true radiative lifetimes of the species. For example, in the case of the I_2 B – X transition, which is spin forbidden with a radiative lifetime of 10^{-6} s, weak predissociation rates ($10^6 - 10^7$ s $^{-1}$), have been observed¹⁷. However, direct lifetime measurements using LIF on alkali metal diatomics suggest that non – radiative dissociation rates 10^3 times slower than the radiative pathway can also be detected¹⁸.

For strong interactions, the fluorescence yield is decreased to such an extent that lifetime measurements are made difficult. In these cases, it may be preferable to carry out absorption studies and to monitor the spectral line widths of the transition. For a Lorentzian line shape, the line width of the individual rotational lines can be related to the lifetime of the predissociated state by a simple formula

$$\begin{aligned}\Gamma \text{ (cm}^{-1}\text{)} &= (2.\pi.c.\tau)^{-1} \\ &= 5.3 \times 10^{-12} / \tau \text{ (s)}\end{aligned}$$

Typically, this technique has been used for strong interactions such as the predissociation in HBr^+ , where a non – radiative lifetime of 10^{-14} s leads to a line width of 400cm^{-1} and was observed by photoelectron spectroscopy¹⁹. New Doppler free spectroscopy has allowed weaker interactions to be observed²⁰.

Other experimental methods have been used to study predissociation such as measuring the energy shifts often associated with the perturbation²¹ and detecting fragments from the dissociating molecule²⁰.

4.2.3 Predissociation : Interpretation

To determine the mechanism and states involved in a predissociation it is useful to consider the symmetries and correlations of the molecular states with those of the fragments. Using the Wigner – Witmer rules²² to carry out this correlation, it is possible to identify a limited number of plausible states which cross the bound potential and correlate with a lower dissociation limit. Knowledge of the configurational character of the interacting states can supplement the electronic selection rules and often eliminate all but one candidate.

After this procedure, experimental investigation into the ν, J dependence and

the absolute magnitude of the interaction should be undertaken to validate the theoretical findings. Full interpretation of the experimental results can be difficult for weak predissociations, since there are many possible mechanisms for such an interaction, including second order effects, where direct interaction between the states is forbidden but perturbation can occur through a third connected state.

There are a number of excellent accounts on perturbation and predissociation, which give a far more detailed explanation of the mechanisms and types of behaviour observed^{13,16}.

4.3 Predissociation in CF

The absence of emission from vibrational levels in the A state above $\nu' = 1$ has been noted by a number of workers, but Thrush and Zwolenik²³ were the first to show that this was due to predissociation and not to unfavourable Franck–Condon factors, by observing the (2,0) band in absorption. Subsequent calculations have shown that the Franck–Condon factors for transitions from the $\nu' = 2$ level are similar in magnitude to those from the $\nu' = 1$ and 0 levels, (see Table 4.1). Thrush and Zwolenik also found evidence for some perturbation in the potential curve by analyzing the molecular constants, and correlated the $A^2\Sigma^+$ state with the atomic states of C (3P) and F (2P). These are the same terms as for the ground state atoms, and so, due to the non – crossing rule, they concluded that the A state must correlate with the ground state atoms. Porter *et al.*⁶ in their comprehensive emission studies of the CF (A – X) transition, also suggested an avoided crossing mechanism, and identified the other state involved as the previously seen $B^2\Sigma^+$ state.

Carroll and Grennan¹¹ detected and analyzed the B – X spectrum and showed the the B state to be a $^2\Delta$ state. They considered the possible states derived from the C (3P) and F (2P) ground state atoms and predicted that an outer arm crossing of a $^4\Pi$ state with the A state caused the predissociation. They were also the first to suggest that the A state is a Rydberg state. A computational study of CF by Hall and Richards²⁴, using LCAO – MO – SCF calculations, indicated that the $^4\Pi$ state lies too high in energy to interact with the A state and proposed that

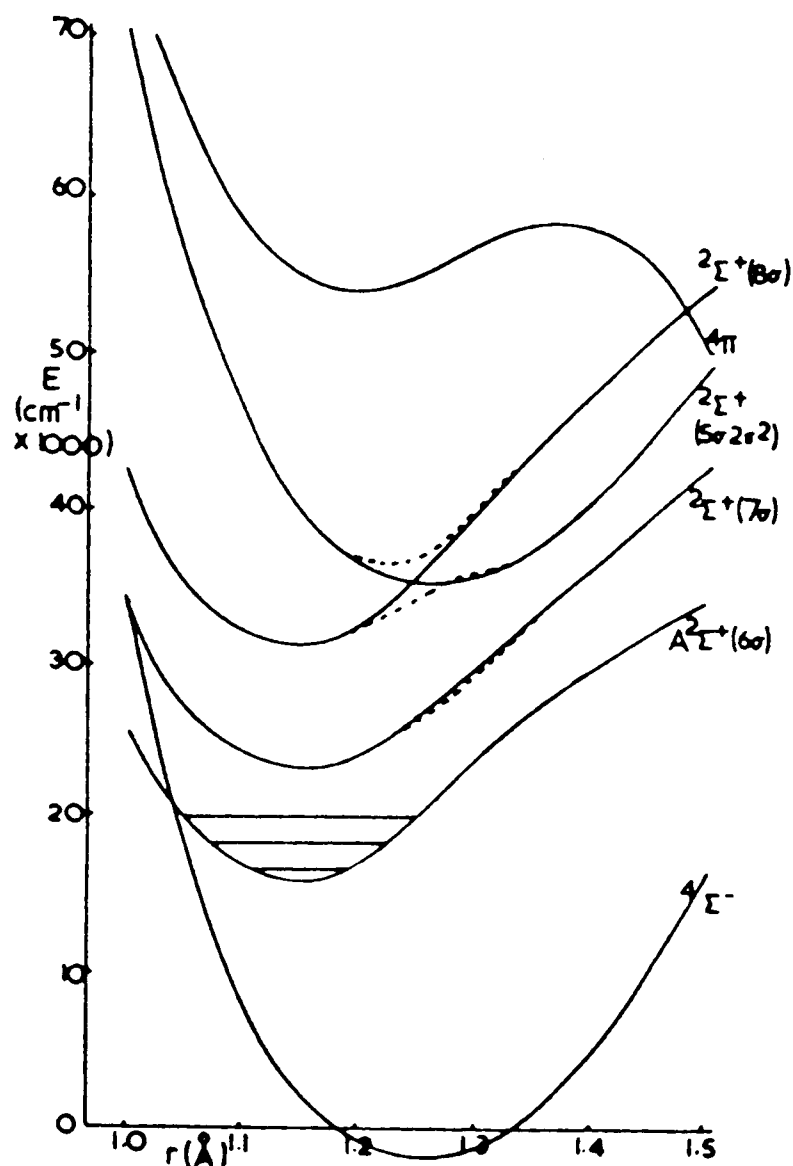


Figure 4.6 Some low lying ${}^2\Sigma^+$ and quartet states in CF, (Hall and Richards²⁴).

an inner arm crossing by a ${}^4\Sigma^-$ state was responsible for the perturbation, see figure 4.6. This was derived by initially considering the lowest energy configurations, which correlate with ground state atoms and comparing the relative positions of the calculated potential curves, but was finally selected by examining the experimental results. These were that although no emission had been seen observed from any J value in the $\nu' = 2$ level, emission had been seen from J levels in the $\nu' = 0$ and 1 bands which lie higher in energy than the $\nu' = 2$, $J = 0.5$ level. This behaviour is consistent with an inner arm crossing with $E_c \geq D_0$, corresponding to predissociation case c⁻ or a⁻, due to the effective potential curves described in section 4.2.1.

The interaction of states with different spins requires a spin orbit coupling operator, but the configurations of the two states, ${}^4\Sigma^- (5\sigma^1 2\pi^2)$ and ${}^2\Sigma^+ (5\sigma^2 6\sigma^1)$, differ by two spin orbitals and so a first order interaction is weak. However, Hall and Richards calculated a larger second order term from an interaction through the ${}^2\Sigma^+ (5\sigma^1 2\pi^2)$ state. This has an electrostatic interaction with the A state and

couples to the $^4\Sigma^-$ state by a spin orbit matrix element. The overall interaction was calculated to be of the order of 1.5 cm^{-1} leading to a predissociation rate of $10^9 - 10^{10} \text{ s}^{-1}$. The interaction of a $^2\Sigma^+$ state with a $^4\Sigma^-$ state via a third state has also been suggested for predissociation in the $A^2\Sigma^+$ state of OH²⁵.

Similar calculations to those of Hall and Richards were performed by White²⁶, who also carried out absorption experiments on CF, analyzing five new states and investigating the predissociation, including observing the (2,0) band by absorption. He found that the variation of the rotational constants, B_v , with v was non-linear, contrary to other Rydberg states (eg. $D^2\Pi$), with a relatively low value for B_2 . Again, no evidence of predissociation was observed for high J levels in the (1,0) and (0,0) transition, but he measured the relative line width of the rotational lines of the (2,0) band as a function of J. The absolute line width was not found and so no measure of the strength of the predissociation was possible, but the line width was found to rise slowly up to J^2 values of about 1000, above which a more marked rise was seen. The experimental results combined with the calculations led to the same explanation as Hall and Richards for the predissociation mechanism. (Later molecular orbital calculations by White *et al.*²⁷ also agreed with this mechanism proposed.) The fact that the interaction involved a third state was tentatively offered as an explanation for the dependence of line width on J.

Experimental evidence for the $^4\Sigma^-$ state has now been obtained²⁸, by observing the spin forbidden $^4\Sigma^- - X^2\Pi$ transition, and this has enabled precise positioning of the potential curve for the $^4\Sigma^-$ state, which was shown to be consistent with the predissociation model. It also indicated that the $^4\Sigma^-$ state is bound and has a well depth of about 1700 cm^{-1} .

More recently, Rendell *et al.*²⁹ have carried out a theoretical determination of the potentials for the B, A and X states of CF, and suggested that the A state does have an avoided crossing and that the predissociation is due to unimolecular decay through a barrier. They calculated the rate of tunneling for the $v' = 2$ case and show it to be $2.4 \times 10^8 \text{ s}^{-1}$, which is slower than the rate obtained by Hall and Richards. However, they do not explain how this mechanism accounts for the experimental

observations, in particular the J dependence of the predissociation. This is discussed later.

4.4 Experimental Observations of CF

As described in section 4.3, the (2,0) band of the A – X transition of CF has only been observed by absorption techniques, but never by emission. The emission studies have generally involved electron impact excitation of CF inside discharges of fluorocarbon precursors. This method of excitation can produce an intense source of radiation, but the process is not specifically selective towards the production of CF in its A state. The absorption measurements again have used a discharge for the production of CF, with a lamp as the ultra – violet source. The laser induced fluorescence technique enables both absorption and emission characteristics of a transition to be studied. In particular, it allows the specific excitation of CF radicals from the ground state to the A state, using a laser as an intense source of radiation, and these excited species can then fluoresce back to the ground state, which permits the study of the emission from a precisely prepared state.

LIF has previously been used to study the (1,0) and (0,0) bands of the transition. Much of the work has been carried out in this laboratory, both on the spectroscopy of CF³⁰, and using LIF as a probe of the spatial and temporal variation in CF concentration, as a function of plasma parameter³. This has illustrated the importance of CF in plasmas, or more particularly that CF is produced directly from electron impact of CF₄, simultaneously releasing three fluorine atoms. Other studies include some time resolved work by Hansen *et al.*³¹ and a rather early observation by Suzuki *et al.*³²

4.4.1. LIF of the CF A²Σ (ν = 2) – X²Π_i (ν = 0) Band

Experimentally, there were a number of considerations and adaptations required to approach this study. Predissociation reduces the expected fluorescence yield from a LIF process and therefore plasma conditions were chosen to give a large concentration of CF. A number of different precursor gases were tried, (CF₄, C₂F₆,

C_3F_8 , CHF_3 and C_2F_4), but contrary to the findings of other workers², CF_4 was found to be one of the better sources under the conditions used. For the majority of the experiments described in this chapter the conditions were 200 mTorr, 200 W and 42 sccm of pure CF_4 . The chopper used in the oxygen atom experiments was also effective in reducing the plasma induced emission in these CF studies, (for LIF of the (1,0) and (0,0) bands this adaptation was not necessary).

The wavelengths required for excitation were available from absorption studies. In this work, simultaneous measurement of LIF of the (1,0) band of the NO (A – X) transition was performed, (also the CF (1,0) and (0,0) with the NO (0,0) and (0,1) bands), to allow comparison between the line positions of CF and the well known line positions of NO. A full spectroscopic analysis of the (2,0) band was however not carried out, but as will be shown, there was excellent agreement between line positions of the simulated and experimental spectra. The wavelengths for fluorescence from the $\nu' = 2$ level have been calculated along with the Franck–Condon factors for these and other transitions from the $\nu' = 0$ and 1 levels. Some of these are shown in Table 4.1.

As emission from the CF (2,0) band had not previously been seen, it was necessary to confirm the identification of the source of the LIF spectrum observed. The experimental LIF excitation and fluorescence spectra are shown in figures 4.7 and 4.8 respectively, together with theoretical simulations and line positions. Although the fluorescence signals were weak, rotational lines can clearly be resolved, and J values up to 26.5 can be assigned before the signal is lost in the noise.

The general form of the excitation spectrum is consistent with the other CF (A – X) bands and fits well to a simulation of the (2,0) band. The fluorescence spectrum is shown to match closely the predicted line positions for the $(2,\nu'')$ transitions. It is possible to extract the experimental Franck–Condon factors of these transitions from the data, but owing to the variation of plasma induced emission with wavelength, the spectrum had to be collected in parts and is not considered reliable enough for such an analysis. The spectrum shown is not corrected for detector sensitivity but it does illustrate the general trends found in

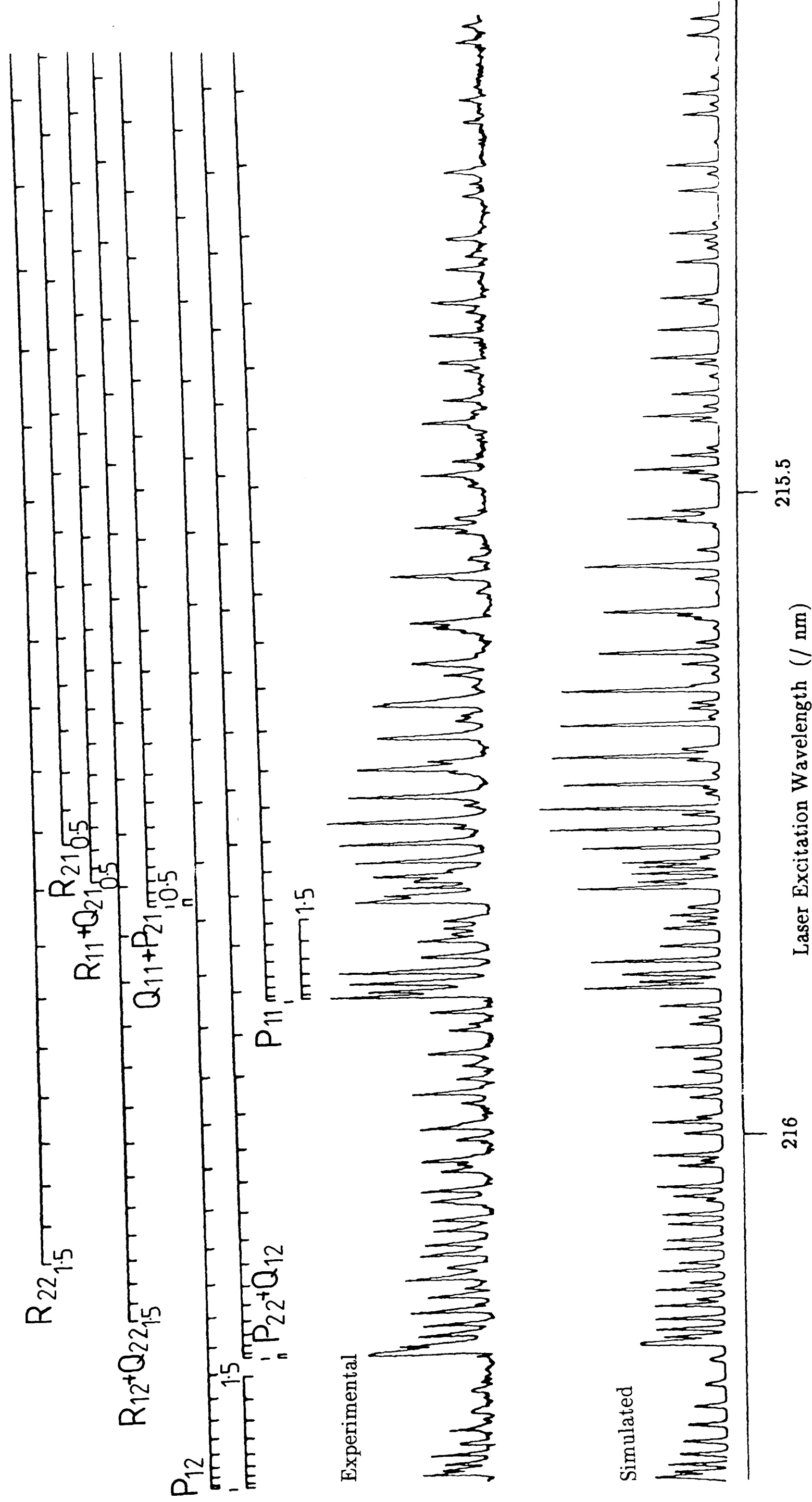


Figure 4.7 LIF Excitation Spectrum of the complete (2,0) band of the $A^2\Sigma^+ - X^2\Pi$ transition of CF.

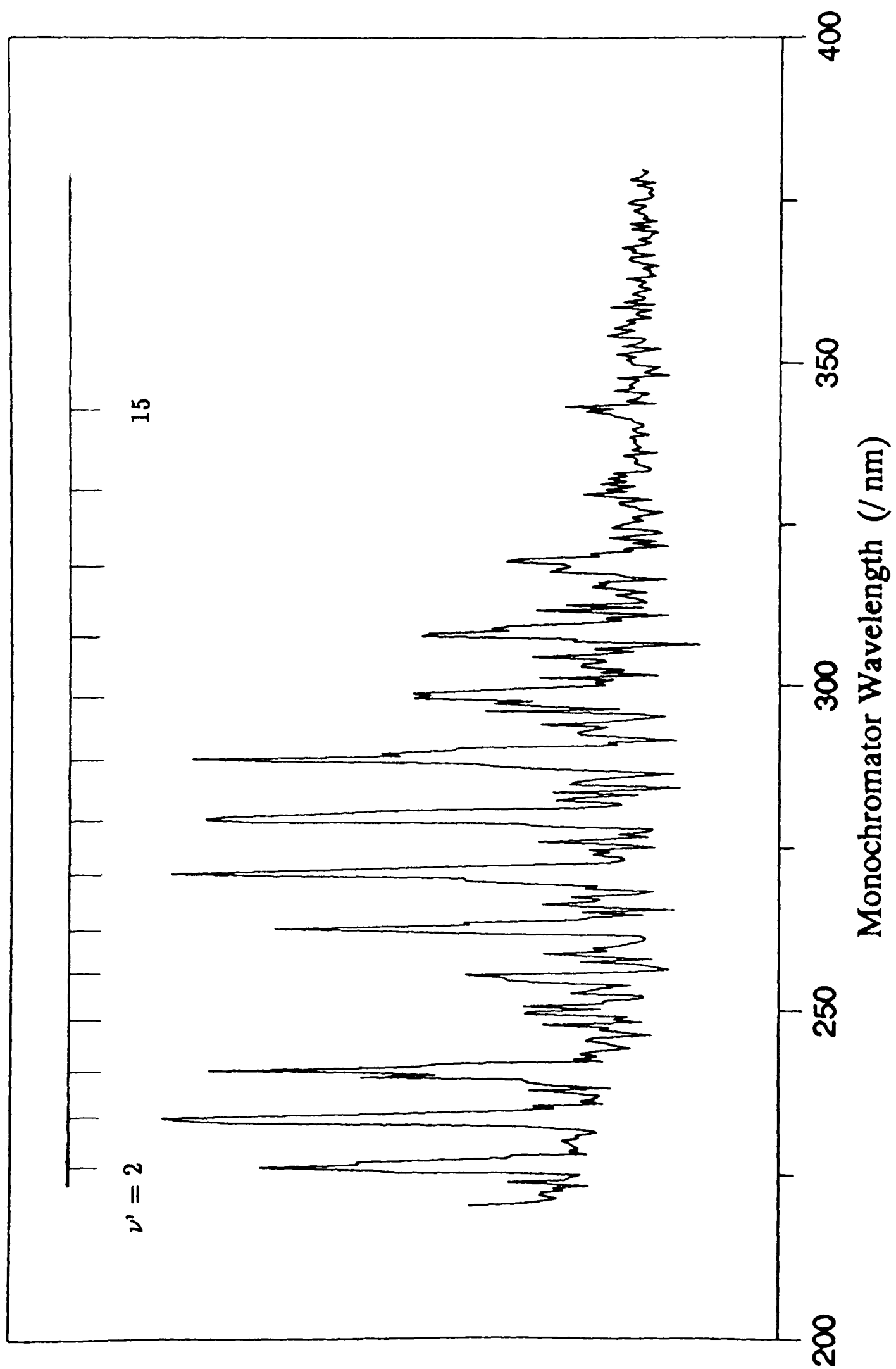


Figure 4.8 Wavelength resolved fluorescence from the $A^2\Sigma^+$ ($\nu = 2$) level of CF, following laser excitation.

the theoretical calculations of Franck–Condon factors³³. It should be noted that the theoretical values do not correlate exactly with the experimental Franck–Condon factors owing to variation of the electric dipole moment with ν' .

Identification of the radical was also tested by comparing the kinetic loss rate of the species, (under a given set of conditions), with that of CF probed using the (1,0) transition. The measured loss rates were the same. Thus, the spectra were attributed to the CF ($A(\nu' = 2) - X$) transitions.

The simulation of the excitation spectrum is based on a computer program developed by Wild³⁴ to aid assignment of $^2\Sigma^+ - ^2\Pi$ transitions. The energy levels, and hence line positions, are determined using formulae given by Herzberg¹⁶ and the rotational line strengths were calculated using formulae by Earls⁵. A more accurate simulation can be obtained by considering the individual rotational wavefunctions, but previous studies have shown this to have little effect on the final result³⁵. The simulation shown uses molecular constants from the studies of Brown¹⁰ and White²⁶ for the ground and excited state respectively. No adjustment to the constants were required to obtain the agreement seen between experiment and simulation, but the resolution of the laser was insufficient to accurately probe and fine tune previous values.

The simulation spectrum shown is based on a Boltzmann distribution for the rotational levels with a temperature of 320K, (similar to experimental measurements), and assumes that all the lines are totally saturated. As mentioned in chapter 1, saturation, the localized depletion of ground state concentration due to laser excitation, is a problem for species such as CF when using pulsed laser systems. For a transition where the upper state is predissociating the effect is even more prevalent, since repopulation of the ground state from radiative decay of the excited state is reduced due to competition with non – radiative predissociation. A study of the dependence of fluorescence signal on laser energy showed that the level of saturation of the (2,0) band was greater than that of the (1,0) and (0,0) bands for a given energy range.

Saturation influences the relative intensities of the rotational lines, such that the rotational line strengths become an inappropriate measure, and in the limit of complete saturation, the line intensities are simply proportional to the populations of each level. In figure 4.9, part of the high J region of the (2,0) experimental spectrum is shown along with two simulations over the same range; one assuming that the transition is totally saturated and the other that it is unsaturated. The relative intensities of lines within a specified branch are, as expected, little changed with saturation, (as within this high J region the line strengths are approximately proportional to J''), but the relative intensities of lines in different bands change markedly. The experimental line intensities correlate with those of the saturated spectrum more closely than those of the unsaturated simulated spectrum. This is further evidence that at the laser energies required to obtain measurable fluorescence signals, there is appreciable saturation of the transition. As discussed in chapter 1 complete experimental saturation is not realizable.

The simulation and experimental spectra of the whole band (figure 4.7) show good agreement, despite the conclusion that complete saturation is not possible. There are no apparent omissions or shifts in line positions, and no dramatic variation in the signal level, and in particular the variation of LIF intensity within a given sub-band shows no obvious decline with increasing J . This suggests that the predissociation has a weak or no dependence on J for the (2,0) band, at least up to the highest levels observed. A Boltzmann plot was used to obtain a rotational temperature from the spectrum, and the result (320 K), compared well with that from the (1,0) and (0,0) bands under like conditions³⁶.

Figure 4.10 shows experimental and simulated spectra for the high J region of the (1,0) band and it can be seen that the line intensities correlate well, with no sudden variation in the intensity of lines as J varies. The highest J transition observed, $J = 36.5$, involves a state which lies nearly 600 cm^{-1} higher than the $\nu' = 2$, $J = 0.5$ level. The complete (1,0) band showed no indication of predissociation even at low J values, where effect of the proposed c^- predissociation mechanism might be expected to be present. This is consistent with previous absorption and

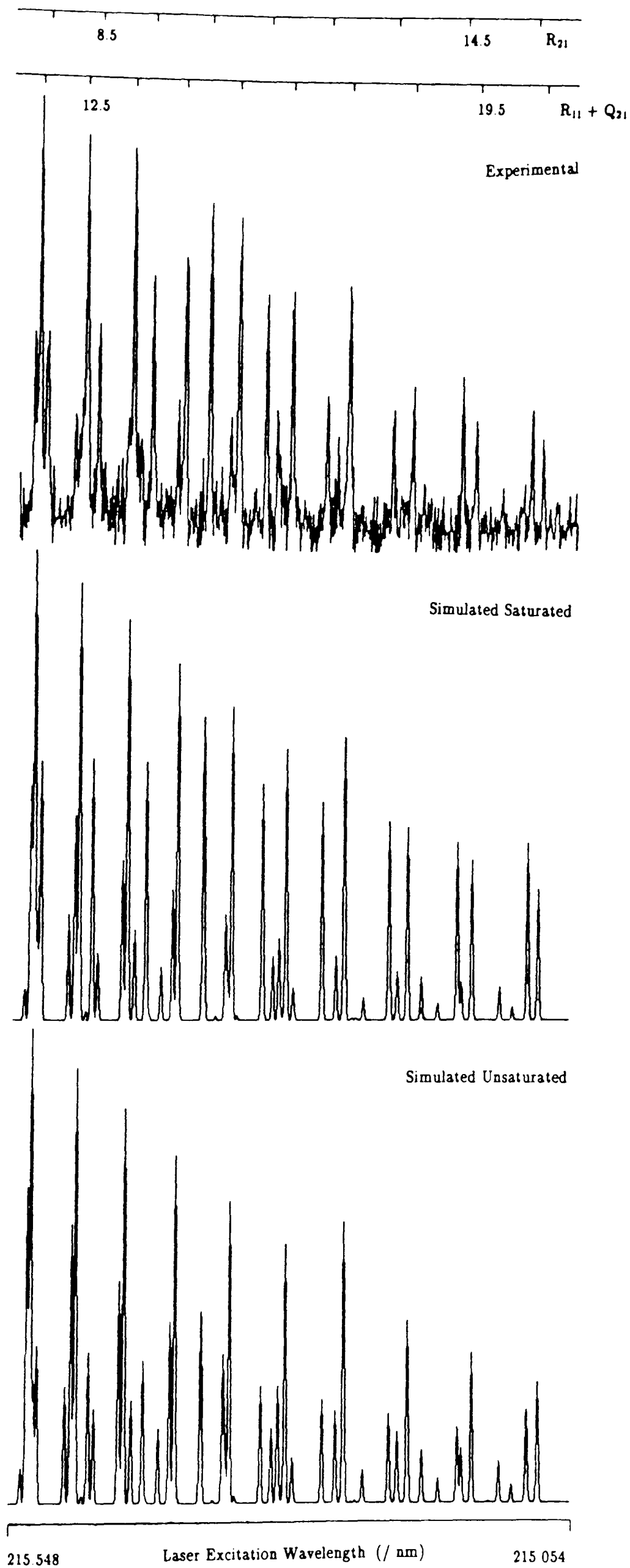


Figure 4.9 LIF excitation spectrum of the high J region of the (2,0) band of the CF (A – X) transition, together with simulations of saturated and unsaturated spectra.

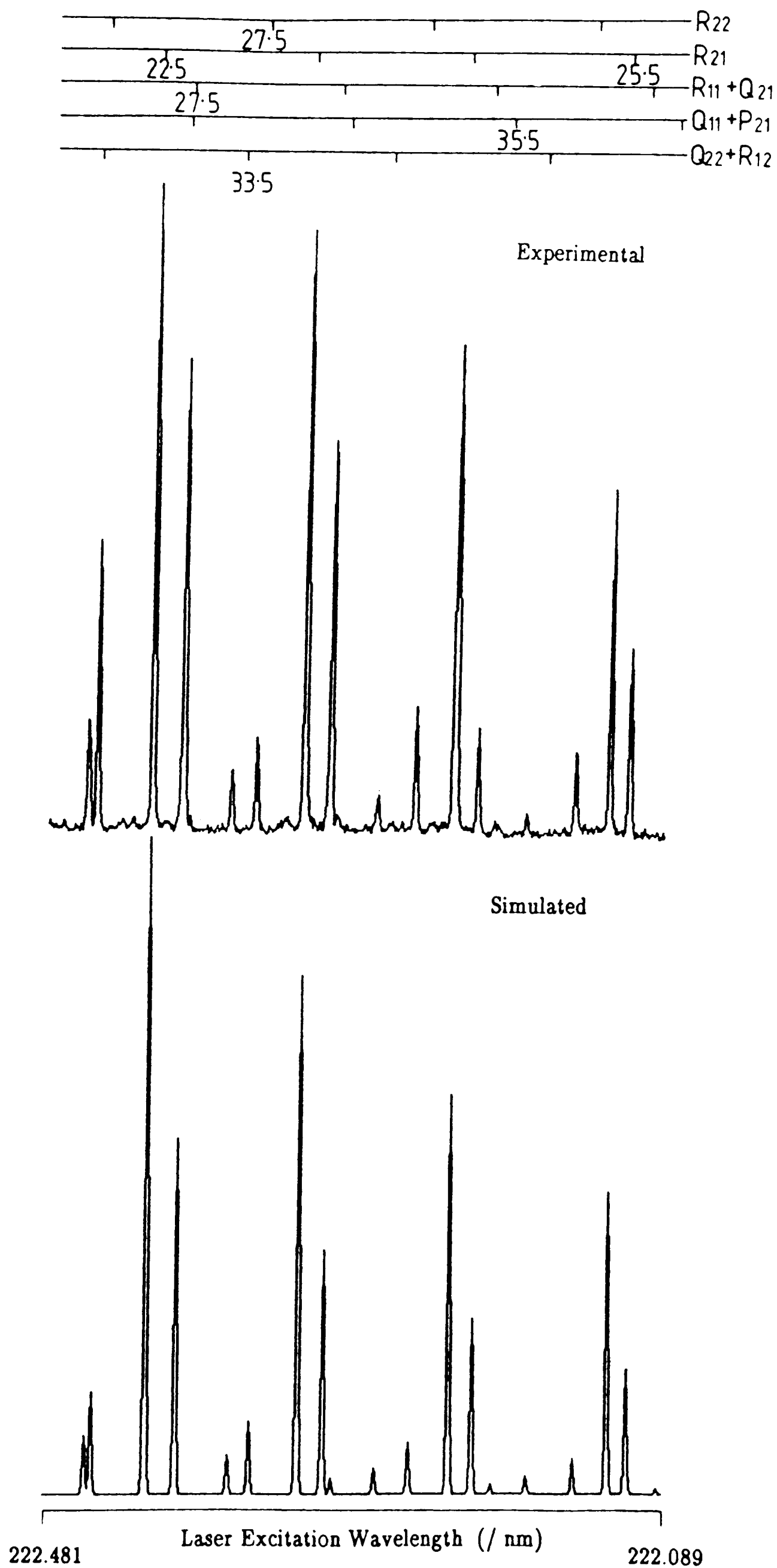


Figure 4.10 Simulated and experimental LIF excitation spectra of the high J region of the (1,0) band of the CF (A - X) transition.

emission studies^{6,26}.

4.4.2. Measurement of the Rate of Predissociation

The next phase of the investigation was an attempt to measure the magnitude of the predissociation, using techniques described in 4.2.2. Analysis of the line widths of the rotational lines showed the features to have widths of about 0.6 cm^{-1} , that is they are restricted by the laser line width. (The Doppler width for CF at 320K is about 0.1 cm^{-1} .) This value for the line width can be used to obtain a lower limit for the lifetime of the A state in $\nu' = 2$, which is $9 \times 10^{-12} \text{ s}$. The calculation however assumes a Lorentzian shape for the line, which may not be true for the lines scanned, because the presence of saturation can influence the line shape. The value for the lifetime is nevertheless a reasonable lower limit, and yields a predissociation rate of about 10^{11} s^{-1} .

A direct measurement of the lifetime was also attempted in this work. The low fluorescence yield meant that use of a fast single shot storage scope was inadequate, and so the SRI fast sampler was used to average the signal over many shots. The sampler was operated with a 1 ns gate and a step size of 0.5 ns. The time response of the fluorescence and the laser pulse were measured at two laser energies, 0.18 and 0.024 mJ, with the laser scattered light coming from 1 Torr of Ar. The results are shown in figure 4.11.

Previous studies in this laboratory³⁷ on the radiative lifetime of the CF $A^2\Sigma^+$ state for $\nu' = 1$ and 0, ($\tau_r = 25.6$ and 26.7 ns respectively), showed the fluorescence to have a rise time slower than that of the laser pulse and a pronounced decay after the laser pulse had finished. For the $\nu' = 2$ level, it can be seen that the fluorescence has a rise time almost indistinguishable from the laser pulse and there is no fluorescence observed after the pulse. Thus, the $\nu' = 2$ level appears to have a lifetime at least as short as the laser pulse rise time, which is about 2 ns. To obtain the actual lifetime for the $\nu' = 2$ level, a much shorter laser pulse would be required. This lifetime is not the true radiative one, and again illustrates the presence of a non — radiative competing channel.

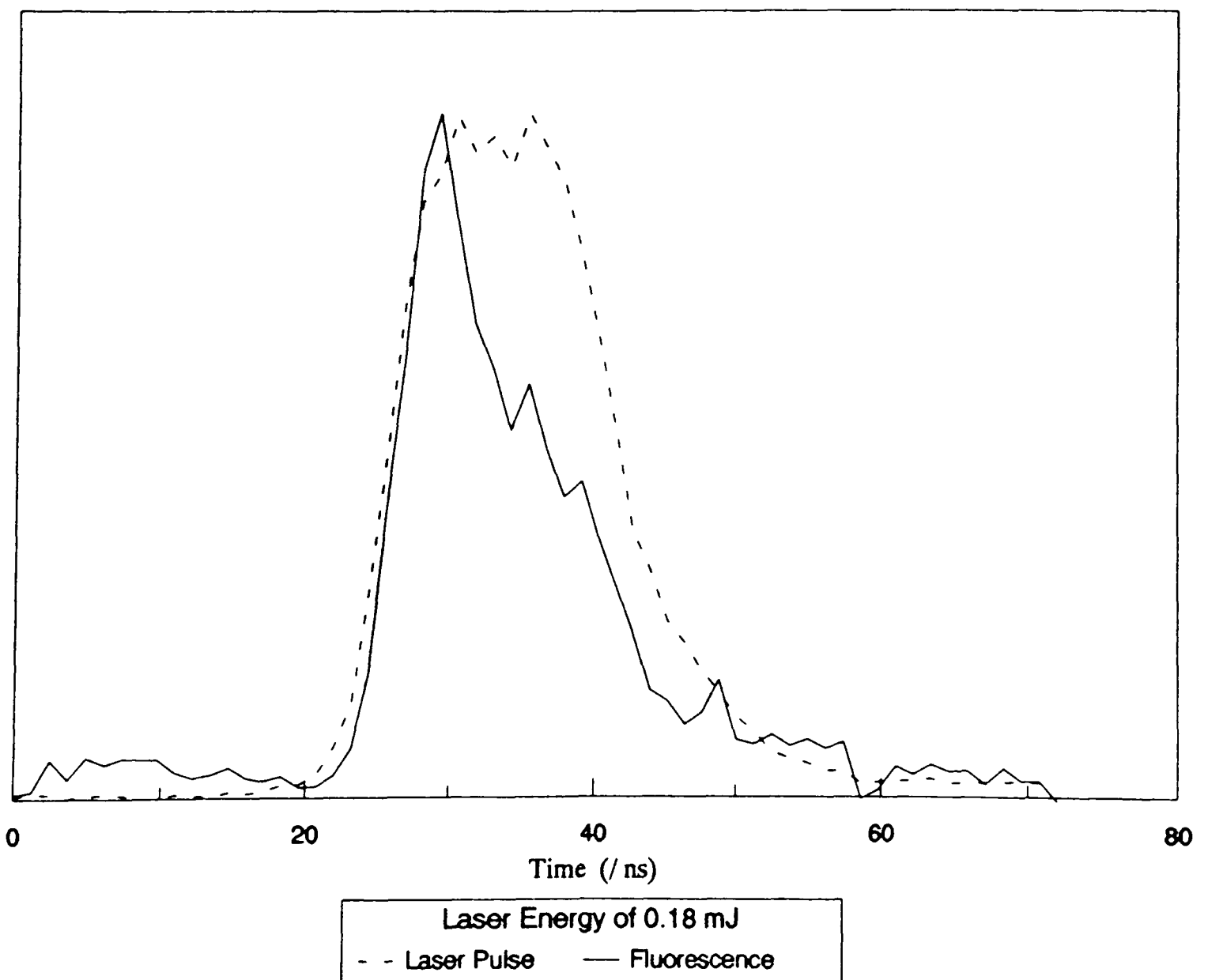
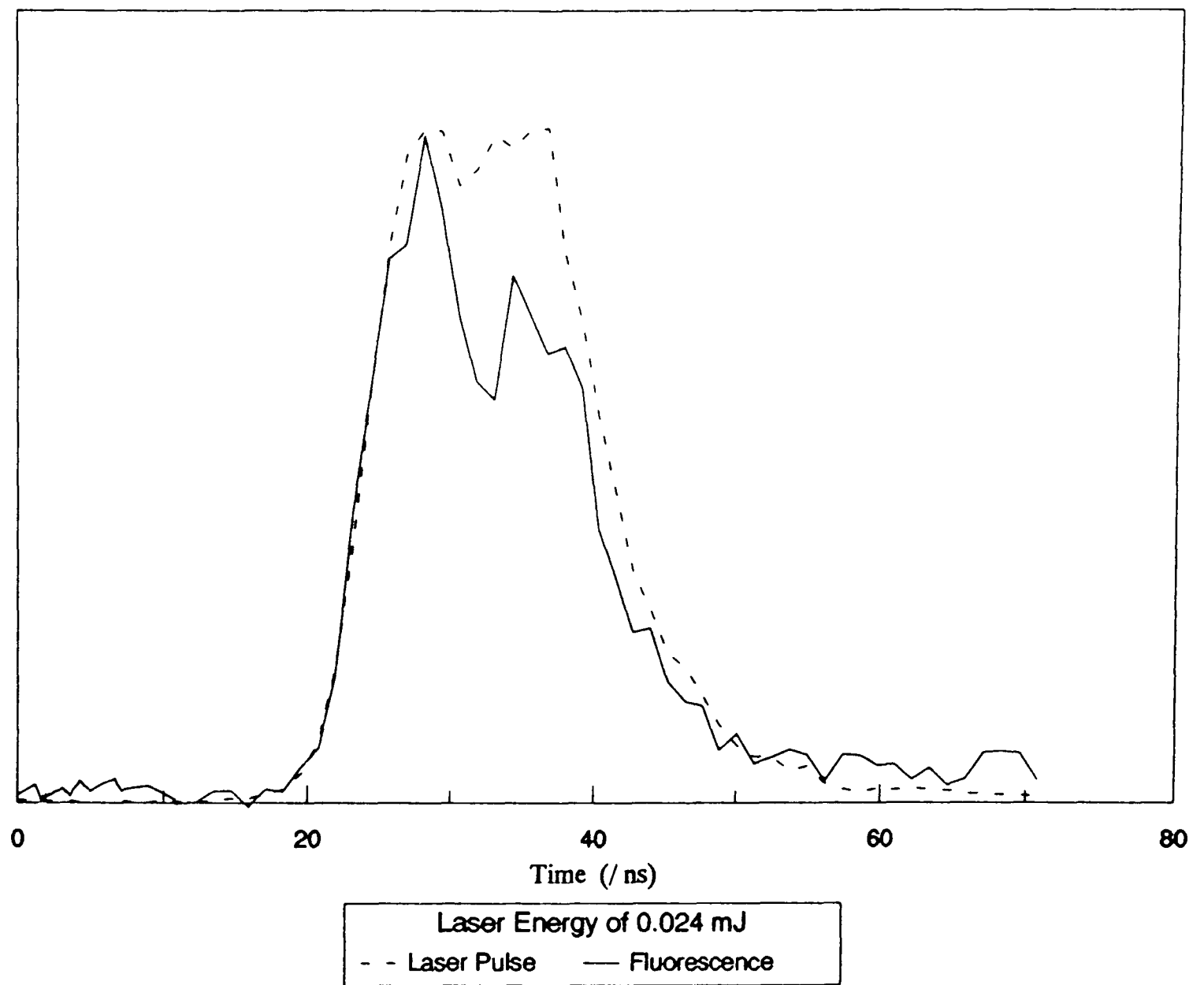


Figure 4.11 Temporal profile of the laser pulse and the fluorescence after excitation of the CF (2,0) band, at two laser energies.

With a lifetime of less than 2 ns and a laser pulse of 20 ns, the fluorescence temporal profile would be expected to follow that of the laser pulse. As can be seen in figure 4.11, this is not the case. The cause of the depletion in fluorescence signal at later times is thought to be a further effect of saturation. The transition is thought to be saturated early in the pulse so that the relative fluorescence signal decreases with time. A simple mathematical model of this system was set up to investigate the behaviour seen, using rate equations for the laser excitation, fluorescence and predissociation processes. The results are given in figure 4.12. As the laser energy increases, the degree and rate of saturation also increase, and so the observed temporal profile decreases more significantly, as seen in the experimental data. The model uses a step function for all laser profiles, (spatial, temporal and spectral), and assumes a predissociation rate of 10^{10}s^{-1} . It does not relate precisely to the experimental conditions, but it does illustrate the observed reduction in fluorescence as a function of time during the laser pulse, and also how this behaviour varies with laser energy. The same model was used to ascertain if saturation of the transition could influence any J dependence of the predissociation rate. The result obtained was that laser powers in excess of 50 MWcm^{-2} (cf. 0.5 MWcm^{-2} used here) are required before such an effect occurs.

Unfortunately, direct lifetime and line width measurements were not able to produce a quantitative measure of the strength of the predissociation, only two limits, greater than $5 \times 10^8\text{ s}^{-1}$ and less than 10^{11} s^{-1} . The final technique attempted was to measure the fluorescence yield from the transition and compare it to that expected if predissociation were not present. This was done by measuring the fluorescence signal intensity from part of the (2,0) band and comparing it to that from the same part of the (1,0) and (0,0) bands, allowing for differences in the Franck–Condon factors for excitation and fluorescence. This comparative technique eliminates the need for the imprecise calculations of laser beam profiles. It does however require knowledge of the wavelength variation in sensitivities of both the fluorescence detection and the dye laser energy measuring instruments, and the Franck–Condon factors for the (2,0), (1,0), (0,0) and (2,3), (1,1), (0,1) bands, used

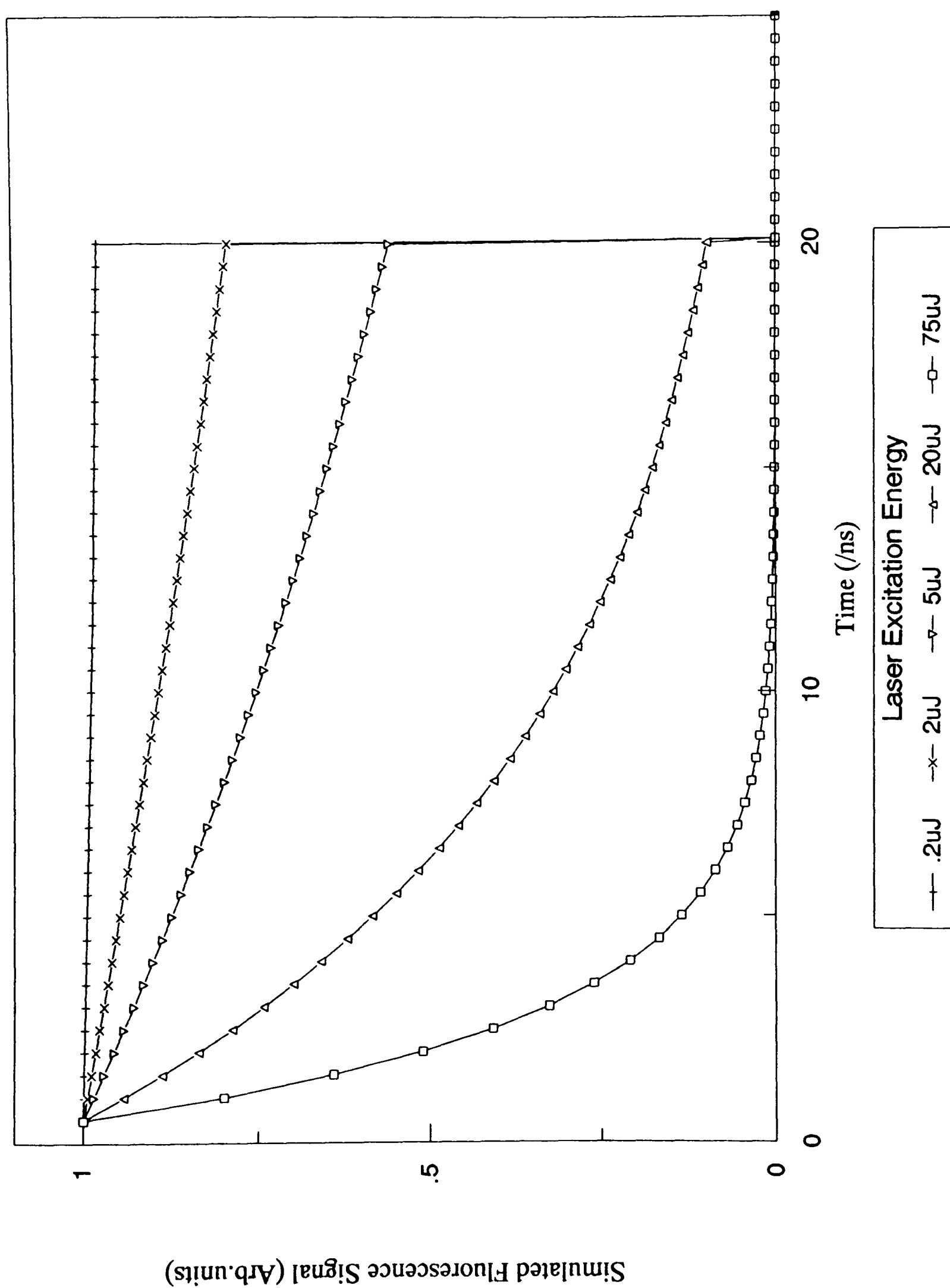


Figure 4.12 Simulated temporal variation of fluorescence after excitation of the CF (2,0) band for a range of laser energies, assuming a predissociation rate of 10^{10}s^{-1}

for excitation and fluorescence respectively, (see table 4.1).

Similar laser energies and plasma conditions were maintained for all the experiments to ensure that the same CF concentration was present and to try to allow for any saturation effects. For the (1,0) and (0,0) transitions, the saturation can be allowed for, but low fluorescence yields made it impossible to probe the non – saturated region for the (2,0) band. This creates a potential source of error in the final result.

The bands used for excitation and fluorescence have relatively large and similarly valued Franck–Condon factors, (Table 4.1), and so a direct comparison of the fluorescence signals yields an approximate level of predissociation.

Excitation			Fluorescence		
Band	FC factors	λ (nm)	Band	FC factors	λ (nm)
(2,0)	0.338*	215.9	(2,3)	0.104*	235.2
(1,0)	0.298*	223.9	(1,1)	0.159*	230.6
	0.176			0.147	
(0,0)	0.106*	232.9	(0,1)	0.205*	240.1
	0.117			0.190	

Table 4.1

* indicates calculated values³³, otherwise experimental³⁰.

The Franck–Condon factors used for a more accurate measure of the predissociation rate were the experimental values obtained previously in this laboratory^{30,36} for the (1, ν'') and (0, ν'') transitions, and theoretical ones for the (2, ν'') bands. This is not a large source of error as the theoretical and experimental factors generally show good agreement for strong factors. Thus, when allowance was made for the experimental considerations discussed above, it was found that corrected relative fluorescence signals from (1,0) and (0,0) excitations were approximately equal, as expected, and were of the order of 65 times greater than

that from the (2,0) band.

Absence of predissociation from the $\nu' = 1$ and 0 levels of the A state allows the reduction in fluorescence yield seen in the (2,0) transition to be attributed to competition of fluorescence with predissociation. The expected radiative lifetime for the $\nu' = 2$ level is approximately 25 ns, so the lifetime associated with non-radiative decay is 0.38 ns, and the rate of predissociation is $2.65 \times 10^9 \text{s}^{-1}$.

This value does not allow for the effect of saturation in the (2,0) transition which would be expected to reduce the rate. The rate, however, does lie between the limits obtained by the other experimental methods and is also consistent with the values suggested by the early calculations of Hall and Richards²⁴.

4.5 Conclusions

The experimental results obtained for this thesis show the first observation of emission from the $A^2\Sigma^+ \nu' = 2$ level and indicate the presence of a J independent predissociation mechanism from that level. The tunnelling mechanism of Rendell *et al.*²⁹ would be expected to produce a rate which increased with J, although such a scheme is consistent with high J levels of $\nu = 1$ being less predissociated than the isoenergetic low J levels of $\nu = 2$, due to centrifugal effects. The inner limb crossing mechanism, where the A state interacts with a $^4\Sigma^-$ state, is consistent with a weak J dependence. The argument outlined in section 4.2 and illustrated in figure 4.5 predicts that for a c⁻ mechanism the predissociation rate decreases with increasing J and that this occurs at higher J for higher values of ν' . However if the position of the crossing point shown in the figure is moved to slightly larger R then it is possible that the overlap of wavefunctions and thus predissociation rate increases with J. No variation with J was observed in this work for the $\nu' = 2$ level up to $J = 26.5$, and there was no evidence of predissociation in the low J levels of $\nu' = 1$. White's²⁶ observation of an increase in predissociation rate at values of $J > 30$ in $\nu' = 2$ could possibly be explained by considering a crossing point at larger R, but such a curve would also predict predissociation from $\nu' = 1$ for the J levels where it is energetically possible. The $^4\Sigma^-$ state has a potential curve which is bound with a

well depth of about 1700 cm^{-1} and so high J states may be restricted from predissociation by a centrifugal barrier, on the outer limb of this potential.

The experimental results do not completely clarify the mechanism, but the lack of J dependence does suggest that it is based on an inner limb crossing. The rate of predissociation has been found and shown to be about $2.6 \times 10^9\text{s}^{-1}$, although there are some uncertainties in this value, owing to unresolvable saturation effects. With respect to the application of LIF to the CF radical in rf discharges, both the (0,0) and (1,0) bands appear unperturbed and can be used, but the (2,0) band is about sixty times weaker in fluorescence, which limits its suitability because of the intense plasma induced emission at these wavelengths.

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Chapter Five

Actinometered Optical Emission

5.1 Introduction

As described in chapter 1, optical emission is extensively used in the study and application of processing plasmas, due to its universal nature and ease of operation. Its major drawback is that it is sensitive to the excited state species not the ground state, but the technique of actinometry, discovered by Coburn and Chen¹ and developed by D'Agostino^{2,3}, has to some extent overcome this problem. The technique involves adding a known concentration of a chemically inert species to the system to act as a monitor of the electron excitation rate in the plasma. By normalizing the emission from the species of interest, X, to that from the actinometer, A, it is hoped to correct for changes in the emission intensity which result from a change in the plasma electrons, rather than the ground state concentration.

The validity of this technique can be checked by comparing the actinometered optical emission, (AOE), with direct measurements of the ground state species. It has been tested previously for only a limited number of species and over restricted ranges of parameter space. This thesis describes the first direct examination of CF₂ actinometry⁴, although there has been a recent publication comparing LIF and AOE over a limited experimental range⁵, which showed a good correlation between the two techniques as a function of gas composition in a CF₄ / O₂ discharge. There is a large difference in the threshold for electron excitation of CF₂ and Ar, (about 5 eV and 14 eV respectively), but despite this some workers have suggested that AOE is a good representation of the ground state³ under conditions where the electron energy distribution is non – variant, (as measured by comparing the emission from a variety of actinometers). However, as is shown below this does not address all the criteria necessary for actinometry to be valid.

Walkup *et al.*⁶ first investigated actinometry of oxygen atoms again using LIF as a probe of the ground state concentration, over the oxygen rich region of CF₄ / O₂ discharges. Two more recent studies used absorption⁷ and electron

paramagnetic resonance⁸ to monitor the ground state, but all showed evidence of a production pathway involving formation of electronically excited oxygen atoms from direct electron impact on molecular oxygen. Such a mechanism had been previously observed in electron beam studies^{9,10,11} and would clearly invalidate any attempts to use such emissions as an indication of ground state oxygen. Walkup *et al.* observed that at high dissociation percentages, (ie. high values of $[O]/[O_2]$), and for systems with low mean electron energy, there was reasonable correlation, although this was partly fortuitous due to the similar behaviour of O and O₂ concentrations.

In work for this thesis, the emission and LIF from the steady state concentrations of oxygen atoms and CF₂ were detected and compared over a wide range of experimental conditions. The interpretation was aided by some measurements of time resolved data, both after plasma extinction, using the time resolved actinometry technique described in chapter 6, and during ignition of the plasma.

5.2 Theoretical Basis for Actinometry

There are three criteria, which are sufficient to ensure that actinometry is valid, but as will be shown there may be regions in the parameter space for which the criteria are not upheld, but where the technique appears to work.

1. The excited state must be produced solely by single electron impact on the ground state species.
2. The excited state must relax primarily by radiative decay.
3. The electron impact excitation cross section for the actinometer and the species of interest must have a similar threshold and variation as a function of electron energy.

In practice, as the thresholds of most of the excitation processes lie in the tail of the EEDF for these plasmas, it is the density of electrons with energies greater than the threshold that is most significant, and not the precise shape of the cross section.

The intensity of emission from an excited state, X_i^* , is given by

$$I_x = [X_i^*].A_{ij}$$

where A_{ij} is the Einstein coefficient for the observed transition, (i upper, j lower).

If X_i^* decays only radiatively, the first order loss rate constant is the sum of the A factors for transitions from the excited state. The production rate can be found from equation 1.3, thus it can be shown

$$[X_i^*] = \frac{[X].n_e}{\sum_j A_{ij}} \int_0^\infty \left(\frac{2\epsilon}{m_e}\right)^{\frac{1}{2}} \cdot \sigma(\epsilon) \cdot f(\epsilon) \cdot d\epsilon \quad 5.1$$

where $\sigma(\epsilon)$ is the cross section for the electron impact excitation to state i from the ground state. A similar equation can be written for the actinometer, and by dividing one by the other, we obtain

$$\frac{I_x}{I_a} \propto \frac{[X^*]}{[A^*]} \propto \frac{[X] \cdot \int \epsilon^{\frac{1}{2}} \cdot \sigma_x(\epsilon) \cdot f(\epsilon) \cdot d\epsilon}{[A] \cdot \int \epsilon^{\frac{1}{2}} \cdot \sigma_a(\epsilon) \cdot f(\epsilon) \cdot d\epsilon} \quad 5.2$$

which is independent of electron density but depends on $f(\epsilon)$.

Under conditions where $f(\epsilon)$ is constant or where the cross sections are identical, the ratio of the integrals are also constant, and so

$$\begin{aligned} \frac{I_x}{I_a} &= \frac{k_x \cdot [X]}{k_a \cdot [A]} \\ \frac{I_x}{I_a} \cdot [A] &= K_x \cdot [X] \end{aligned} \quad 5.3$$

Thus, as the concentration of the actinometer is constant, it can be seen that if the three criteria are upheld, the actinometered emission signal, (left hand side of equation 5.3), is proportional to the ground state concentration. In the event that the excited state is formed by electron impact of another species⁶ or by a non electron impact process, such as a metastable reaction¹², then equation 5.1 is no longer valid and the technique can break down. Even if the concentration of the

second species varies in a similar manner to the species of interest, the excitation cross sections may differ and so a change in $f(\epsilon)$ will influence the emission seen. There are situations however where, if the component of the emission from a second pathway is small and constant with changes in plasma parameters, it still may be possible to extract useful information, (see chapter 6).

The possibility of secondary relaxation mechanisms is rarely a problem, owing to the short lived excited states associated with the intense emissions used. Such is the case for CF_2 , Ar and F emission. For excited oxygen atoms, the collisional quenching rate is very rapid, (as described in chapter 3), and this could effect the emission results in the same way as the LIF data, but such an effect is easily allowed for by a simple quantitative change in the quantum yield of emission.

Previous studies have shown that the presence of rare gas, or indeed any actinometer, can influence the discharge being studied if the concentration is too high. In the case of a rare gas actinometer, it is thought that the presence of metastables are the cause of the perturbation, probably due to their influence on the physics of the discharge, rather than due to chemical reactions between molecular and metastable species¹³. This perturbation has been shown to be negligible at the low concentration of actinometer, (<10% by volume), used in the present studies.

5.3 CF_2 : LIF and Actinometered Emission

5.3.1 CF_2 Actinometry : Steady State Studies

The emission intensity from electronically excited CF_2 and Ar, CF_2^* and Ar^* , was measured over a range of experimental conditions. For CF_2 , the A (0,5,0) – X (0,0,0) band was monitored owing to its high relative intensity and lack of other overlapping transitions, as shown in figure 5.1. All the CF_2 bands are however superimposed on a continuum emission stretching from 250 – 330 nm with a maximum around 300 nm. The most probable source of this emission is CF_4^+ , and a similar feature has been seen in electron beam studies¹⁴ and synchrotron studies^{15,16} on CF_4 . Some workers³ assigned the band to a transition of CF_2^+ , using the similar behaviour of CF_2 and the continuum emission, and thermodynamic

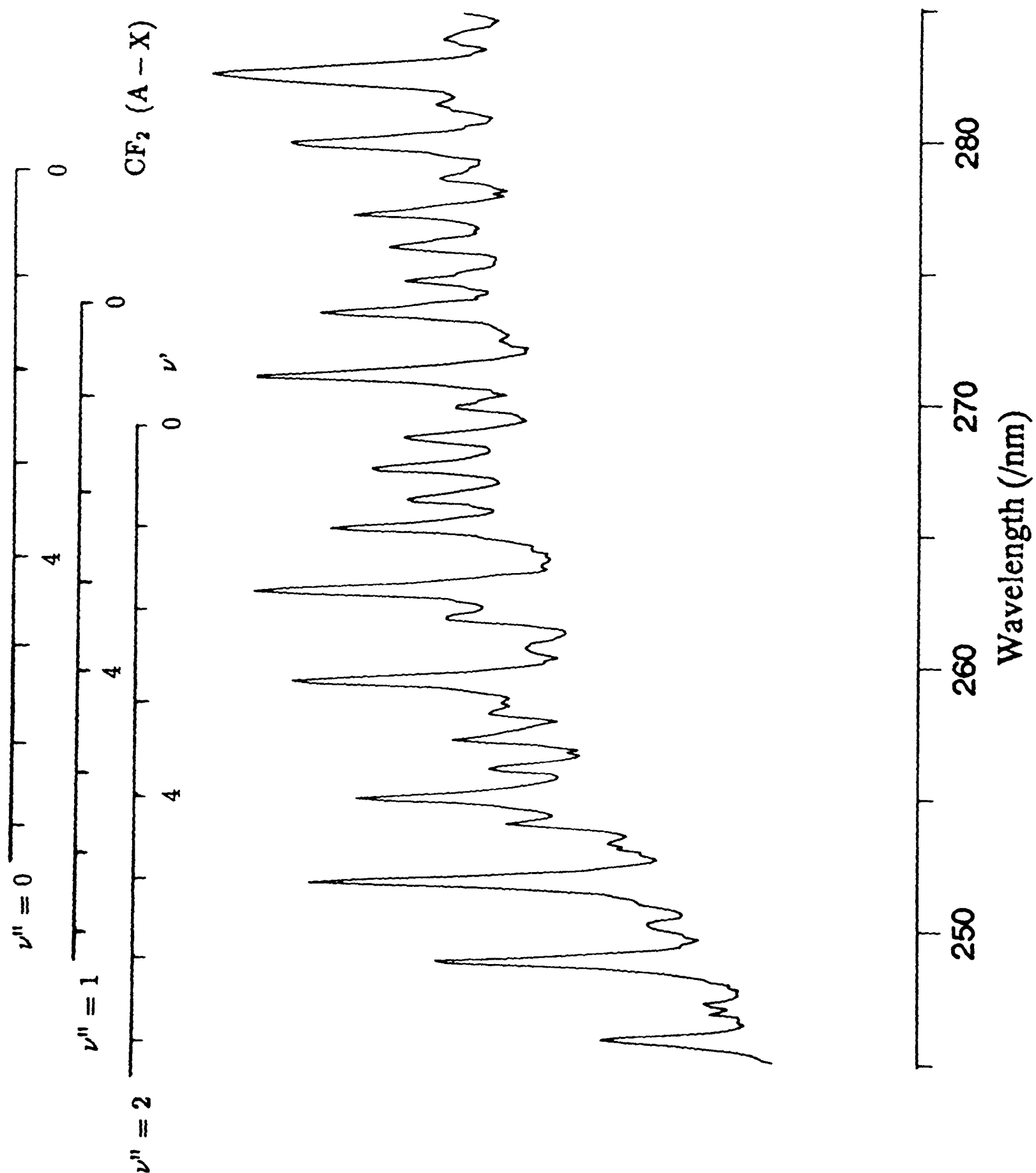


Figure 5.1 Part of the emission spectrum from a 50 mTorr, 200 W CF_4 plasma, showing bands from the CF_2 ($\tilde{\text{A}}^1\text{B}_1 - \tilde{\text{X}}^1\text{A}_1$) transition.

arguments as an explanation. However, previous work in this laboratory^{17,18} has shown a poor correlation between the continuum and the CF₂ ground state concentration, and illustrated a close dependence on CF₄ pressure and electron density, (as measured by Ar emission).

To extract the CF₂ emission signal from the spectra, it is necessary to subtract the continuum component, which requires that the CF₂ emission peaks are fully resolved. Previous attempts¹⁷ to determine the vibrational temperature of CF₂ using the relative intensities of the transitions, indicated that many of the bands behaved similarly with changes in plasma parameters, and so monitoring the (5,0) transition was considered to be a good representation of the total CF₂ A – X emission.

λ (/nm)	Upper level	Lower level	A factor (/10 ⁸ s ⁻¹)	Threshold Energy (/eV)
<u>750.4</u>	4p'[$\frac{1}{2}$]	4s' [$\frac{1}{2}$] ⁰	0.47	13.5
104.8	4s' [$\frac{1}{2}$]	3p ⁶ ¹ S	5.10	
<u>687.1</u>	4d [$\frac{1}{2}$] ⁰	4p [$\frac{1}{2}$]	0.029	14.7
965.8	4p [$\frac{1}{2}$]	4s [$\frac{3}{2}$] ⁰	0.272	
<u>703.0</u>	6s [$\frac{3}{2}$] ⁰	4p [$\frac{5}{2}$]	0.278	13.1
801.5	4p [$\frac{5}{2}$]	4s [$\frac{3}{2}$] ⁰	0.366	

Table 5.1

Several Ar lines were monitored, (750.4, 703.0 and 687.1 nm), in both the steady state and time resolved experiments, details of which are given in table 5.1. The first of these lines has been extensively used for actinometric purposes. As can be seen from table 5.1, all three lines chosen have non – metastable lower states so that there should be no complications of self absorption or radiation trapping¹⁹. However, although the lines behaved similarly under steady state conditions they showed some differences as a function of time after ignition, (see figure 5.2). As the

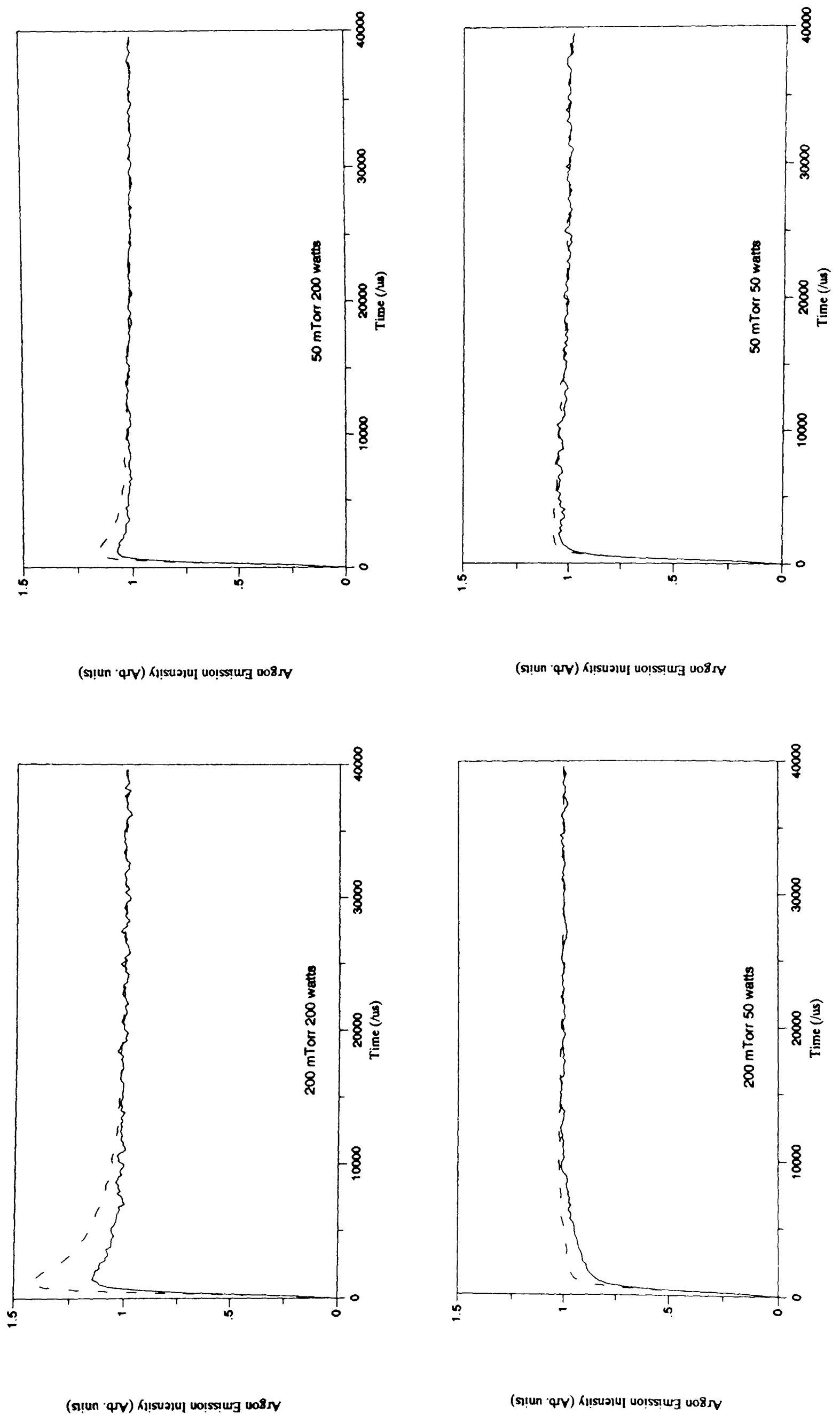


Figure 5.2 Comparison of the time dependence of the emission from two argon lines under four sets of plasma conditions, (750.4 nm — — — 678.1 nm ———).

time constant associated with the variation is of the order of a few milliseconds, one possible cause is the build up of metastable concentration. As shown, metastables should not affect the radiative decay of the excited state but they may influence the production rate. Full analyses of the rate equations for the production of a variety of excited states of Ar have been done²⁰, and it has been shown that the state from which 750.4 nm emission occurs, is formed predominantly by direct electron impact of the ground state atom, ($> 86\%$). Thus, the 750.4 nm line was used for most of the steady state and time resolved measurements of Ar emission, and the others were used for experimental convenience under conditions where their behaviour was similar to that of the 750.4 nm line. For this study, neon was also used as an actinometer, monitoring the 650.6 nm line, ($2p^53s \left[\frac{1}{2}\right]^0 - 2p^53p \left[2\frac{1}{2}\right]$), which has a lower state optically connected to the ground state. In order to test the applicability of the excited state emission as a monitor of the ground state, the CF₂ LIF signal was measured by tuning the laser to the centre of the A (0,11,0) – X (0,0,0) transition and monitoring the fluorescence at (11,4) as a function of plasma parameters. Such a measurement is a reasonable representation of the total ground state concentration, since it fulfils the criteria described in section 1.4.2.

The emission and LIF data were taken under identical conditions on the same apparatus, and the results from Ar and CF₂, for three different pressures, over a range of rf powers are given in figures 5.3 – 5.5.. The result of combining and comparing the data directly, by plotting AOE against LIF is shown in figure 5.6.

It can be seen that for the lowest pressure data at 50 mTorr, there is a fairly strong correlation between the two techniques, although there is a small intercept on the AOE axis, (which will be discussed later). At 100 mTorr, the agreement is still reasonable, at least qualitatively, but for the 200 mTorr data, the use of AOE as a measure of the ground state concentration of CF₂ could seriously distort any attempt to interpret the plasma. There is good correlation between the signals up to a power of 100W, but there appears to be a sudden change above this. This change is most clearly observed in the CF₂ emission data and is not strongly reflected in the argon signal. It should be noted however, that the CF₂ ground state concentration

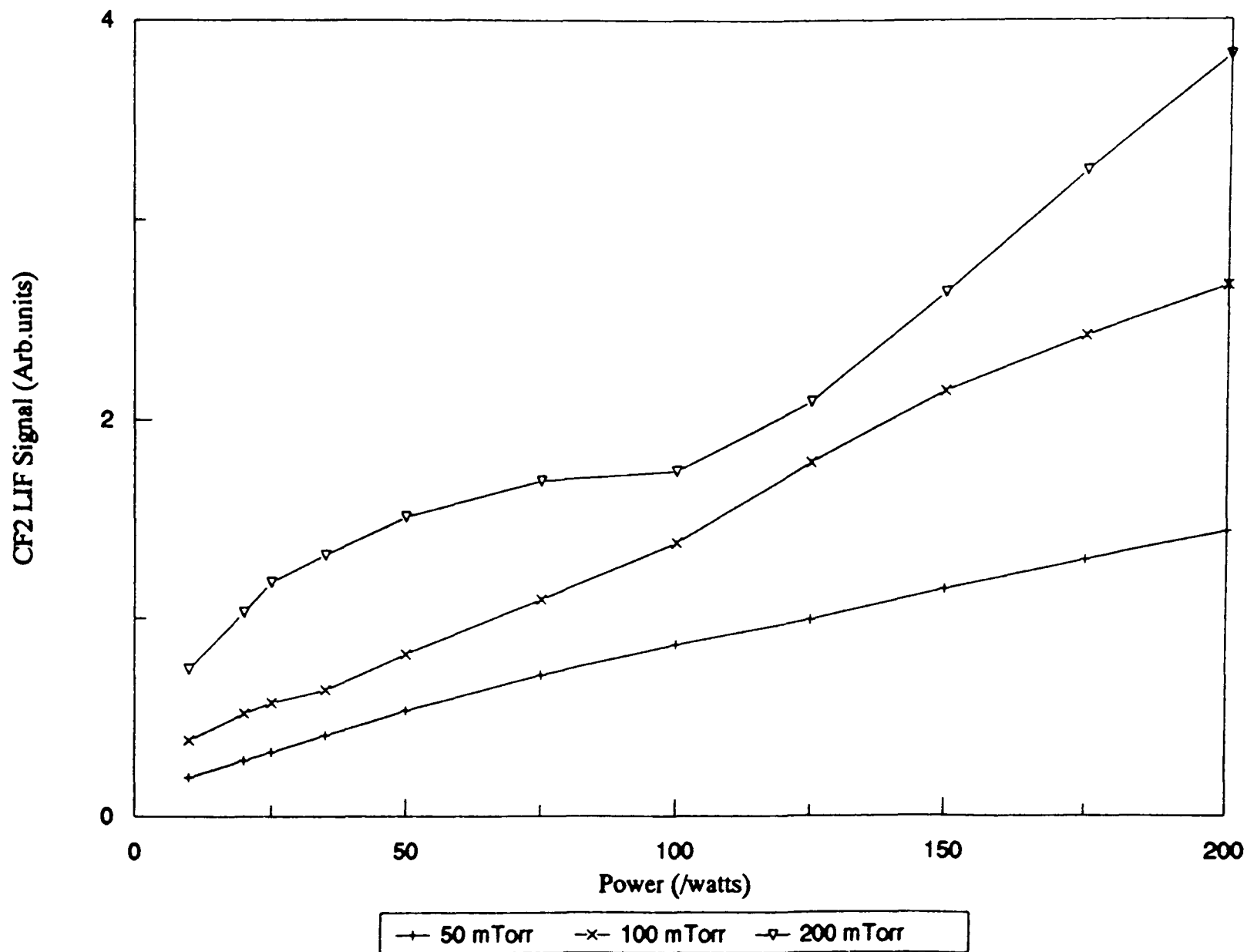


Figure 5.3 Variation of the CF₂ LIF signal as a function of power and pressure in a CF₄ plasma.

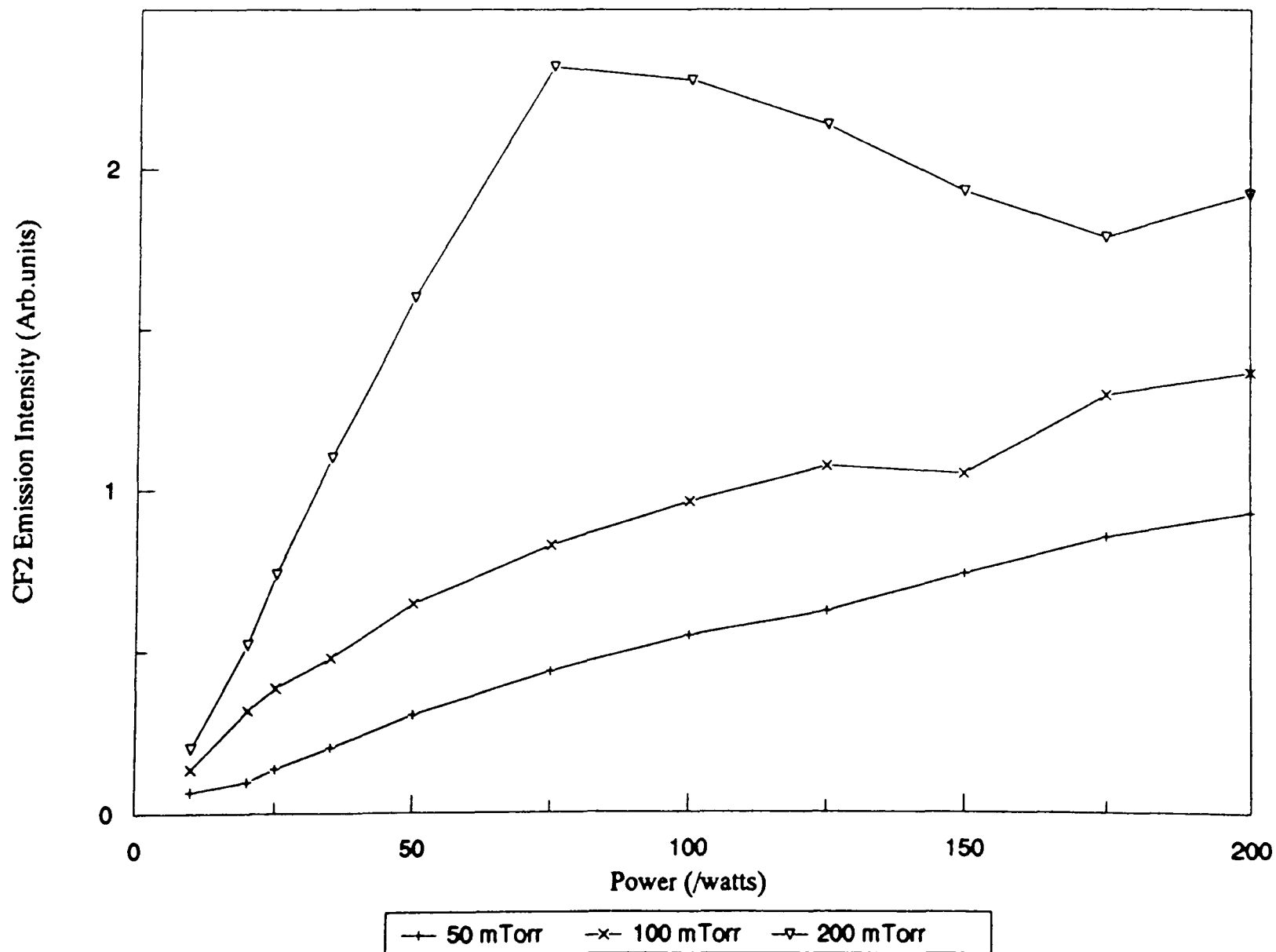


Figure 5.4 Variation of the intensity of CF₂ emission as a function of power and pressure in a CF₄ plasma.

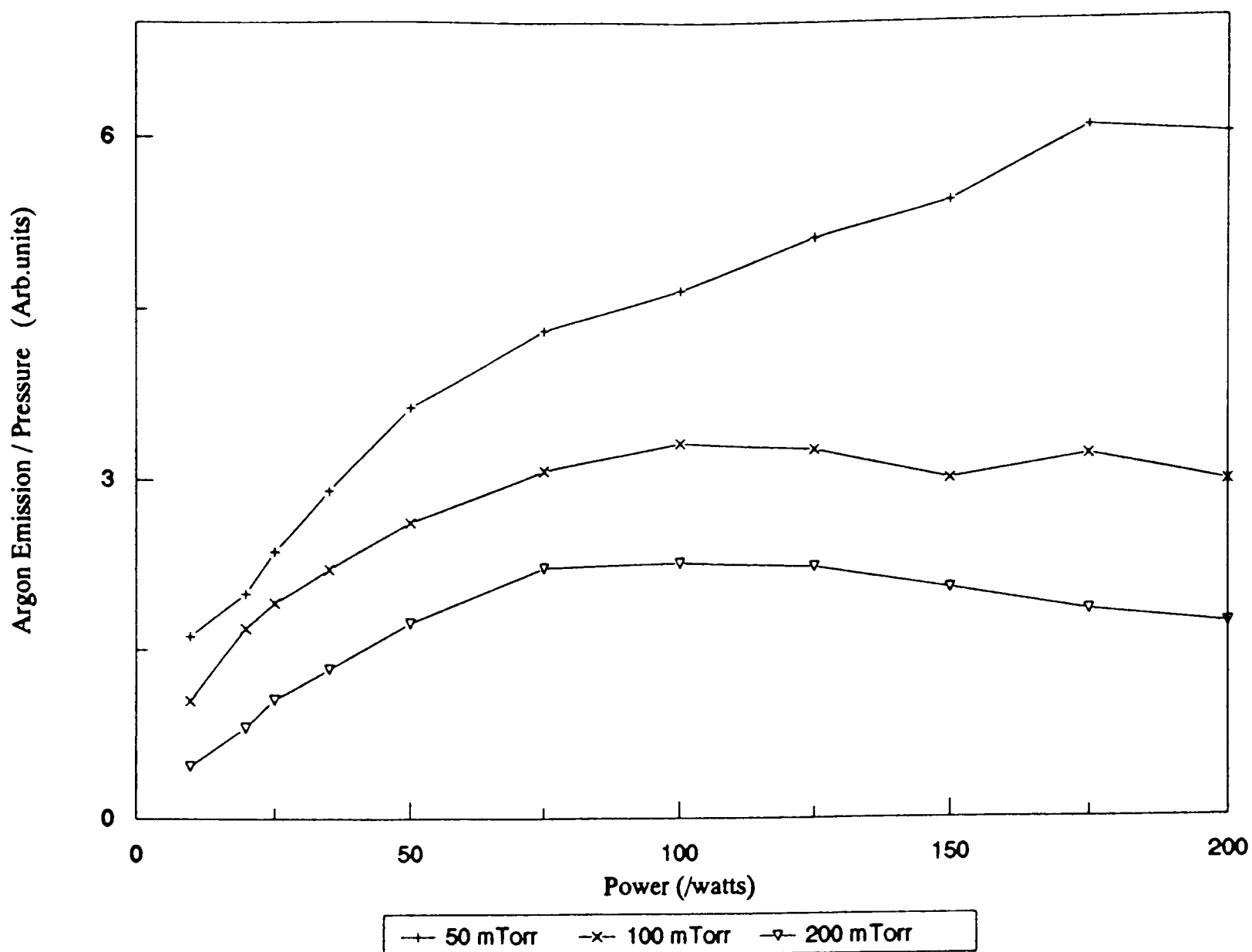


Figure 5.5 Variation of the intensity of argon emission as a function of power and pressure in a CF_4 plasma.

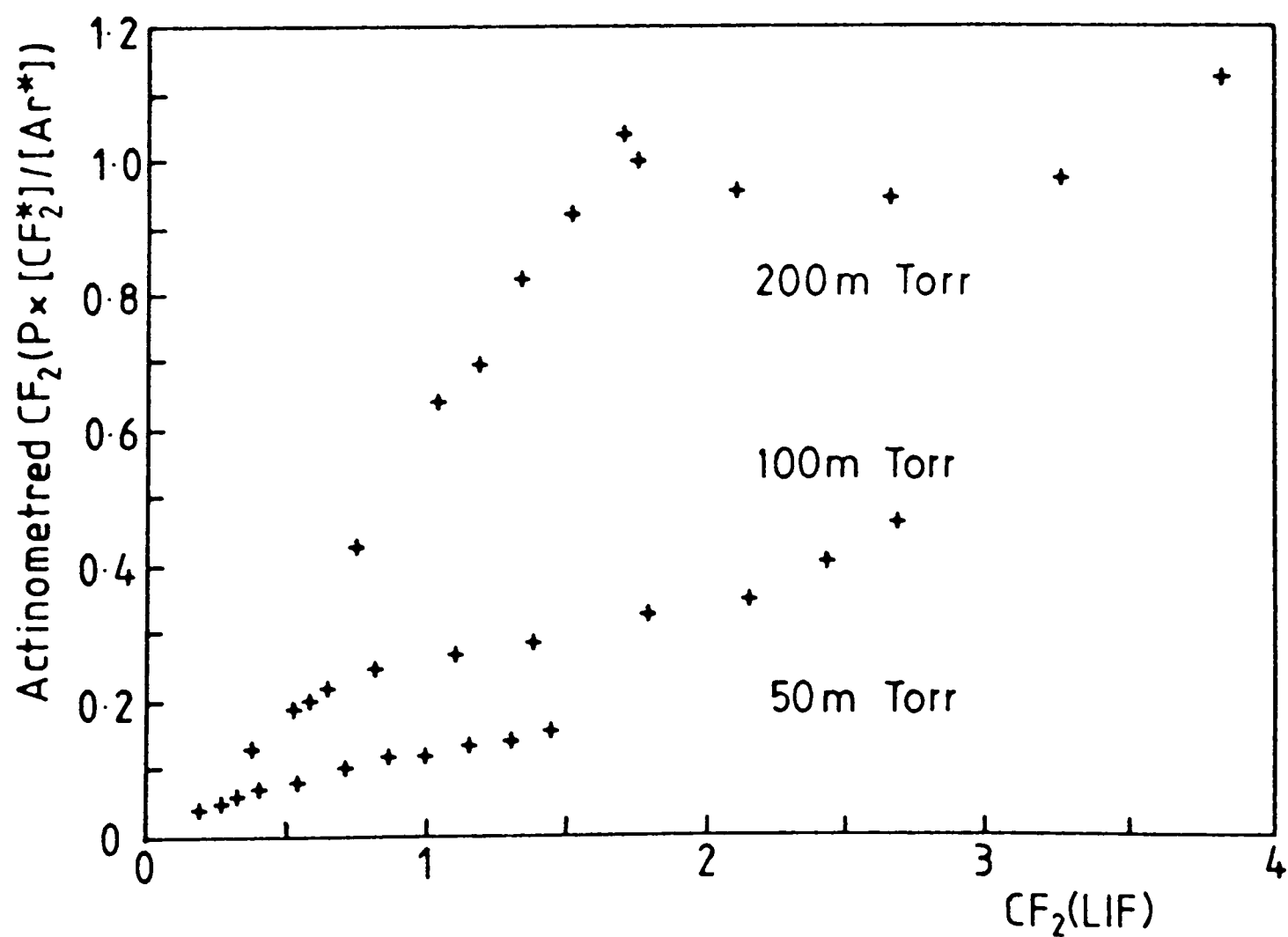


Figure 5.6 Variation of the actinometered CF_2 emission signal with that from CF_2 LIF, at 50, 100 and 200 mTorr, varying power to change the radical concentration.

also behaves non – uniformly under these conditions.

One possible explanation for the behaviour of CF_2 was that the optical emission was not probing the same spatial region as the LIF. The optical emission for these initial experiments was collected as a spatial average from the plasma, with the window ports acting as the limiting aperture. It was thought that, because of the non – uniform nature of the plasma induced emission, the emission collected might be weighted by a region not probed by the laser, (the laser probed a volume 1 cm above the driven electrode surface). Thus, some spatially resolved experiments were done using two slits to limit the emission from the plasma, which enabled a resolution of about 2 mm. The spatial variation of CF_2 AOE was measured as a function of rf power, and the variation was found to be almost independent of position, (as shown in figure 5.7). Thus, spatial variation of the emission does not appear to be responsible for the observed strange behaviour of CF_2 emission at high power and pressure.

The second actinometer, neon, which was added to the system, has a threshold for electron excitation of 18.6 eV and so comparison with the argon emission, ($E_{\text{th}} = 13.5\text{eV}$), can illustrate a variation in the high energy tail of the EEDF. The results can be seen in figure 5.8, where the ratio of the argon to neon emission is plotted against power. This reveals that an increase in power causes a larger increase in the fraction of electrons with energy greater than 18.6 eV than those with energy greater than 13.5 eV, (ie. an increase in the high energy tail, although this is not necessarily related to the electron temperature of the bulk electrons). This change in EEDF is however sufficient on its own to question the use of actinometry for CF_2 , because of the large difference between threshold energies of this species and those of the gas actinometers.

5.3.2 CF_2 Actinometry : Time Dependent Studies

To overcome the complications of a change in the electron energy distribution on the AOE measurements, a second method was employed, which used time instead of plasma parameters, as a means of varying the ground state CF_2

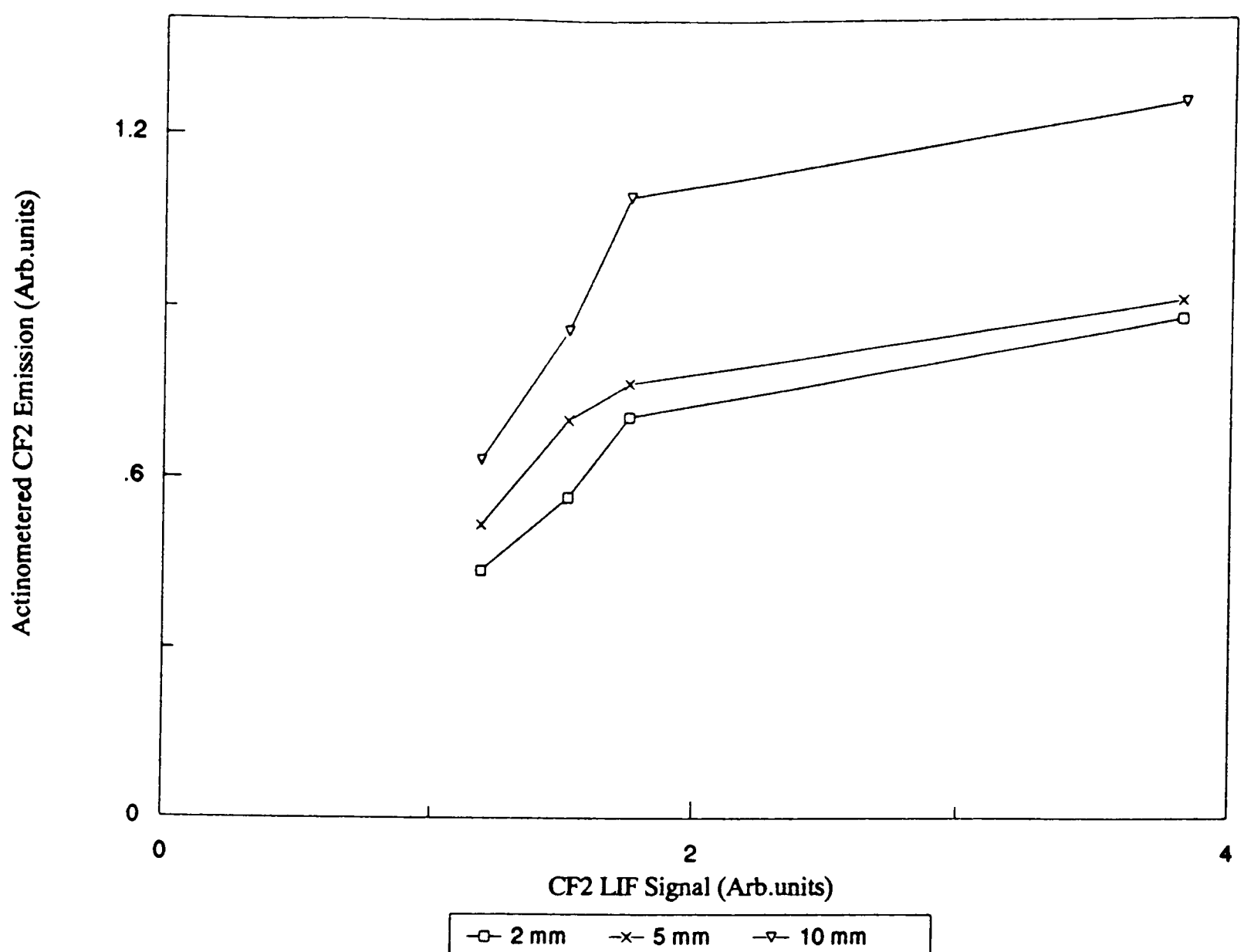


Figure 5.7 Variation of the actinometered CF₂ emission signal with that from CF₂ LIF, as a function of distance from the driven electrode.

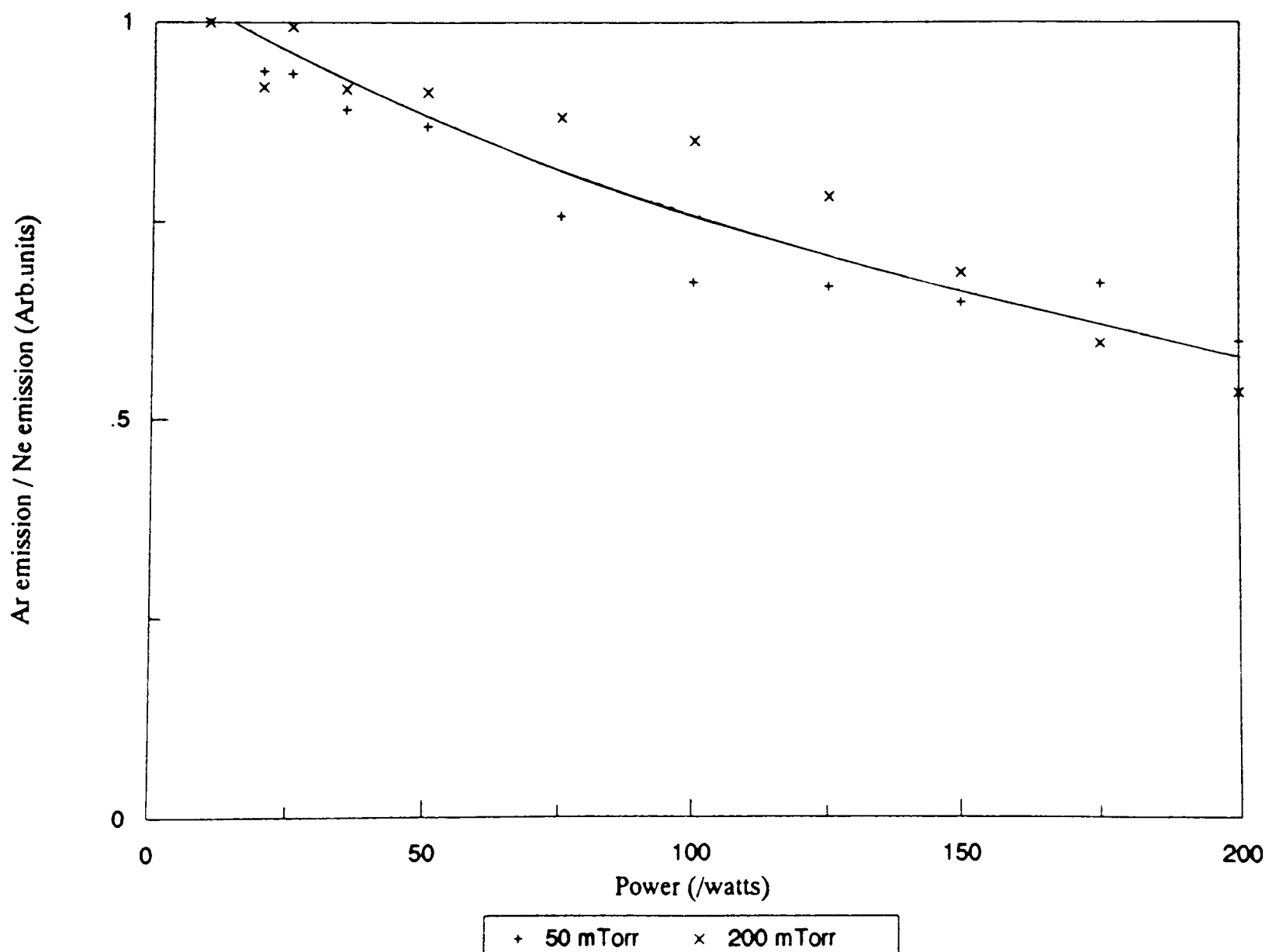


Figure 5.8 Ratio of the emission from the actinometer Ar (750 nm) to that of Ne (651 nm) as a function of power. (The actinometers were used separately).

concentration. This was done by following the rise in the concentration of CF_2 after plasma ignition, as measured by AOE and LIF, making sure that all the CF_2 produced in the previous plasma pulse had been removed. The premise was that after an initial breakdown period, the EEDF and the plasma density remain constant and so should not influence the emission from CF_2 . This relies on the electron distribution being unaffected by changes in the precise chemical composition of the plasma, which is a reasonable approximation as the major electron interactions involve feedstock gases, and their concentrations are not significantly depleted on plasma ignition. Some measure of the validity of this assumption can be gained by studying the argon emission signal as a function of time after ignition, (see figure 5.2). In all cases, the steady state level is reached on a much faster time scale than that of the temporal CF_2 behaviour, and anyway the CF_2 emission was actinometered so that any variation in electron density was allowed for.

The overshoot of the signal at high power and pressure is thought to be due to the breakdown mechanism of the plasma. During ignition, the low concentration of any charged species causes the electric fields to rise up to the high levels required for electric breakdown. At this point, the ions and electrons are generated by collisions with the accelerated electrons, which has the effect of reducing the rf fields. The rf power output can be seen to stabilize after a few microseconds, but the effect of the high initial breakdown voltages appear to last for longer, particularly at high rf power and plasma pressure.

The time dependent CF_2 emission was measured in two ways; i. by obtaining a full two dimensional array of time and wavelength, so that spectra of the CF_2 band were collected at a variety of time delays, (see figure 2.3), and ii. by following the time variation in the intensities of just the peak and background wavelengths, thus using a peak height method of analysis of the spectra. Both methods produced very similar data, but the former was used for the majority of CF_2 studies to ensure that any variation in the band shape was allowed for and that the correct background was subtracted. (In experiments involving atomic species, Ar, F and O,

the latter method was used because of the flat backgrounds surrounding the lines of interest and the fact that the observed line widths were instrument limited.) A number of different CF₂ bands were monitored, ((4,1),(3,1),(6,0) and (5,0)), and as with the steady state measurements, the behaviour observed was independent of the band. The LIF data were taken by firing the laser at various delays after the plasma was ignited and used the same transition as before.

The AOE and LIF results have again been plotted against each other and are given in figures 5.9 – 5.12. The scales used relate to the final steady state values of the AOE and LIF signals. It can be seen for the first three plots that, except for an intercept on the AOE axis, there is very good agreement between AOE and LIF. The size of the intercept increases with decreasing pressure, but even at 50 mTorr, it only accounts for 10% of the steady state level. One interpretation of this is the presence of a direct pathway from electron impact of CF₄ to form CF₂*.



The rate of this process depends on the concentration of CF₄ and the electron energy distribution, both of which are invariant during these experiments. This component is thus expected to be constant, whilst that from electron impact of ground state CF₂ will vary with ground state concentration.



This is consistent with the data shown in figures 5.9 – 5.11. The energy threshold for dissociative excitation of CF₄ to CF₂* is higher than that for the direct excitation of the ground state species, and so the former would be expected to be more significant under conditions of high electron temperature. The electron temperature is known to fall as the gas pressure is increased, and so an increase in pressure should reduce the intercept on the AOE axis, as observed experimentally.

This model does not explain the result at 200 W, 200 mTorr, (figure 5.12),

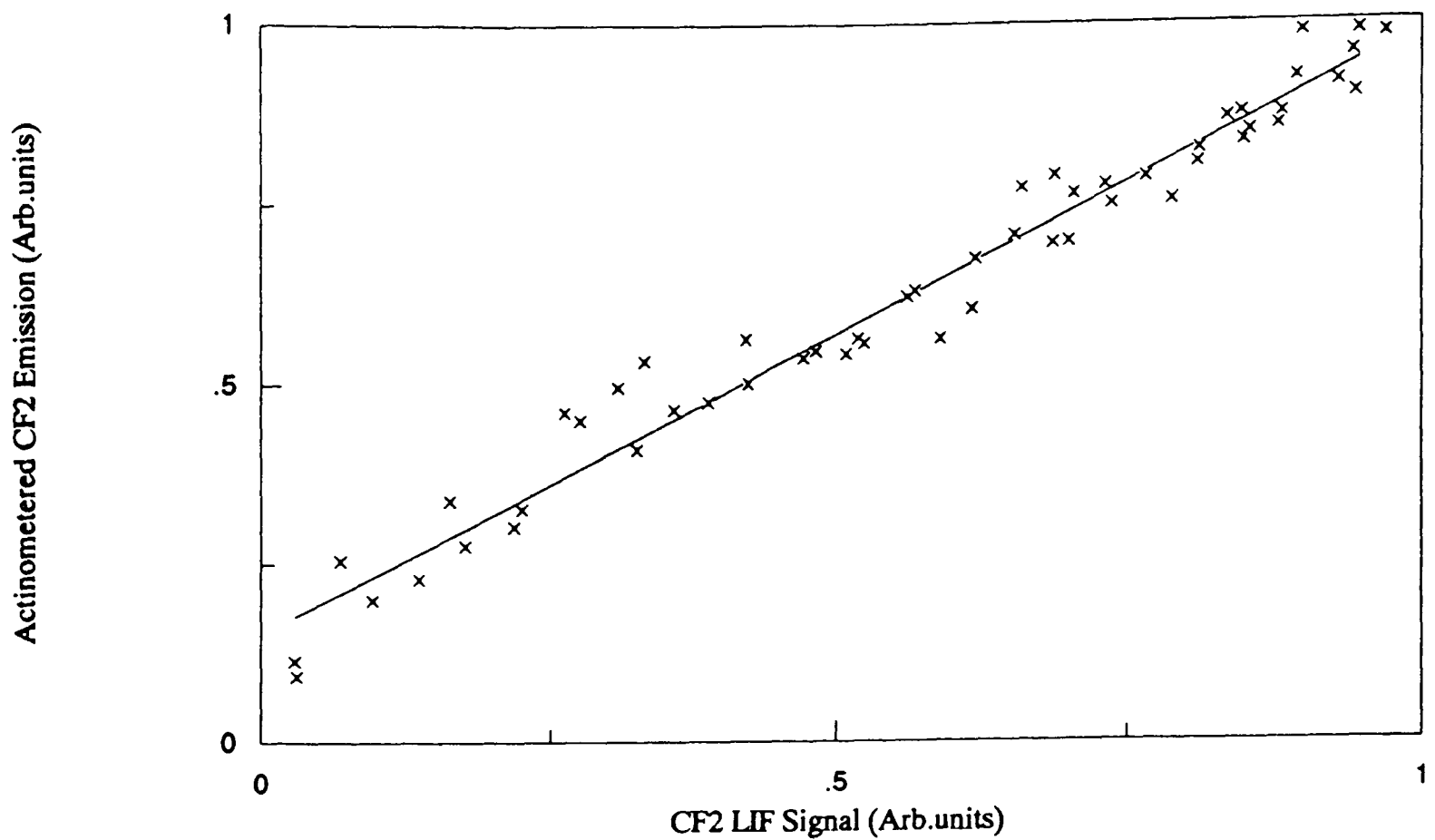


Figure 5.9 Variation of actinometered CF_2 emission with CF_2 LIF as a function of time after plasma ignition in a 50 mTorr, 200 W CF_4 plasma.

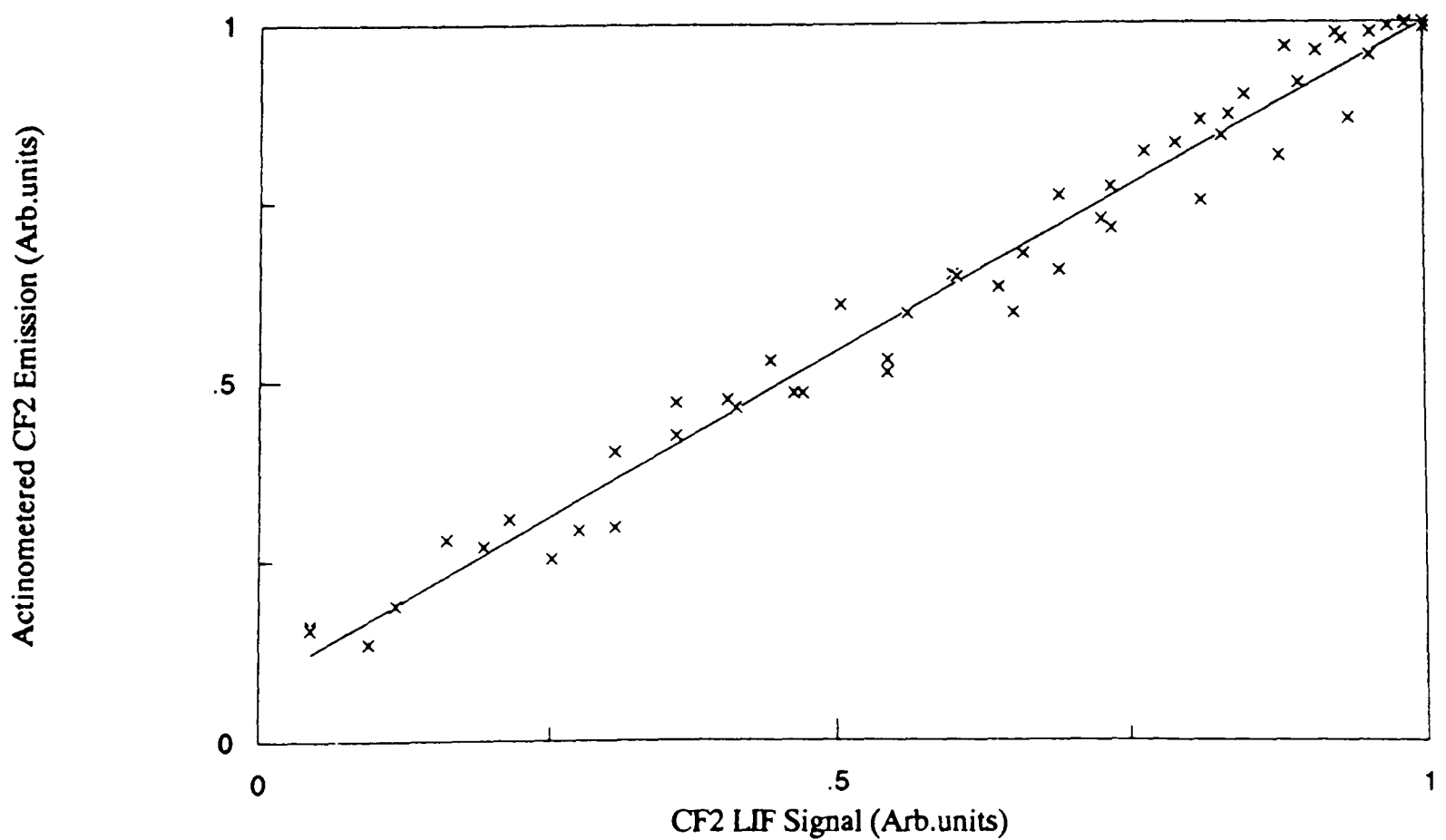


Figure 5.10 Variation of actinometered CF_2 emission with CF_2 LIF as a function of time after plasma ignition in a 100 mTorr, 200 W CF_4 plasma.

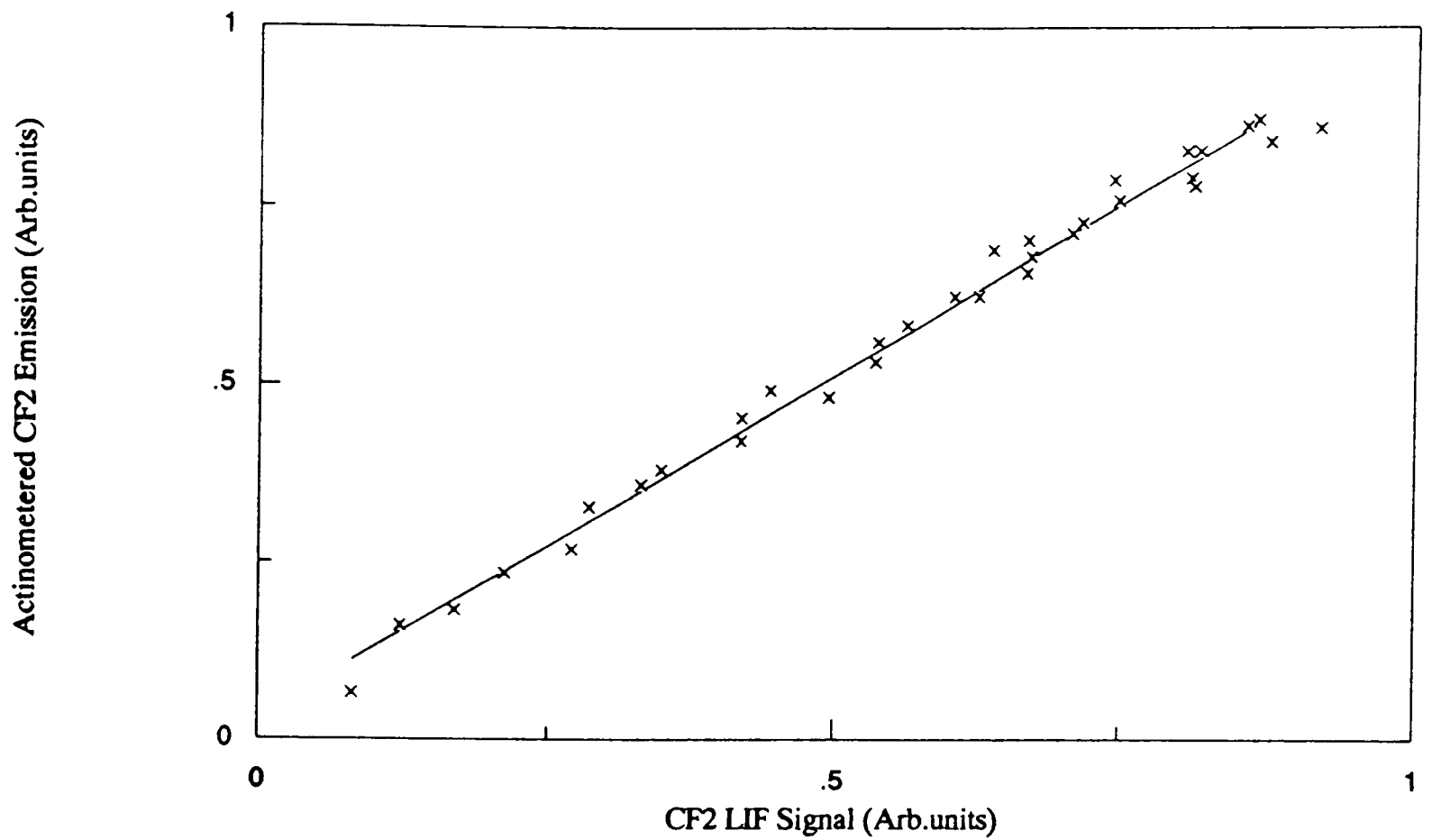


Figure 5.11 Variation of actinometered CF₂ emission with CF₂ LIF as a function of time after plasma ignition in a 200 mTorr, 50 W CF₄ plasma.

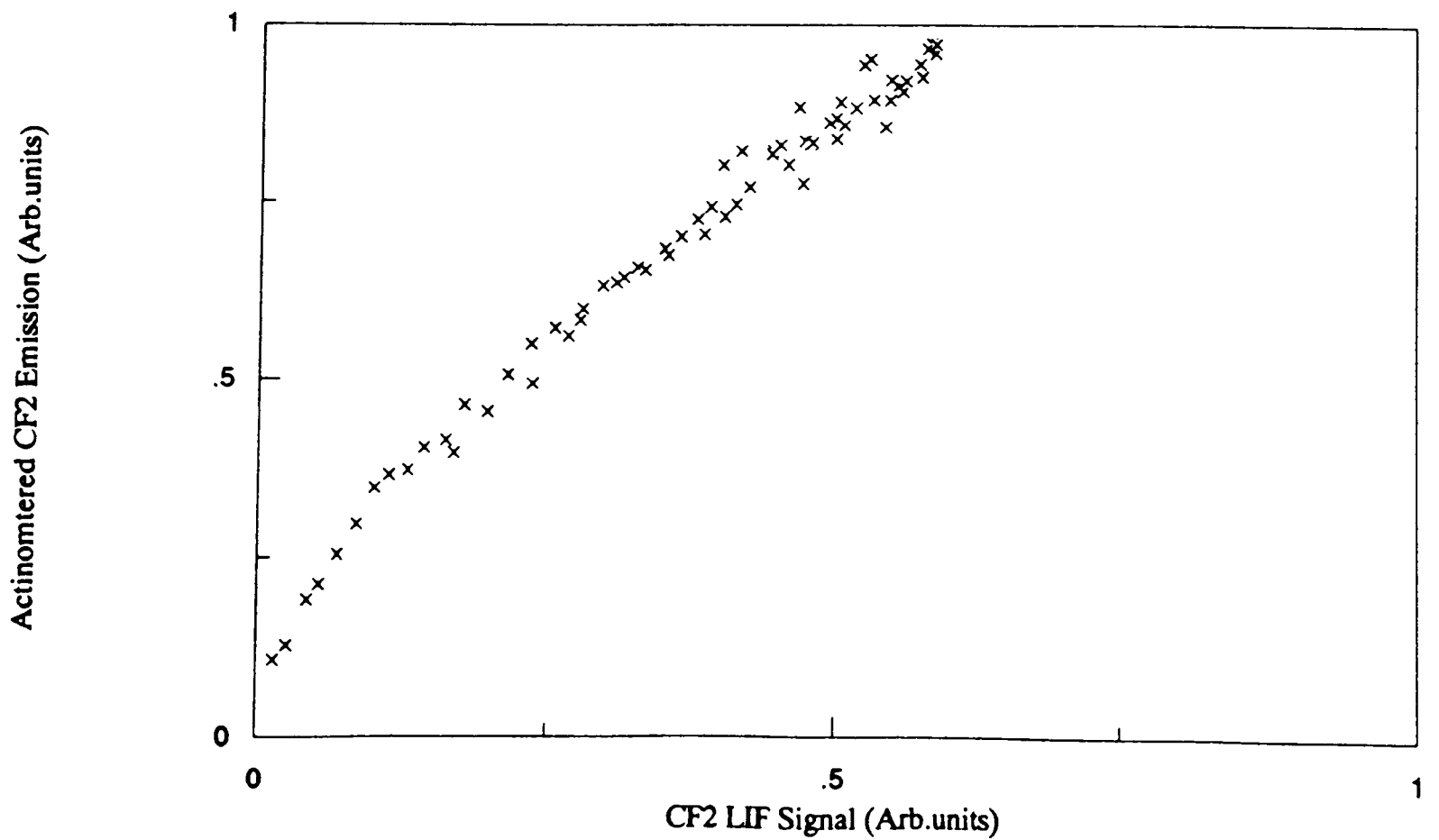


Figure 5.12 Variation of actinometered CF₂ emission with CF₂ LIF as a function of time after plasma ignition in a 200 mTorr, 200 W CF₄ plasma.

The reason for this can be seen from the temporal profiles of AOE and LIF for conditions of 50 mTorr, 200 W and 200 mTorr, 200 W, in figure 5.13. For the 50 mTorr data, the rise times obtained are seen to be very similar as expected from the discussion above, but the 200 mTorr results illustrate significantly different time scales for the two techniques, that for AOE being about four times that for LIF. Spatially resolved experiments on the time resolved rise data were carried out and showed the rise time for the actinometered emission to be independent of position. Thus, spatial variation of the emission was unable to explain the difference in the rise times observed at high plasma power and pressure. The rise time of the emission must depend on the kinetic rise time of the species, which is responsible for the production of the CF_2 excited state, since the excitation function has a much more rapid rate, as shown by the argon emission. The identification of such a species has not been found but it is interesting anyway to note the apparent change in production mechanism for the CF_2^* state. This change also seems to be exhibited in the steady state observation of CF_2 emission and CF_2 ground state.

The CF_2 region of the emission spectra from a CF_4 plasma recorded at 200 mTorr, with 50 and 200 W, are shown in figure 5.14 and these are illustrative of the differences observed between these two experimental conditions. The relative steady state emission intensities from a variety of species were seen to exhibit a large variation as the power was increased; CF_2 emission showed a slight rise, but the ratio of CF_2 to continuum decreased significantly, and the carbon atom emission at 248 nm which was not observed at 50 W, was very strong at the higher power. Direct observation of the plasma was itself sufficient to perceive a fairly sudden change in the discharge, with the plasma appearing almost white at low power and blue at high power.

This type of behaviour was also seen in CF_4 / O_2 plasmas, although the power at which the apparent transition occurred varied with gas composition, (see figure 5.15). It is probable that the cause of this rapid transition is due to the physics of the discharge rather than the chemistry, and a measure of the full EEDF in such plasmas would be of great interest. A transition such as the $\alpha - \gamma$ regime

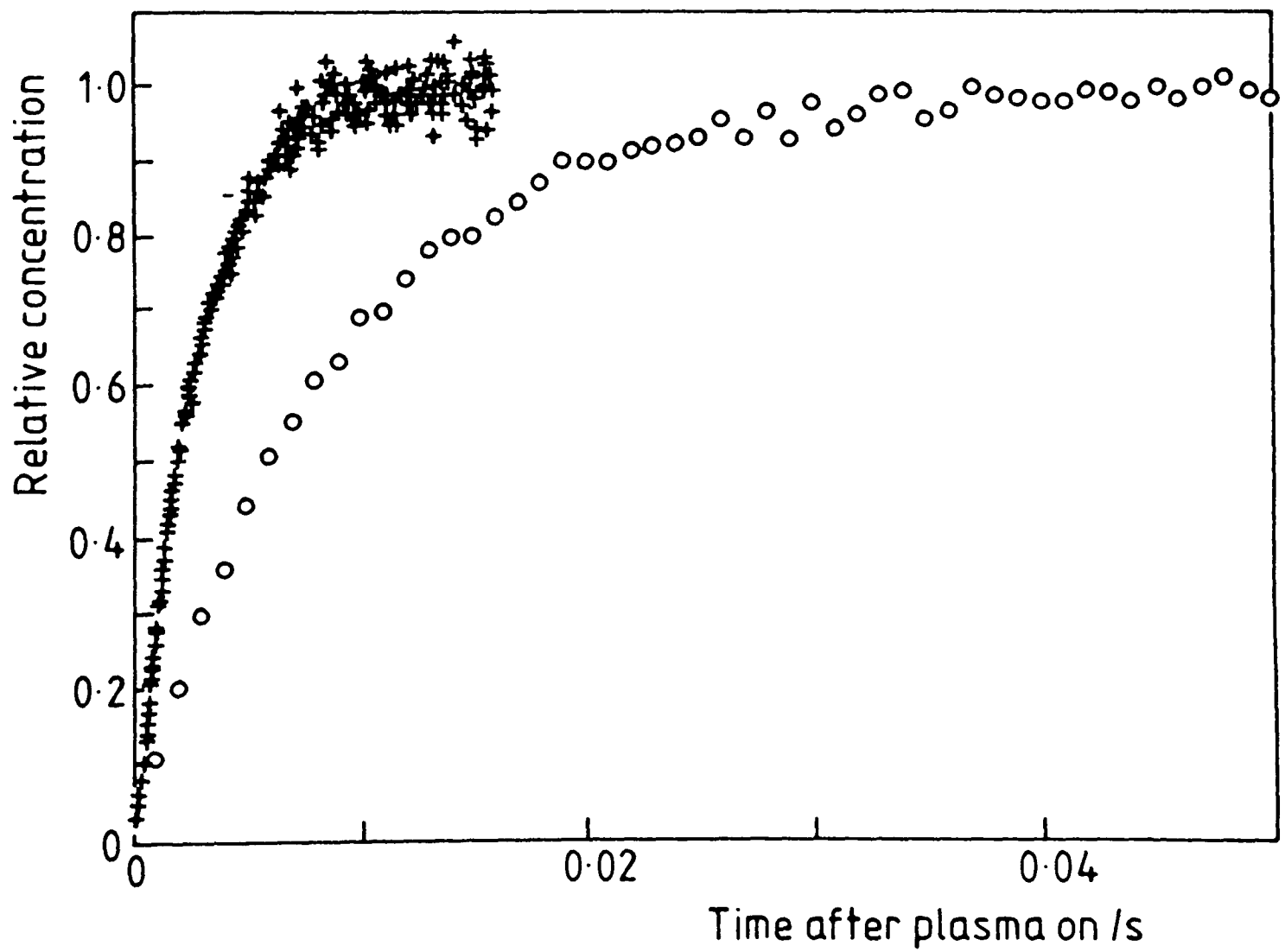
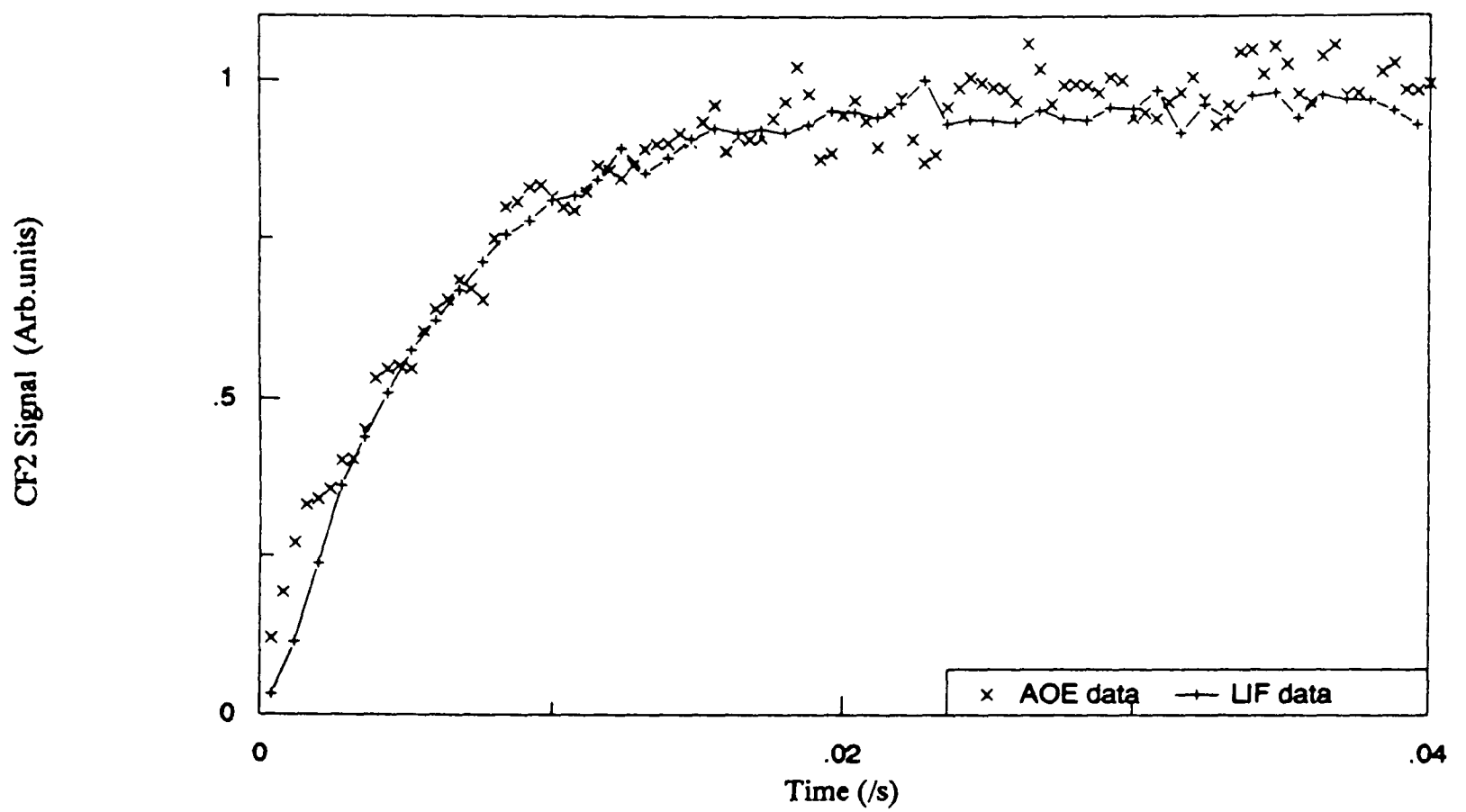


Figure 5.13 Temporal profiles of AOE and LIF of CF_2 in a CF_4 plasma at (a) 50 mTorr and (b) 200 mTorr, (+ AOE, o LIF)

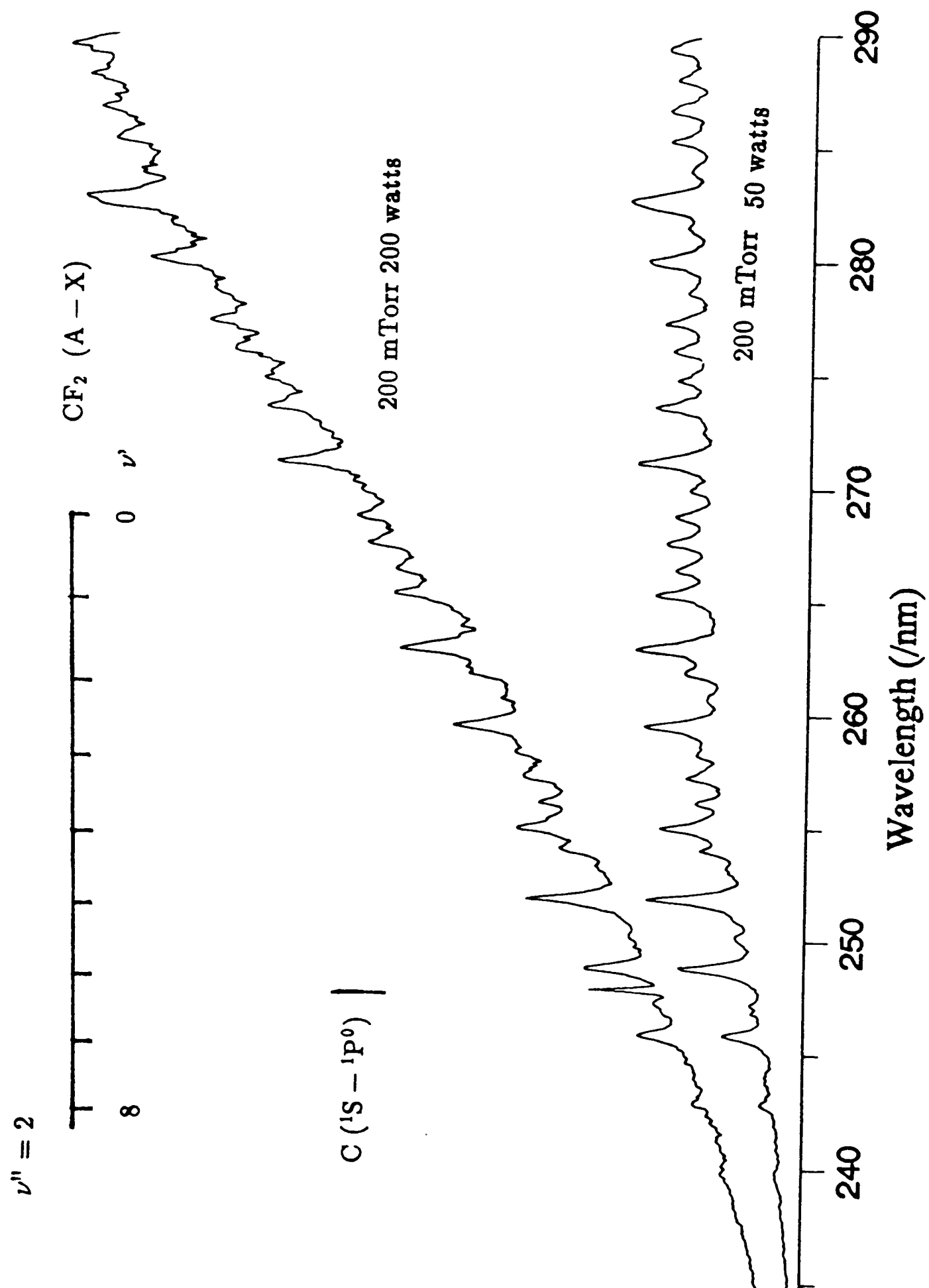


Figure 5.14 Part of the emission spectra from a CF_4 discharge illustrating the CF_2 (A - X) transition region, taken at two sets of plasma conditions.

transition observed in other rf systems,(see chapter 1), may partly explain the results obtained. The "blue" plasma observed at high power and also lower pressure, may be associated with the secondary electron production mechanism, (γ), whilst the "white" plasma depends on wave riding to sustain the discharge, (α).

Lower mean electron energies, with highly energetic secondary electrons are related to the γ regime. This might explain the apparently low level of excitation of ground state CF_2 to CF_2^* , which has a low threshold (5eV), but the high levels of excitation of CF_4^+ and C, which require high energy electrons. The variation in the transition power as a function of gas composition, may be the result of a change in the degree of secondary emission from the electrode, due to changes in the energy and nature of the impinging ions, and / or the nature of the electrode surface itself²¹.

Such speculations need to be tested by direct measurements of the electron energy distribution function, but the problems associated with Langmuir probes in these discharges and the absence of other experimental techniques which can measure the distribution, have made such an analysis unobtainable for this thesis.

The major conclusions for this section are that in terms of the criteria discussed in section 5.2, rare gas actinometry of CF_2 emission should be employed with great caution as a measure of the ground state CF_2 concentration, owing to the difference in the threshold energies and to a direct pathway from CF_4 to excited state CF_2 . It has been shown that the actinometered data was quantitatively, and in some cases qualitatively, a poor representation of the ground state. It may be possible to apply AOE over a limited experimental range, but it should be stressed that the experimental range needs to be clearly defined first by measurements of the ground state concentration.

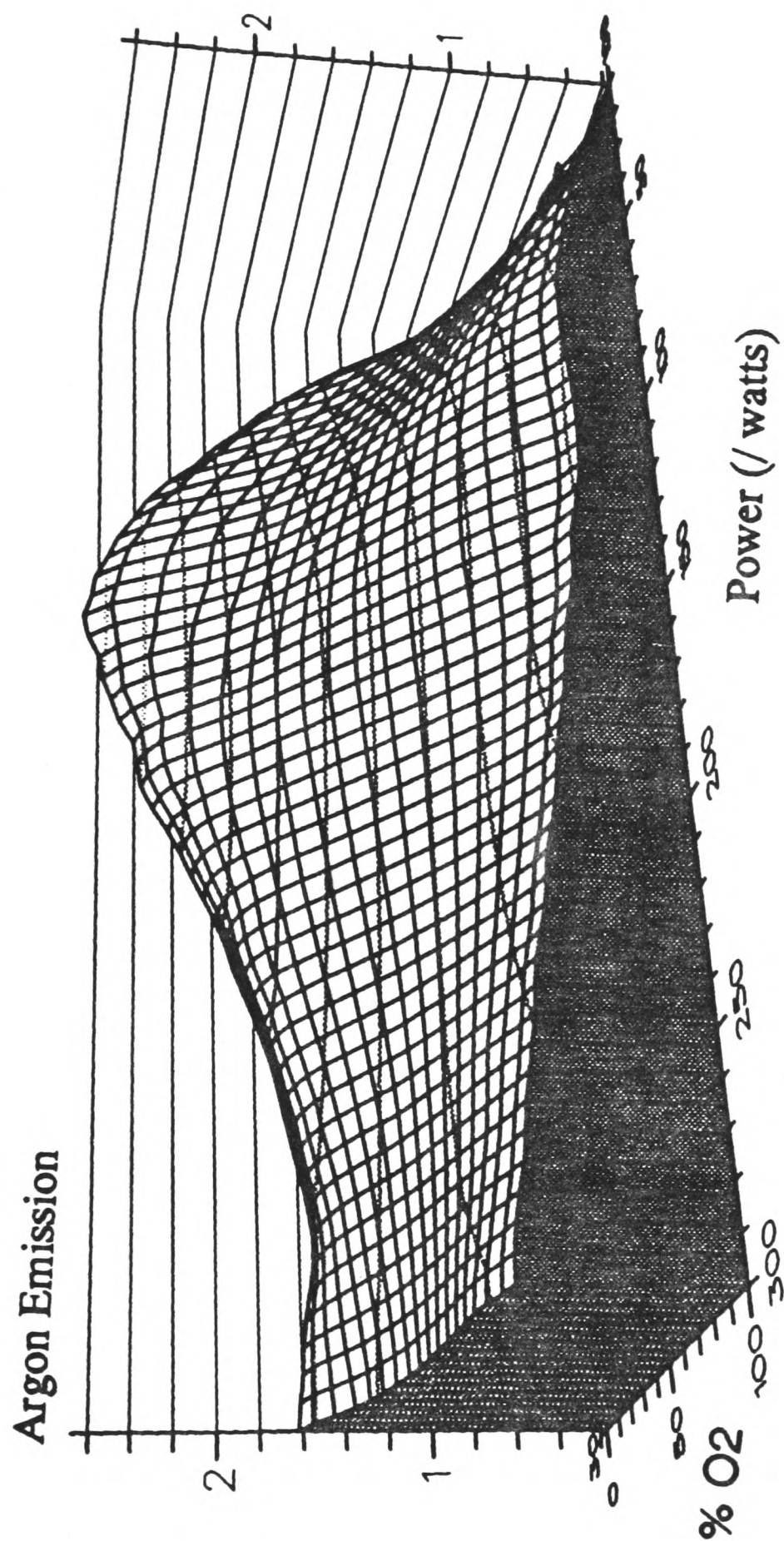
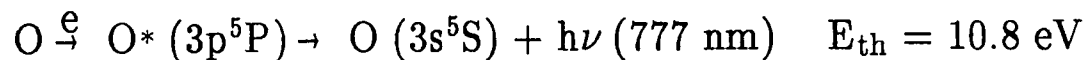
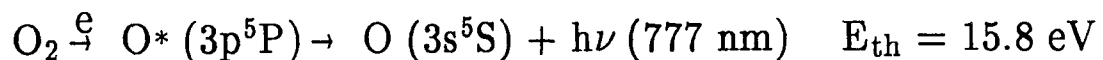
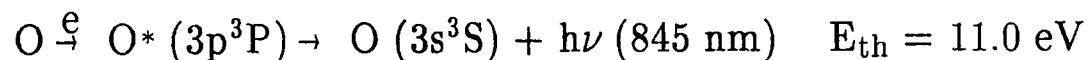
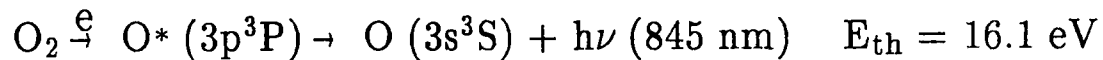


Figure 5.15 Variation in the intensity of argon emission as a function of rf power and gas composition, illustrating changes in the excitation processes in the plasma, (at 200 mTorr).

5.4 Oxygen Atom Actinometry

Two photon laser induced fluorescence was used as a ground state probe for an investigation into the application of actinometry for oxygen atom emission, with great care taken to avoid the experimental complications described in chapter 3. For the oxygen emission, the 845 nm line, and to a lesser extent the 777 nm line, were monitored, because they are intense and are commonly used in the diagnostics for processing plasmas. The thresholds for single electron impact excitation of these lines are 11.0 and 10.8 eV respectively, so that argon should act as a better actinometer for changes in the EEDF than in the CF₂ case. However, as discussed in section 5.1, previous studies have shown the presence of a dissociative excitation mechanism to produce excited state oxygen, O*, from molecular oxygen. This is true for excitation to the upper levels of both of the lines of interest and the processes are summarized below



The dissociative and direct excitation mechanisms have been studied in some detail^{9,11,22,23,24}, due to the interest in oxygen emission from the atmosphere, and all the cross sections have either been measured or calculated. These are shown schematically in figure 5.16. Theoretical calculations on the excitation of oxygen atoms^{22,23} have shown that radiative cascading from higher states accounts for a significant proportion of the production of the upper state, particularly for the 777 nm line. Julienne and Davis²² discuss optically thick and thin cases corresponding to situations where radiation trapping is important or negligible respectively, and produced theoretical cross sections of the excitation of oxygen atoms for both cases, (where radiation trapping is significant this increases the cascading component). For

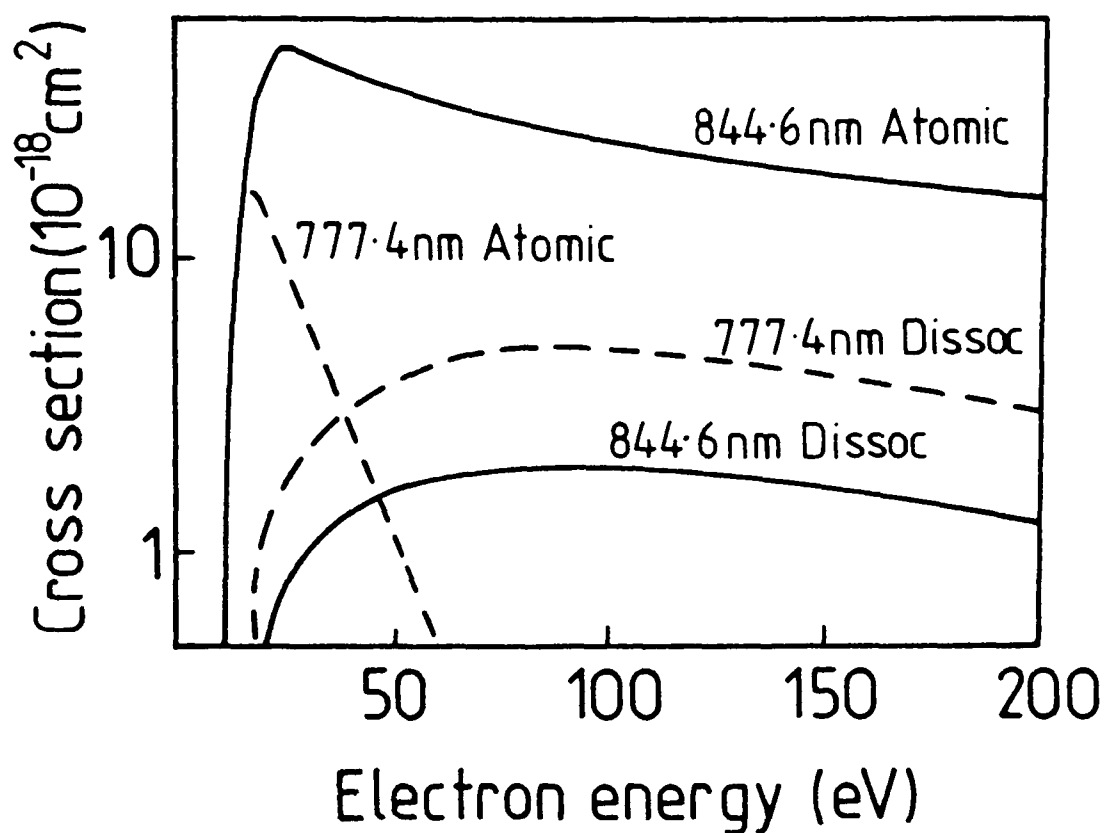


Figure 5.16 Schematic of the cross sections for atomic excitation²² and dissociative excitation²⁴ of oxygen leading to emission, shown as a function of electron energy.

the plasmas used in this study, the relatively low oxygen atom densities measured are consistent with the optically thin case, and it is these cross sections that are shown in figure 5.16. For dissociative excitation, there have been a number of experimental measurements of the cross sections^{9,10,11}, and those shown are from Schulman *et al.*, although there is good agreement between the measurements²⁴.

Walkup *et al.*⁶ considered a variety of other possible mechanisms for the production of O*, such as dissociative recombination and ion – ion or ion – electron recombination, but concluded that the electron impact mechanisms described above are the most important in processing plasma environments. Analysis of the line width of the 777 nm line provided further evidence for the dissociative mechanism, in the form of translationally hot oxygen atoms. However, more recent work²⁵ has questioned whether self absorption of the emission due to the build up of the metastable lower state, (3s⁵S), may be responsible for the observed line shape. The overall conclusions were that in the plasma, both the 777 nm and the 845 nm lines have a dissociative component, but that for the 845 nm line the direct atomic

excitation is still significant, a conclusion which has been suggested by other workers^{7,8}.

For dissociative and direct excitation, the equations from section 5.2, can be extended to give⁷

$$\begin{aligned} \frac{I_0 \cdot [\text{Ar}]}{I_{\text{ar}}} &\propto \left[\frac{k_0}{k_{\text{ar}}} \cdot [\text{O}] + \frac{k_{02}}{k_{\text{ar}}} \cdot [\text{O}_2] \right] \\ &= K_0 \cdot [\text{O}] + K_{02} \cdot [\text{O}_2] \end{aligned} \quad 5.6$$

where k_i relates to the production rate of the excited state from i , (ie. for the two cases, $i = \text{O}$ and O_2), and thus K_0 and K_{02} are only constant under conditions where $f(\epsilon)$ is unchanged, (for $\epsilon > E_{\text{th}}$ of all the excitation processes). From equation 5.6

$$\frac{I_0 \cdot [\text{Ar}]}{I_{\text{ar}}} \cdot \frac{1}{[\text{O}_2]} = K_0 \cdot \frac{[\text{O}]}{[\text{O}_2]} + K_{02} \quad 5.7$$

Thus, for conditions where K_0 and K_{02} are constant, it is possible to determine the relative magnitude of the two components, by plotting the actinometered signal divided by the O_2 pressure against the dissociation fraction. As the thresholds for excitation are similar, the criteria for which this technique is applicable can be slightly relaxed.

The aim of this study was to extend previous work to a larger parameter space, in particular to lower O_2 percentages, and to try to determine the relative importance of the mechanisms which produce excited state oxygen.

5.4.1 Oxygen Actinometry : Steady State Measurements

Actinometered 845 and 777 nm emission and the two photon LIF measurements of oxygen atoms are given in figure 5.17, over the full range of gas composition for CF_4 / O_2 discharges. The results indicate that both emission lines show a reasonable correlation with ground state concentration, although at very high and very low percentages of O_2 the agreement is not so good, particularly for

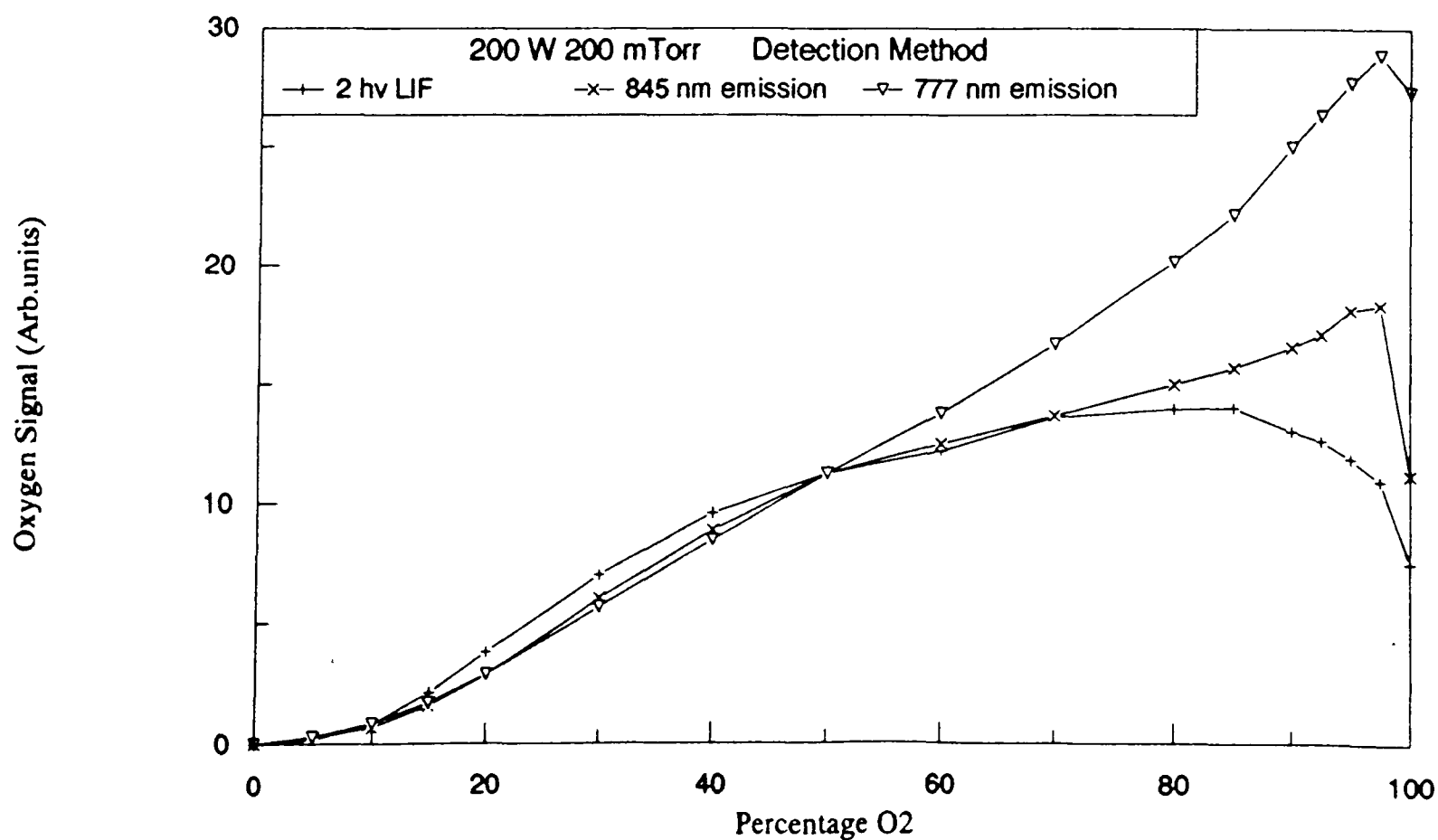
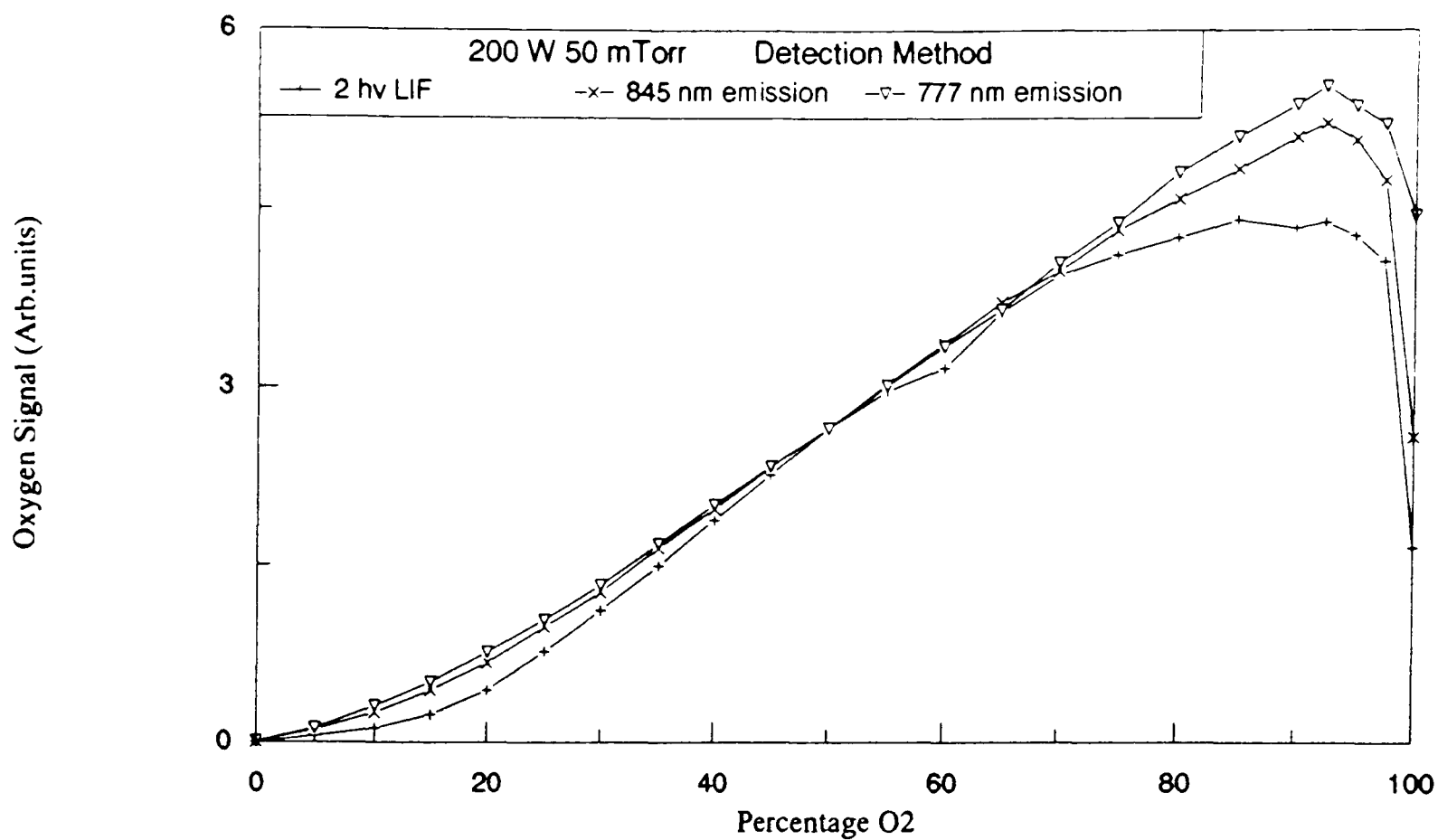


Figure 5.17 Comparison of the two photon LIF measurements of atomic oxygen with the actinometrered emission signals from both the 777 and 845 nm lines, as a function of gas composition. (The data were normalized at 50% O₂).

the 777 nm line. However, both O and O₂ increase monotonically as O₂ is added to CF₄, and so both excitation mechanisms would be expected to show similar behaviour, making the agreement somewhat fortuitous. The regions of poorest agreement are where the oxygen atom variation is furthest from that of O₂, which are the conditions where the dissociation fractions are lowest, (as discussed in chapter 7 these are conditions of highest O loss rate).

A plot of the actinometered emission divided by O₂ pressure against dissociation fraction, as described by equation 5.7, is shown for both emission lines in figures 5.18 and 5.19. The equation can only be used to compare the components of the production mechanism where there is little variation of the high energy tail of the EEDF, ($\epsilon > 10.8$ eV). Previous studies in this laboratory¹⁷, using a selection of argon emission lines, with different excitation thresholds, have suggested that there is little change in this region of the distribution, but that there is a reduction in electron density, as O₂ is added to a CF₄ discharge. Similar conclusions have been reached by other workers, where Langmuir probe^{5,26} and emission from excited states with different thresholds²⁷ have been used. In this study however the 200 mTorr pressure region has been shown to exhibit behaviour consistent with a transition in the excitation processes, and hence in the electron energy distribution. As can be seen, this effect is also apparent in the 200 mTorr data of figures 5.18 and 5.19, and so it is not possible to extract the relative proportions of the O* excitation processes for this condition.

At 50 mTorr, the 845 nm data does show a dependence consistent with equation 5.7, and a measure of the slope and intercept produce a value for k_0/k_{02} of 24, ie. the rate of excitation of oxygen atoms is 24 times that of molecular oxygen. These rates when multiplied by their relative concentrations predict that for example for a 50 mTorr, 85% O₂, 200 W plasma, the contribution to the emission from oxygen atoms is about 2.5 times that from O₂. The 777 nm data are not as well described by equation 5.7, but a similar analysis suggests that the contribution from O and O₂ are comparable. The higher molecular contribution to the 777 nm line is consistent with the observations made from figure 5.17.

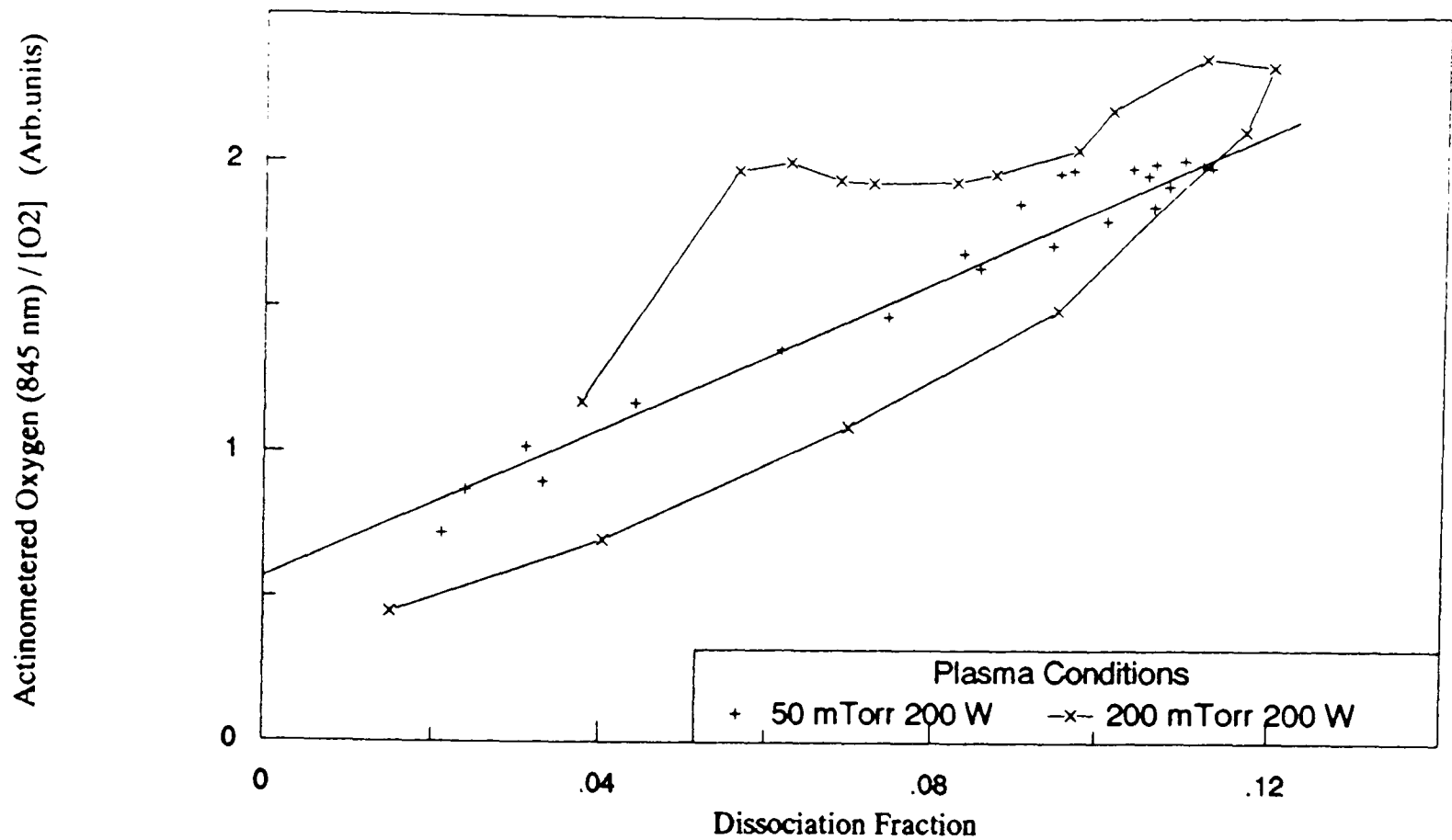


Figure 5.18 Variation of actinometered emission divided by O₂ pressure against dissociation fraction (see text), using the 845 nm emission line and measured as a function of gas composition.

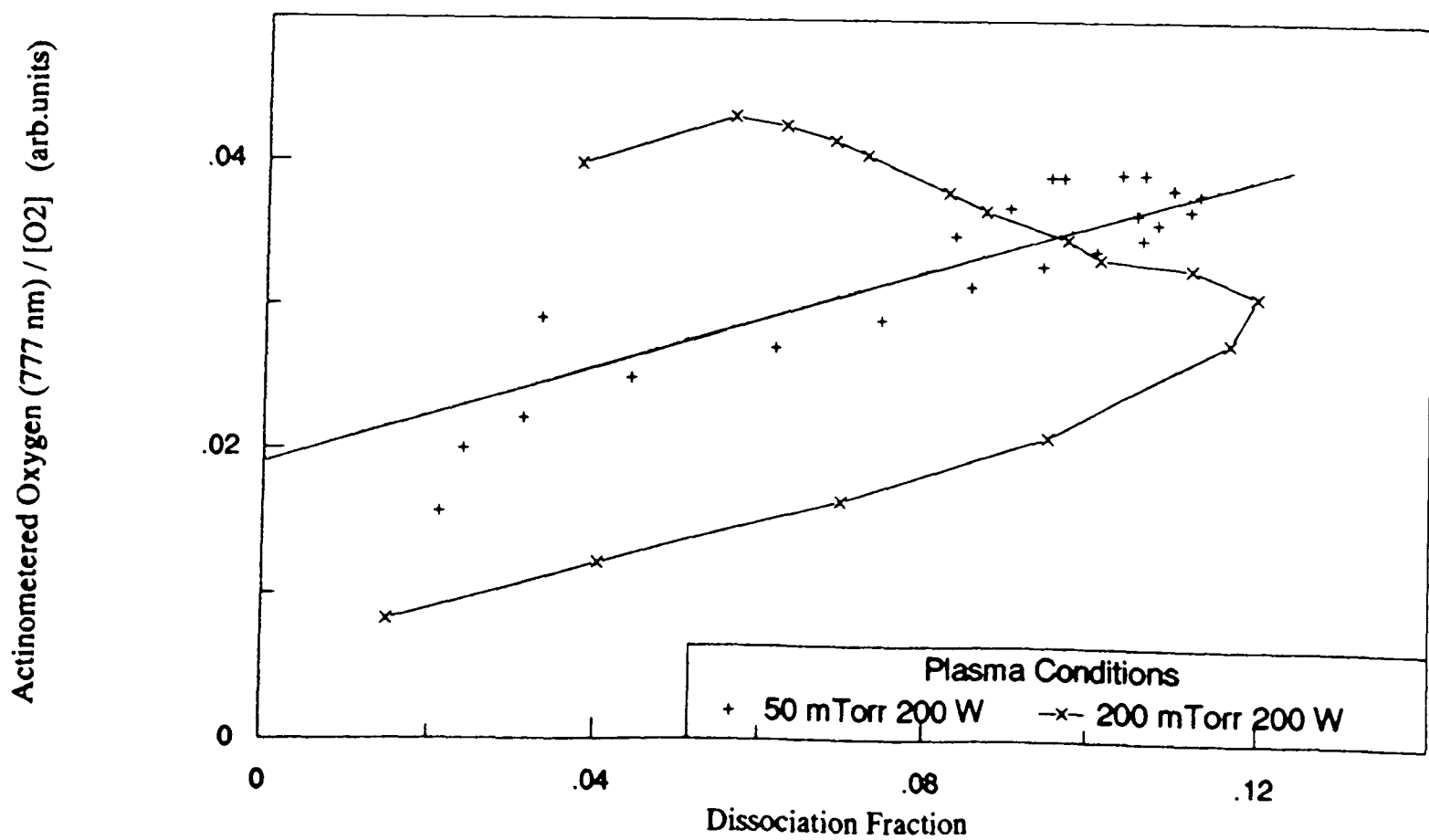


Figure 5.19 Variation of actinometered emission divided by O₂ pressure against dissociation fraction (see text), using the 777 nm emission line and measured as a function of gas composition.

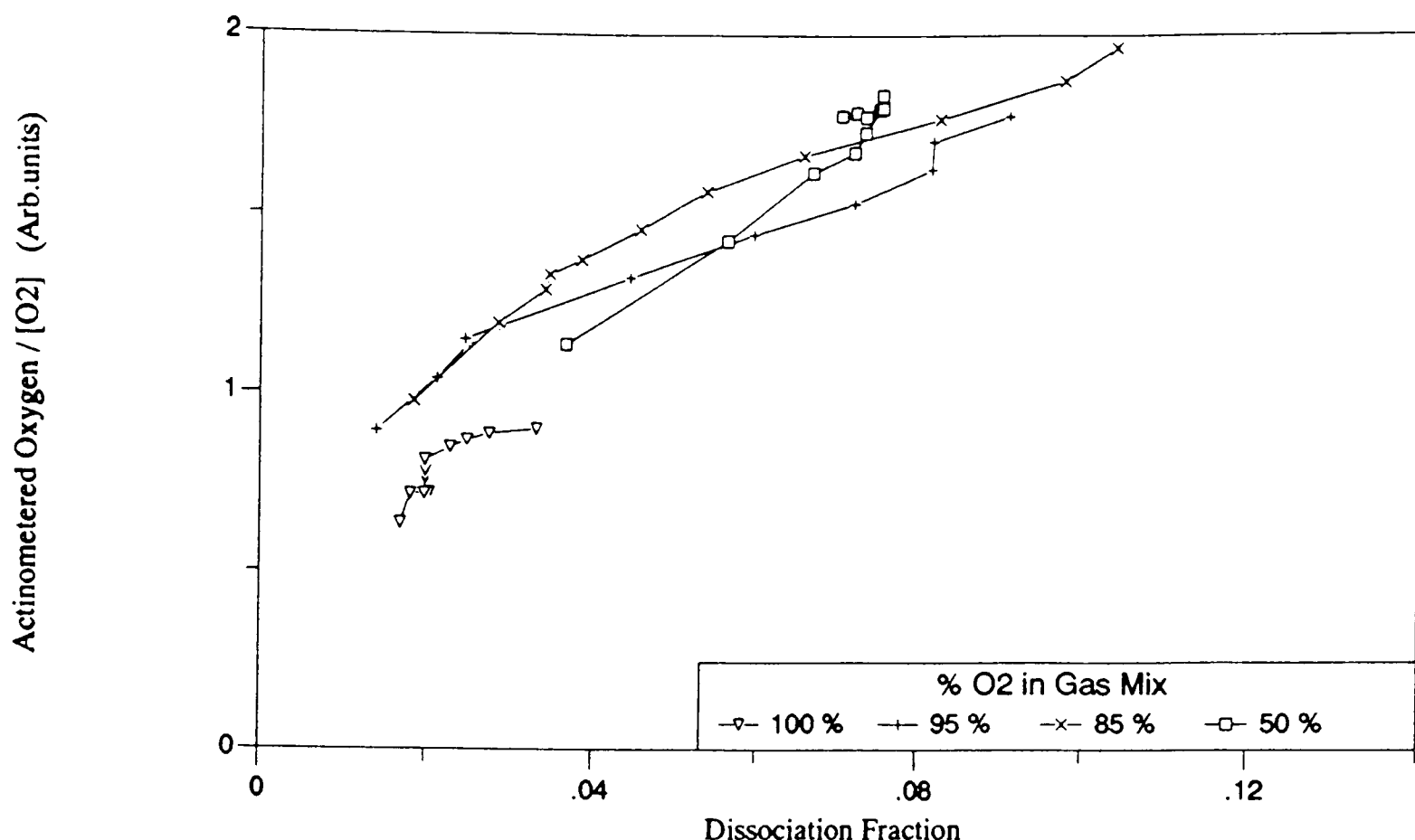


Figure 5.20 Variation of actinometered emission divided by O_2 pressure against dissociation fraction (see text), using the 845 nm emission line and measured as a function of rf power at a variety of O_2 percentages.

A similar analysis has also been done for 845 nm emission as a function of power, and the results are given in figure 5.20. The plot shows some curvature at low dissociation fractions, but the four different gas compositions show similar overall behaviour and lie on top of each other. Using this data, k_0/k_{02} is 12.5, and so predicts that at 50 mTorr, 15% O_2 , 200W, the dissociative mechanism contributes about 45% of the production of the excited state. This value is more than the value obtained from the composition result, but the slight curvature in figure 5.20 and the question raised by the actinometer signals measured as a function of power in a CF_4 plasma, (see figure 5.8), place in doubt the application of equation 5.7 to the data.

From the cross sections discussed above and an assumed electron energy distribution function, it is possible to calculate expected values for the k_0/k_{02} ratio, by substitution in equation 1.3. These calculations have been performed, taking the distribution to be a Druyvesteyn function (equation 1.2) for a variety of mean energies. Results are shown in Table 5.2 for the 845 nm emission.

$\langle \epsilon \rangle$ (/eV)	3.0	3.75	4.5	5.25	6.0	6.75	7.5
k_0/k_{02}	$\sim 10^7$	7×10^4	3200	495	145	124	77

Table 5.2

Langmuir probe measurements^{28,29} in CF_4 plasmas at 50 mTorr have produced $\langle \epsilon \rangle$ of 4.5 – 6 eV, ($T_e = 3 - 4$ eV), and thus values of 3000 – 100 in k_0/k_{02} are predicted for these conditions. These values are far higher than those observed experimentally, but the steep dependence of k_0/k_{02} on the mean energy show the sensitivity of this ratio to the precise form of the high energy electron tail of the distribution. Better knowledge of this region of the distribution is required for these calculations to be done more accurately.

Further direct comparisons of AOE, using the 845 nm line, and LIF data have been carried out over a large parameter space of gas composition, pressure and power. The overall results show that the AOE data is particularly poor where the dissociation fraction changes significantly. Thus, AOE correlates reasonably well with LIF for changes in pressure and gas composition, but poorly with power variation, (some of the results are shown in figures 5.17, 5.21 and 5.22). AOE of oxygen atoms using the 845 nm line does follow the observed changes in ground state oxygen atom concentration, but the correspondence is partly due to the similar variation in the molecular oxygen concentration.

5.4.2 Oxygen Actinometry : Time Dependent Measurements

The mechanism of excitation has also been studied by time dependent techniques. The intense plasma induced emission at 845 nm restricts the conditions for which rise time data can be obtained by two photon LIF and so the investigation was done using the time resolved actinometry technique, (described fully in chapter 6). This technique follows the rise of emission during plasma ignition, as a function of the delay time from the previous pulse. The initial signal level can be regarded as a measure of the concentration of species responsible for the production of the

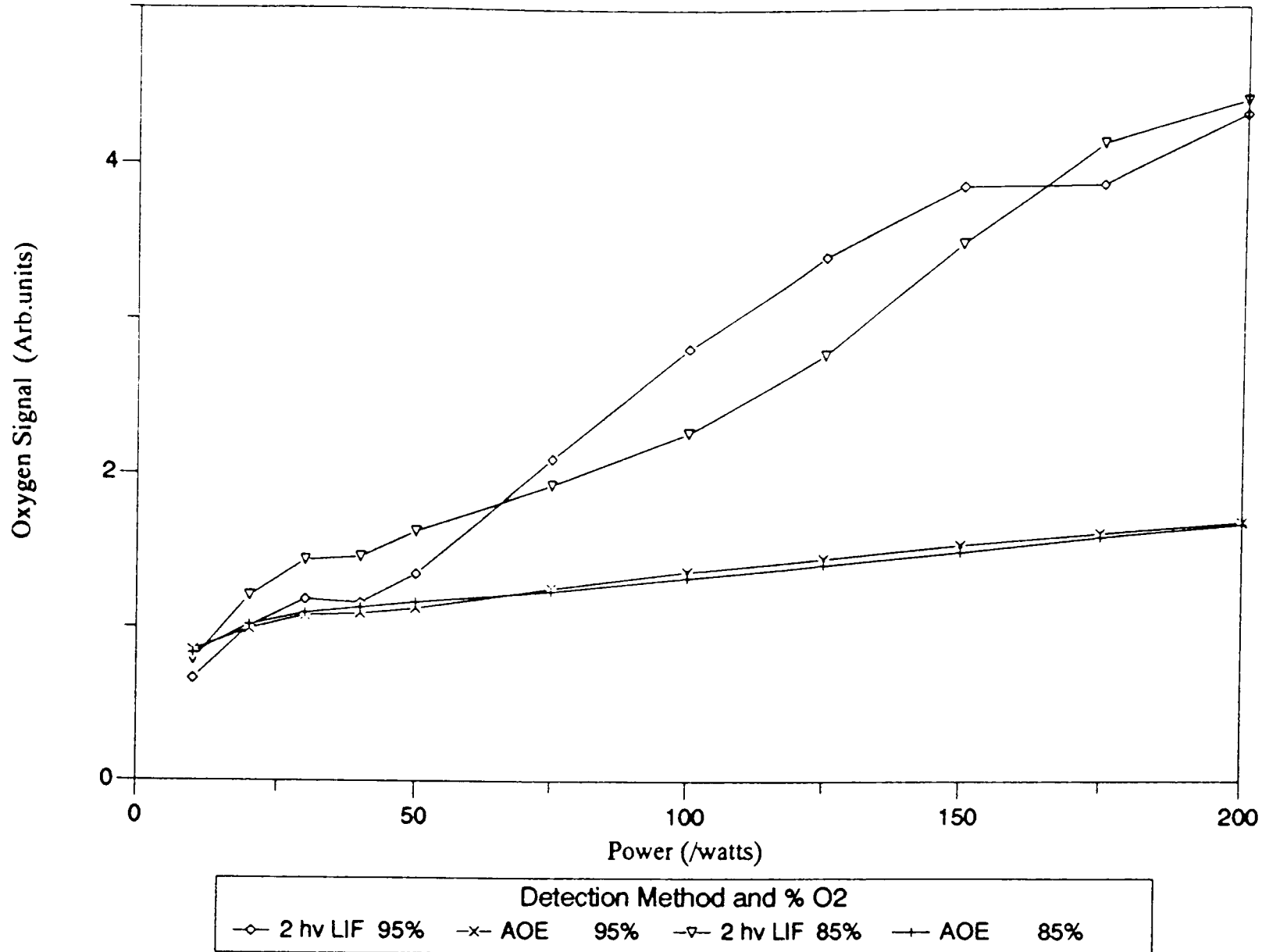


Figure 5.21 Comparison of LIF measurements of oxygen with actinometered emission signals using the 845 nm transition, as a function of rf power, (50 mTorr).

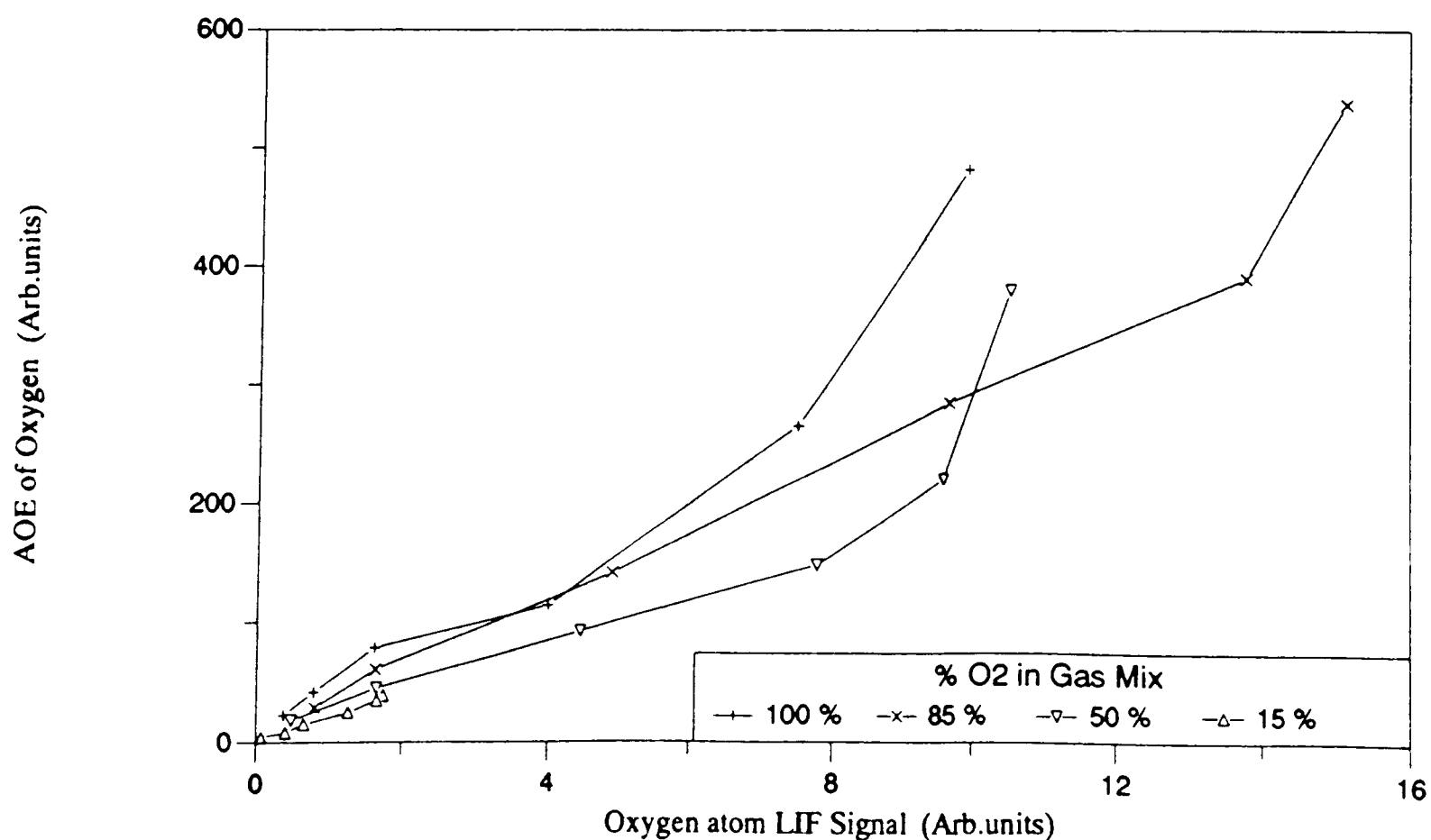


Figure 5.22 Variation of actinometered optical emission (845 nm), with LIF of oxygen atoms as a function of pressure for several gas compositions.

emitting excited state. For fluorine atom emission at 703.7 nm, the ground state atoms are the major species responsible, and so the technique is able to follow the concentration of the ground state as it falls with increasing delay time. Thus, the technique can be used to obtain kinetic measurements, (see chapter 6).

For 845 nm emission of oxygen, O_2 and O are both precursors for the excitation process, so the initial emission level will be dependent on the relative concentrations and rates of excitation of the two species. At long time delays after plasma extinction, the concentration of oxygen atoms will tend to zero and so only O_2 will contribute to the emission. The initial emission levels have been plotted against delay time for a 50 mTorr, 85% O_2 , 200 W plasma, in figure 5.23. If it is assumed that only ground state O and ground state O_2 act as precursors for the emission and that the concentration of O_2 is approximately constant with time after plasma extinction, (O_2 concentration will be considered later), then the contributions of each mechanism can be assigned as shown in figure 5.23a, (A from O_2 and B from oxygen atoms). This suggests that under steady state conditions, 40% of the emission is from molecular oxygen, (ie. $k_0/k_{02} = 15$), which lies between the values observed from the steady state measurements.

Similar results have been obtained for a number of other experimental conditions and for the 777 nm line. The results are given in table 5.3.

The contribution from O_2 is smallest for conditions of high pressure and low power, where $\langle \epsilon \rangle$ is expected to be low, and for high values of the dissociation fraction, $[O]/[O_2]$. The 777 nm data shows a higher O_2 contribution than for 845 nm under like conditions, as suggested by the steady state measurements, although the contribution, (80%), is higher than predicted, (50%).

A more detailed examination of the processes can be carried out by comparing the decay trace from TRA to that from LIF. This has been done for two sets of experimental conditions, and these are shown in figure 5.24 as semi-log plots. (The "constant" contribution from O_2 excitation has been subtracted from the optical emission data to leave the dependence on O .) It can be seen that the apparent loss rate as measured by TRA, is slightly lower than the true decay rate

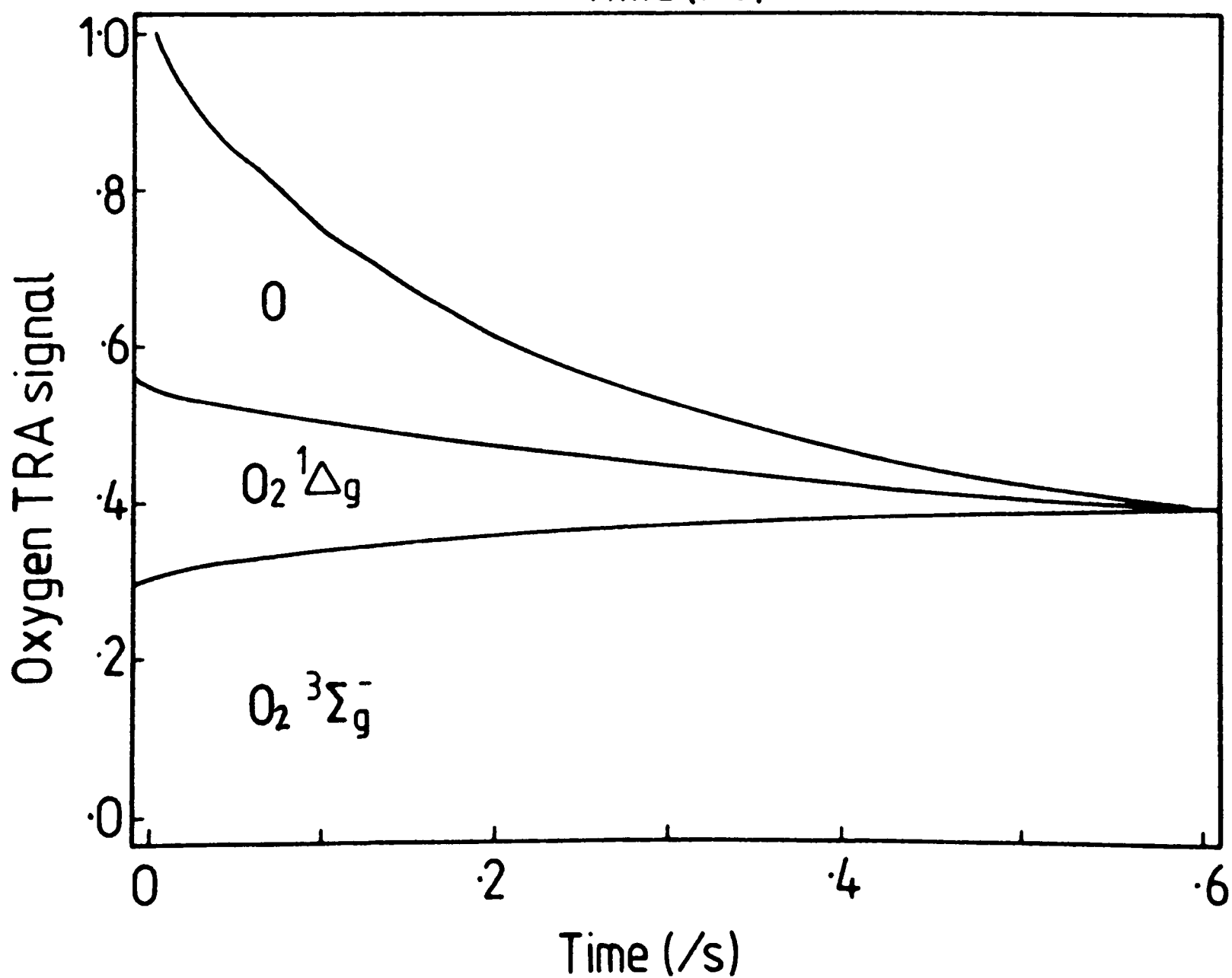
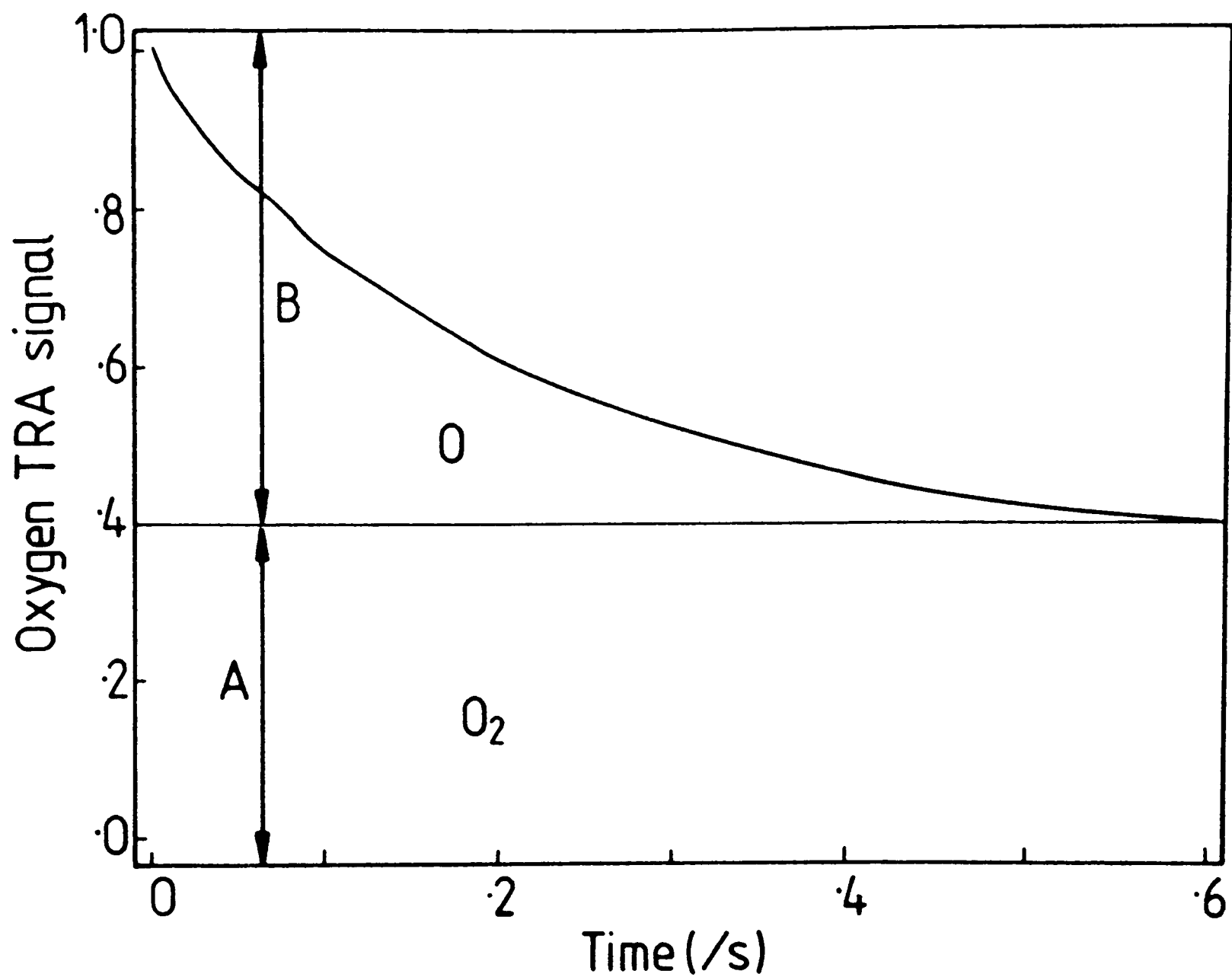


Figure 5.23 Time resolved actinometry data for oxygen emission at 845 nm in a 50 mTorr, 200 W 85% O₂ plasma, indicating the components to the total emission as deccribed in the text.

produced from the LIF data. Under the experimental conditions used, oxygen atoms are lost predominantly by reaction at the walls, so the disagreement observed was first thought to be a result of the known sensitivity of the loss rate to the precise nature of the surface, (ie.chamber history). However, the effect was found to be reproducible.

Line (/nm)	Power (/W)	Pressure (/mTorr)	% O ₂ in mixture	[O]/[O ₂] (%)	% contribution from O ₂ [*]
845	100	50	85	5.4	37
	200	50	85	10.4	42
	200	100	85	10.7	40
	100	500	85	6.7	11
	100	50	100	2.0	80
	100	50	85	5.4	37
	100	50	50	7.2	28
	100	50	15	3.6	37
777	100	50	85	5.4	80

Table 5.3
 * – A/(A + B) from figure 5.23a.

The concentration of ground state molecular O₂ is in fact depleted when the plasma is ignited, possibly by up to 20%, due to the formation of oxygen atoms and O₂ metastables, but after extinction of the plasma this concentration will build back up by the flow of O₂ into, and other species out of, the reactor. (This pump out rate is about 3s⁻¹ for a pressure of 50 mTorr). When this is taken into account and with the LIF signal used as a measure of the true oxygen atom decay rate, the temporal behaviour can be modelled. Atomic and molecular components sum to produce the total emission, so if the distribution function is assumed constant with time, the total intensity is given by

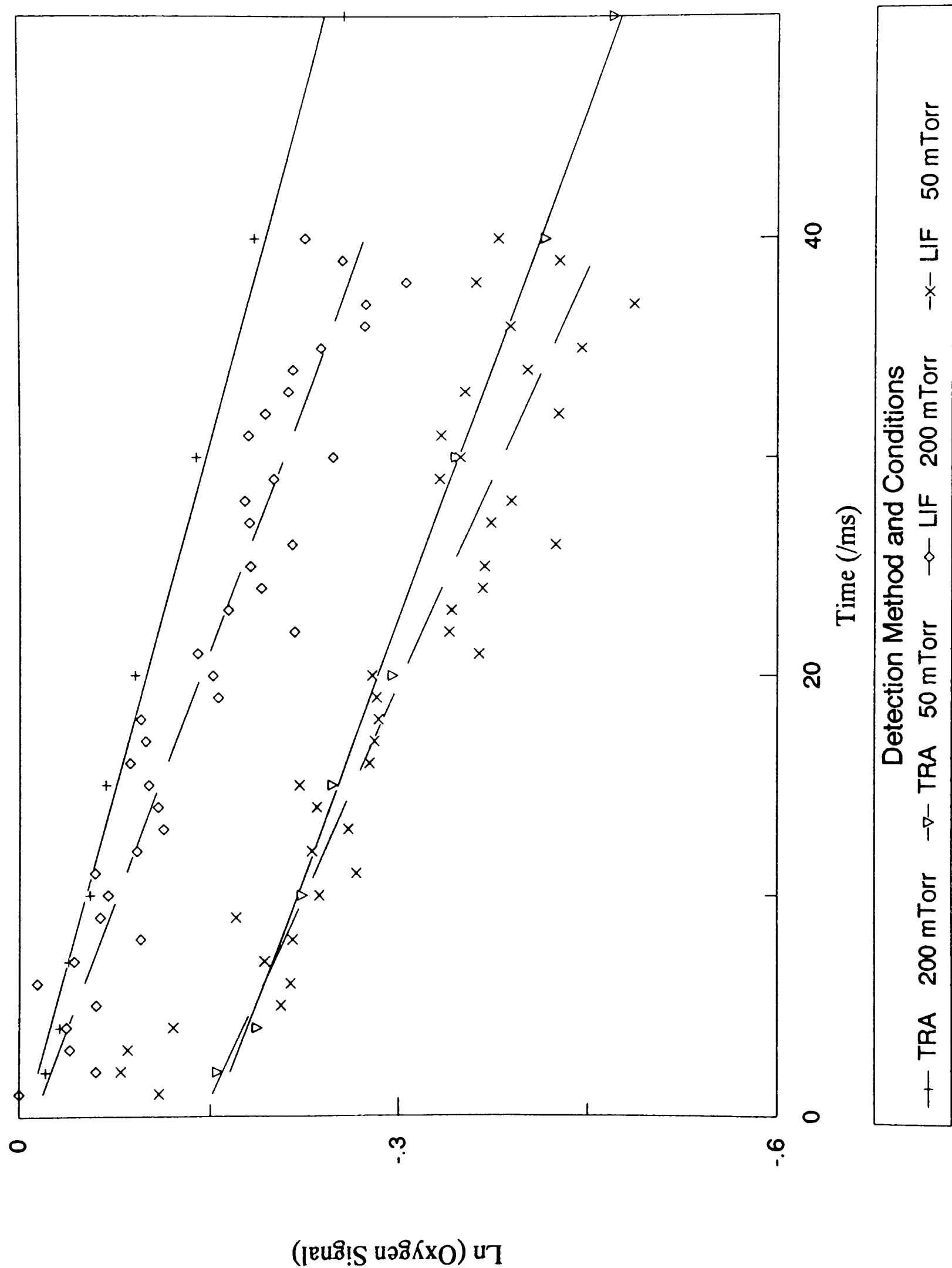


Figure 5.24 Comparison of the time dependent data observed by LIF and TRA for a 50 mTorr, 200 W 85% O₂ plasma.

$$\begin{aligned}
I(t) &\propto k_0.[O] + k_{02}.[O_2] \\
&\propto k_0.[O]_0.\exp(-k_1.t) + k_{02}.[O_2]_0.(1 + 0.2(1 - \exp(-k_2.t))) \\
&\equiv A.\exp(-k_1.t) + B - C.\exp(-k_2.t)
\end{aligned}$$

where k_1 is the true oxygen atom decay rate, (from LIF experiments), k_2 is the pump out rate, $[X]_0$ is the steady state plasma concentration of X and A, B and C are positive constants. The resulting dependence of $I(t)$ on time is not a true single exponential decay, but an approximate effective first order decay coefficient can often be assigned. The influence of the increase in O_2 concentration with time is to make the effective decay coefficient greater than the true oxygen atom loss rate, which contrasts the experimental observation.

This suggests that another process is taking place which has not yet been considered. O_2 discharges are known to generate high concentrations of metastable molecular oxygen species, in particular $O_2\ ^1\Delta_g$. This can be produced by electron impact²⁴ or by heterogeneous recombination of oxygen atoms³⁰, and has been measured at concentrations of 10 – 20 % of the ground state³¹. $O_2\ ^1\Delta_g$ is chemically inert³², with a long radiative lifetime and so its main loss mechanism in these plasmas will be pump out, (a lifetime of about 300 ms at 50 mTorr). The electron impact dissociative excitation of $O_2\ ^1\Delta_g$ has not been studied, but it is reasonable to suppose that its cross section might lie between that of atomic oxygen and ground state O_2 .

Adding such a mechanism to the simple system described above produces

$$I(t) = A.\exp(-k_1.t) + B + C'.\exp(-k_2.t)$$

The effective decay coefficient can now be lower than k_1 , and to obtain a decrease comparable with the experimental result, the $O_2\ ^1\Delta_g$ contribution to the 845 nm emission needs to be about half that from atomic oxygen, see figure 5.23b. Fitting the model to the experimental data thus predicts the following contributions to the

emission under steady state conditions;

$$\text{O} : \text{O}_2 : \text{O}_2 \ ^1\Delta_g \qquad 0.43 : 0.36 : 0.21$$

which requires electron impact excitation rates in the ratio 11 : 1 : 5 assuming concentrations of 10% O and 10% O₂ ¹Δ_g. This is at least consistent with the expected relative rates.

In order to investigate this mechanism and the relative magnitudes of the contributions, a more extensive study is required, involving direct measurement of O₂ ¹Δ_g and its temporal decay, as well as a measure of the cross sections for dissociative excitation from O₂ ¹Δ_g with the precise form of the high energy tail of the electron energy distribution. Such an investigation was not carried out for this thesis.

Measurements to find the relative components of the different excitation processes have not produced completely consistent results, with the steady state data showing the O₂ contribution to the 845 nm line to be 29%, with a value of 37% from time resolved data, (50% and 80% respectively for the 777 nm line), for a 50 mTorr, 85% O₂, 200 W plasma. The time resolved results have questioned the possible additional O₂ ¹Δ_g pathway, and the presence of quenching in the upper state, (and self absorption for the 777 nm line), will also affect the analysis of the optical emission detected. Thus, it can be seen that actinometered optical emission from oxygen is poorly correlated to the true ground state atomic concentration, and that its widespread application is due to the ease of operation and the fortuitous similar variation in excited state precursors.

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Chapter Six

Time Resolved Actinometry

6.1 Introduction

As discussed in chapter 1, measurement of steady state concentrations allows only a limited analysis of the plasma based processes and direct monitoring of the time dependence of species is required to obtain separate information on the production and removal rates. Such rate studies have been made for a variety of plasma species, CF^1 , $\text{CF}_2^{1,2}$ and oxygen atoms, (see chapter 7), using time resolved laser induced fluorescence. Fluorine atoms are another key species in CF_4 / O_2 plasmas, but they cannot conveniently be observed by LIF, since the first optically allowed transition occurs in the vacuum ultra violet. However, they are readily detected by optical emission, and so a new technique, Time Resolved Actinometry, (TRA), was developed³ during the period of this work, which uses optical emission to obtain kinetic information on the plasma based species.

One method of collecting temporal information from emission is to follow the rise in the intensity as a function of time after plasma ignition. As the production rate generally rises very rapidly to its steady state level, the rise time measured is related to the decay rate of the species being detected. However, any slow variation in the production process affects the time trace taken. Chapter 5 illustrated conditions for which the rise time of CF_2 has been followed by LIF and AOE and a reasonable agreement has been shown with decay times from plasma afterglow measurements. For a 50 mTorr, pure CF_4 , 100 W plasma, the rate associated with the rise was 190 s^{-1} , whilst the afterglow decay rate was 140 s^{-1} . The difference is thought to be due to the effect of negative ions and / or the level of ion bombardment of the electrode surfaces⁴. Similar agreements have been seen for LIF measurements of O and CF, although, because of the intense plasma induced emission, rise time data can be difficult to obtain by laser induced fluorescence. The rise in fluorine atom emission for a 50 mTorr, pure CF_4 , 200 W plasma is given in figure 6.1, and it can be seen that the trace is not a single exponential rise, and

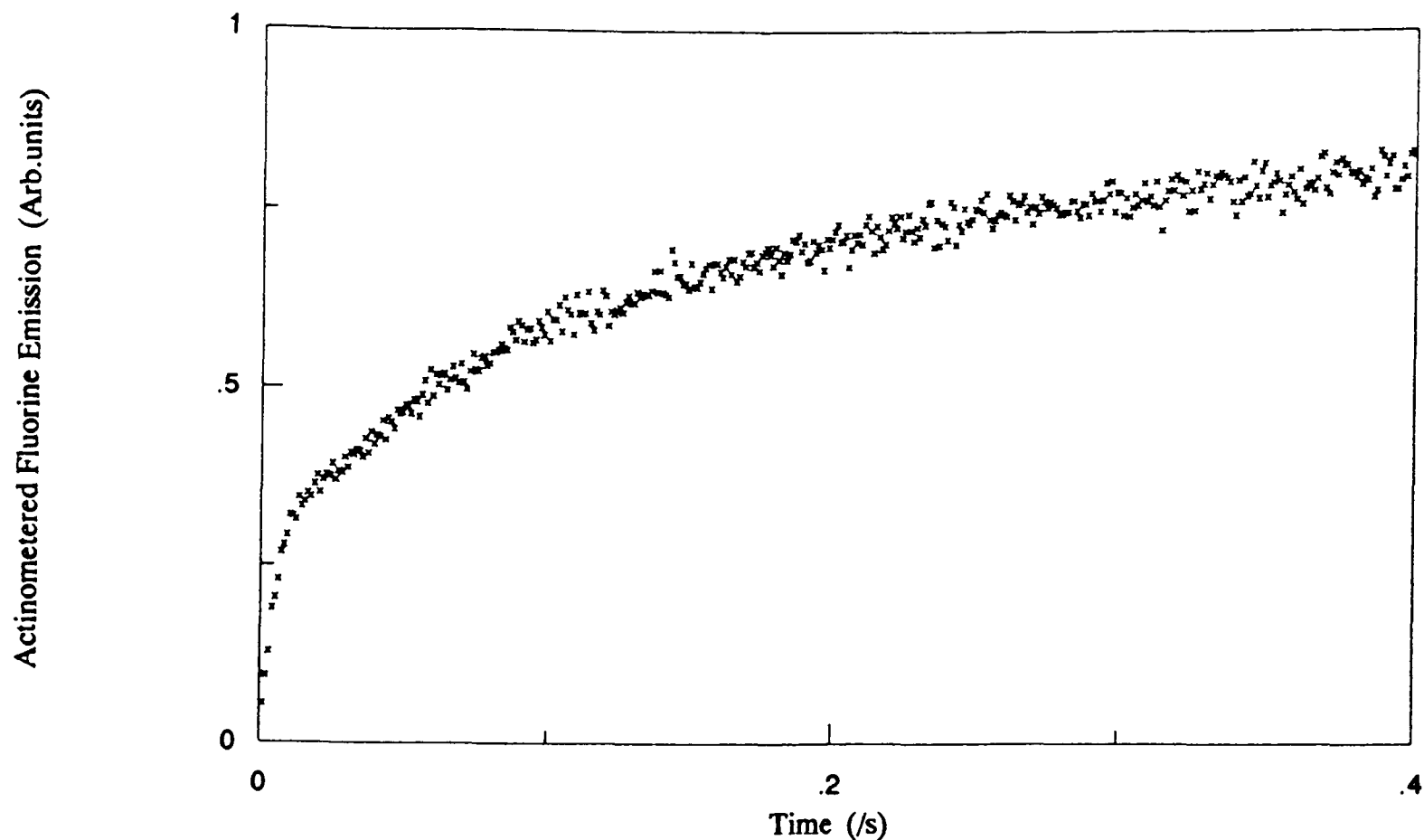


Figure 6.1 Temporal variation of actinometered fluorine emission after plasma ignition.

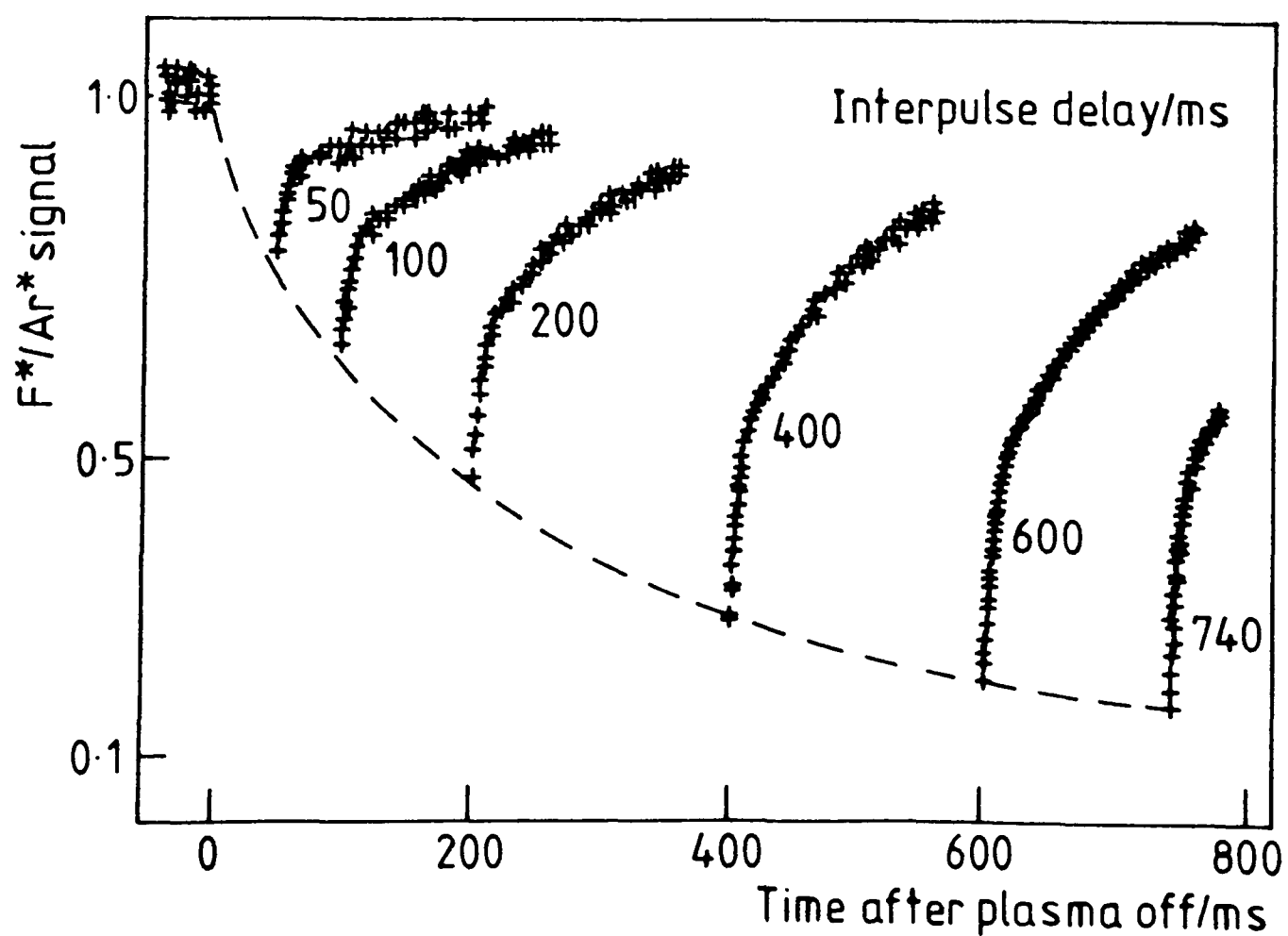


Figure 6.2 Variation of actinometered fluorine emission on plasma ignition for a range of interpulse delays. The dashed curve joining the initial levels indicates the decay of fluorine atoms obtained from such data.

suggests the presence of a complex mechanism. Thus, a method of obtaining the time dependence after plasma extinction was devised.

6.2 Time Resolved Actinometry : The Technique

Emission from the discharge ceases in less than $10\ \mu\text{s}$ after extinction of the plasma, owing to the rapid loss of high energy electrons responsible for excitation of the emitting levels, and the short radiative lifetimes of the excited states, and so it does not directly reveal the change in concentration of ground state molecular species which takes place on a longer time scale. However, the plasma can be re-ignited with a delay τ after extinction, before the complete removal of the ground state of a particular species of interest. The actinometer signal reaches close to its steady state value in a short time (tens of microseconds) compared to τ , showing that the concentration of the high energy electrons rapidly approaches its equilibrium value. The emission signal caused by excitation of the species under investigation will rise very rapidly to an initial level which is dependent on the concentration of the ground state species remaining (providing that the conditions of actinometry are met). The signal then rises more slowly (millisecond time scale) as the concentration of the species approaches once more its steady state value. As the delay time τ increases, this initial level of emission decreases due to a fall in the fraction of ground state species remaining from the previous pulse. This is shown experimentally in figure 6.2 for a variety of delay times, for actinometered F atom emission, and schematically in figure 6.3. Providing the plasma is on long enough before extinction to ensure steady state concentration of all the species, this technique can be used to examine the steady state loss rate of the species of interest.

This method has some analogies with laser induced fluorescence, but with the plasma acting as the excitation source as opposed to a laser. Plasma excitation is universal to all species in the plasma unlike the specificity of laser excitation, but once again the detected signal is related to the excited state concentration and so the actinometry criteria need to be met. As the plasma parameters are not being varied, it is specifically the production mechanism that is most relevant to these

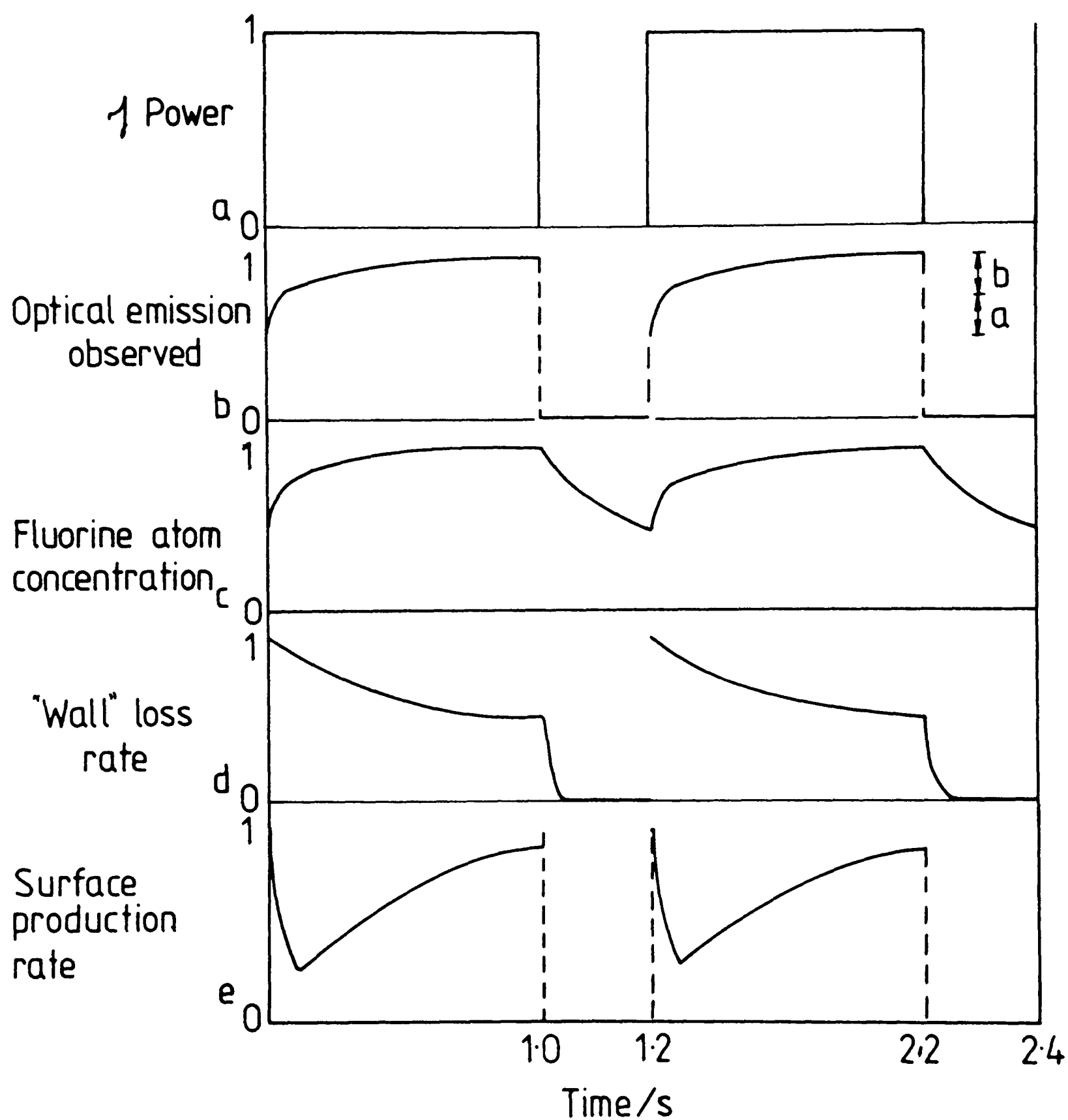


Figure 6.3 Schematic representation of the temporal variation of (a) rf power, (b) fluorine optical emission, (c) fluorine atom concentration, (d) wall loss rate (see text) and (e) surface production rate (see text)

studies, (criterion one from section 5.2). Thus, as described in chapter 5, this technique is sensitive to the time variation of species responsible for the production of the emitting excited state, (eg. O and O₂ for O* production), and it may be possible to investigate the presence of more than one excitation channel, if the time dependence of the precursor species are different.

6.3 Validation of the Technique : CF₂ Kinetics

The time resolved actinometry technique was first applied to CF₂ emission so that the technique could be validated by comparison with time resolved laser induced fluorescence data. Conditions were chosen where actinometry has been shown to exhibit a reasonable correlation with the ground state species, (see chapter 5). The TRA data was extracted from the initial levels of a set of rise curves and plotted against time delay. The raw TRA data was found to approach a non-zero final value (5–10% of the initial signal, the precise magnitude depending on plasma conditions), since even at very long delay times, there was a small instantaneous rise in the emission signal^{3,5}. As discussed in section 5.3.2, one interpretation of this is a direct pathway by electron impact on CF₄ to form excited state CF₂. This component was subtracted as a constant from all delay times and was thus assumed to be independent of the delay, an assumption which would be consistent with a direct pathway.

Comparisons of LIF and TRA results are shown in figure 6.4 for two sets of experimental conditions, so that a variation in decay rate was measured. It can be seen that there is excellent agreement between the two techniques, particularly at 50 mTorr and in the tail of the decay of the 200 mTorr data (times > 8 ms after plasma extinction). For early times of the 200 mTorr result, the TRA data indicates a faster decay rate than that of LIF. Previous LIF studies¹ have shown that for a species which is predominantly lost by wall reaction, the initial decay rate measured near the surface is faster than that measured away from it. As much of the optical emission emanates from the plasma – sheath boundary, which for a 200 mTorr plasma is approximately 4 mm from the electrode surface, the TRA data may be

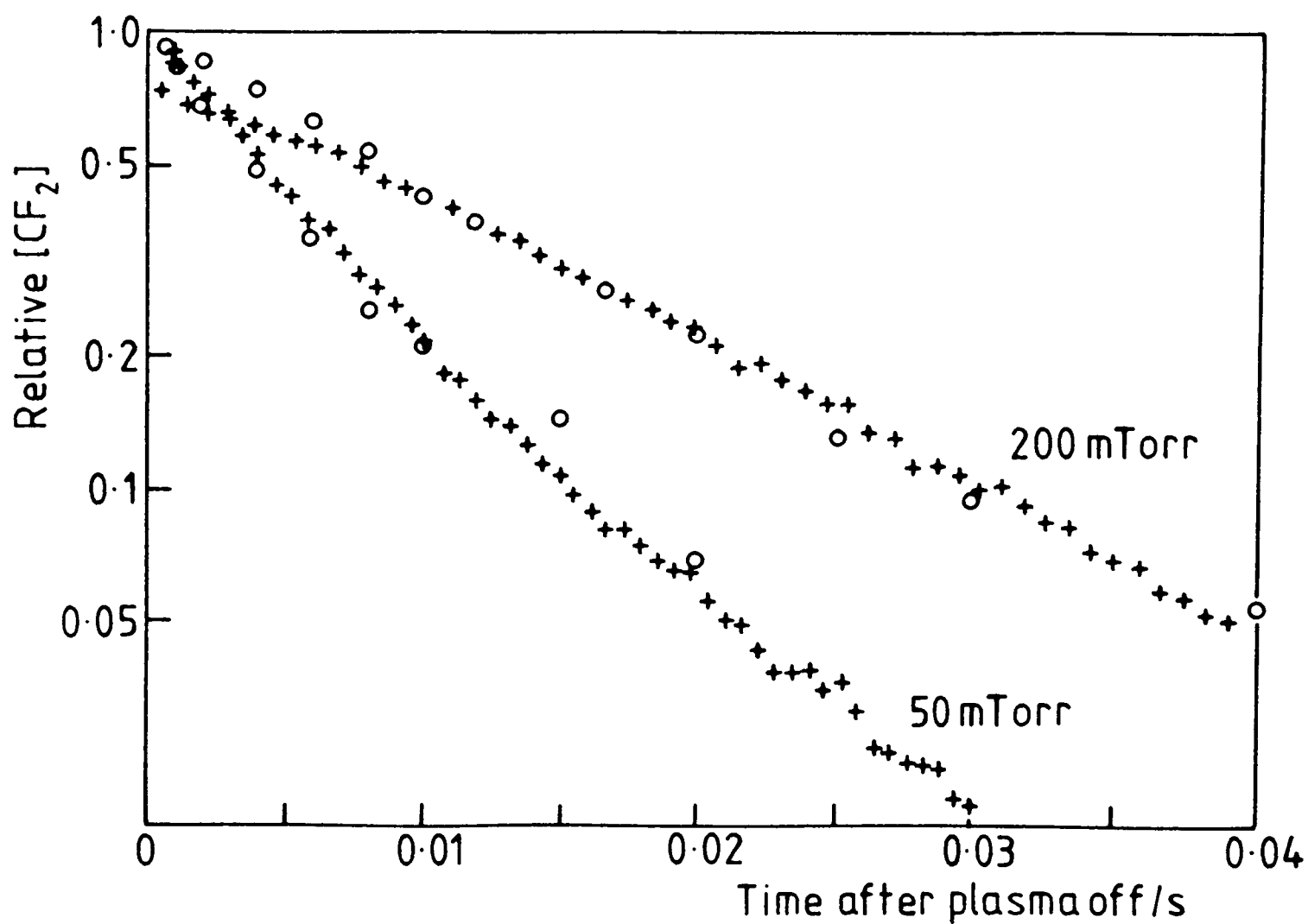


Figure 6.4 Semilogarithmic plot of the variation in concentration of CF₂ after plasma extinction at 50 mTorr and 200 mTorr, measured by LIF (+) and TRA (o). The concentrations are normalized to their respective steady state values.

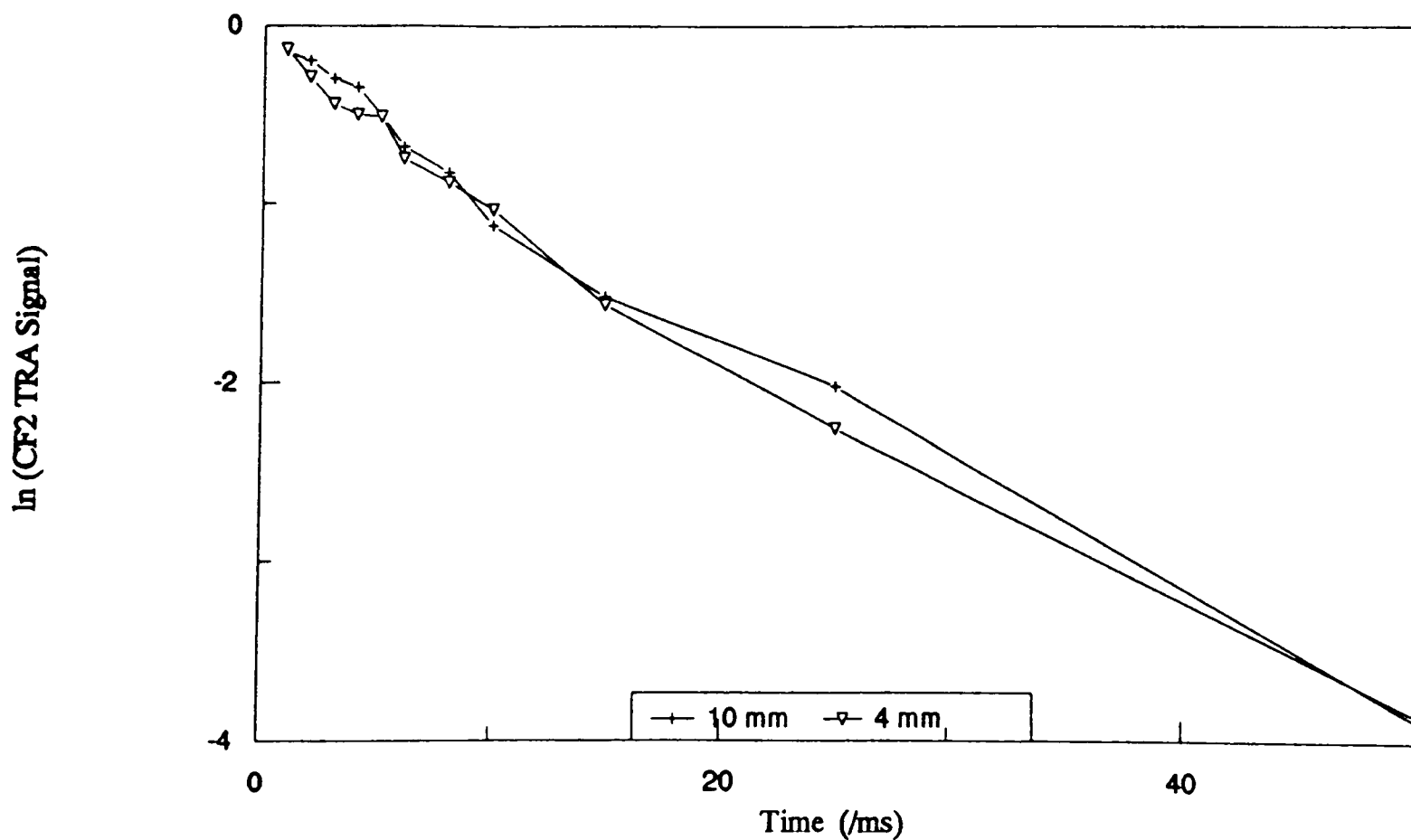


Figure 6.5 Semilogarithmic plot of the variation in concentration of CF₂ after plasma extinction measured at two distances from the driven electrode surface, by TRA in a 200 mTorr, 100 W, CF₄ plasma.

weighted by the loss rate of the CF_2 radicals in that region. This would contrast with the LIF data, which probed a region 10 mm above the surface. Thus, spatially resolved TRA experiments were carried out, using slits to produce a resolution of about 2 mm, and the decays were taken at 4 and 10 mm above the electrode surface. The results are given in figure 6.5, and show that spatial variation does not explain the slight discrepancy observed at early times in the 200 mTorr data.

As described in chapter 5, the technique was also tested on oxygen atoms, again comparing the results with LIF. In this case, the presence of other excitation mechanisms for excited state production invalidate the actinometry technique so good agreement is not expected. However, the method does highlight the dissociative excitation mechanism and allows some attempt to calculate the relative contributions of the excitation processes.

6.4 Fluorine Atom Kinetics

The kinetics of fluorine atoms were followed by TRA, after both plasma ignition and extinction. The time required for the emission signal to reach a constant steady state value was found to be of the order of seconds as opposed to milliseconds for the CF_2 radical under similar conditions, as can be seen in figure 6.1. A consequence of this is the lack of dependence of the CF_2 concentration on that of F atoms, and it adds evidence to the model in which gas phase chemistry has little effect on the CF_2 concentrations in these low pressure plasmas^{1,4}. The plasma also needed to be extinguished for these longer time periods in order to remove all residual F atoms in the TRA experiments. As with the CF_2 case, even at very long delays there is a small component of the F atom emission, which rises instantaneously on ignition of the plasma. The most probable cause of this is again a direct production pathway from electron impact on CF_4 to excited state fluorine.

The size of the direct component was found to depend on the plasma conditions and on the emission line monitored. For a 50 mTorr CF_4 plasma an increase in power produced an increase in the direct component observed, (50 W 5%, 100 W 6.5%, 200 W 10%), probably due to an increase in the density of high

energy electrons, required for dissociative excitation. The relative contribution of the direct component was also found to increase when silicon wafers were placed in the chamber. The wafers significantly reduced the concentration of fluorine atoms without influencing the electron energy distribution, and so the observation was as expected.

A number of fluorine atom emission lines with different upper states were monitored to study the direct component effect, (see table 6.1).

Wavelength (/nm)	Upper State	Lower State	Threshold Energy (/eV)
703.7	$3p^2P^0 (J=1\frac{1}{2})$	$3s^2P (J=1\frac{1}{2})$	14.7
720.2	$3p^2P^0 (J=1\frac{1}{2})$	$3s^2P (J=\frac{1}{2})$	14.7
685.6	$3p^4D^0 (J=3\frac{1}{2})$	$3s^4P (J=2\frac{1}{2})$	14.5
690.2	$3p^4D^0 (J=2\frac{1}{2})$	$3s^4P (J=1\frac{1}{2})$	14.5
643.8	$3p^4S^0 (J=1\frac{1}{2})$	$3s^4P (J=1\frac{1}{2})$	14.5

Table 6.1

The time response of the emission from like upper states was identical, but those with different excited states showed some variation, (see figure 6.6). The differences were found to be due to the magnitude of the initial rise, and hence the size of the dissociative excitation component. Figure 6.7 shows the rise curves for the 703.7 and 685.6 nm lines, where the initial level has been subtracted. The time dependence is now seen to be independent of the emission line monitored, and this which was shown to be the case for a variety of different time delays, τ .

The direct production of F^* from CF_4 by electron impact has been observed in electron beam studies^{6,7}, with emission at all the wavelengths monitored in this work. Blanks *et al.*⁷ measured the absolute emission cross sections for a number of lines over a range of electron impact energies. In agreement with van Sprang *et al.*⁶, they showed the 685.6 nm line to have a higher cross sections than that of the

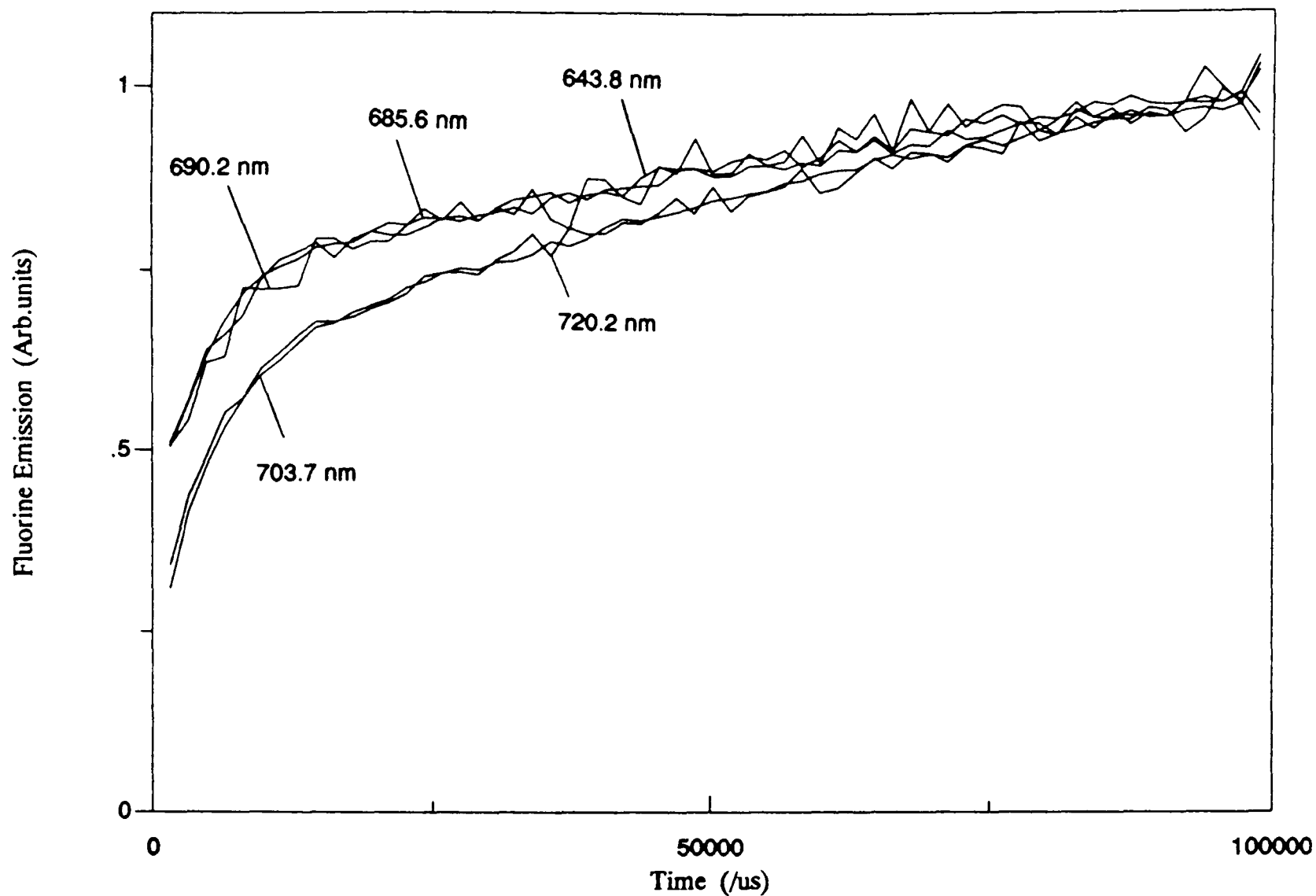


Figure 6.6 Temporal variation of fluorine emission for a variety of transitions measured on plasma ignition after a delay of 400 ms. (Data normalized at $t = .1$).

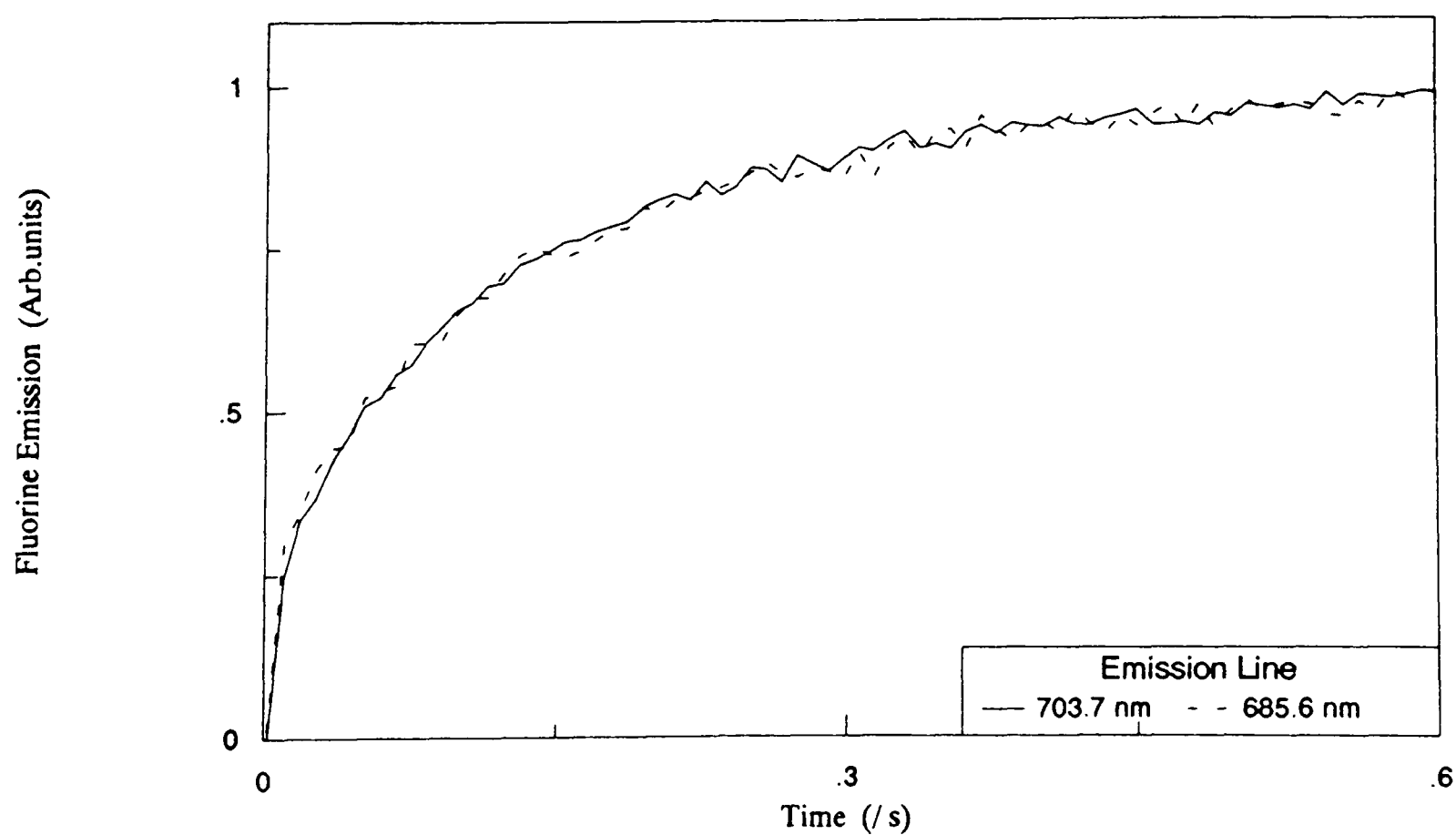


Figure 6.7 Comparison of the temporal variation in intensity from the 703.7 and 685.6 nm emission lines after plasma ignition, modified by subtracting the initial signal levels from both sets of data.

703.7 nm line, and thus the emission intensity observed was higher for the former line. This is in agreement with the results shown in figure 6.6, which shows a larger fraction of the emission being produced instantaneously for the 685.6 nm line. The actual intensity of the emission from the 703.7 nm line in a CF₄ rf plasma was found to be greater than the 685.6 nm line, but in such an environment excitation of the ground state atomic species is the major source of F*, and not dissociative excitation of CF₄. The threshold for excitation was shown to be 41 eV, (van Sprang *et al.* suggest 28 eV), which lies very high in the electron energy distribution function for the discharges studied here, and this explains the relatively low contribution they afford to the total fluorine atom emission and enables the actinometry technique to be applied to this species. The dissociative mechanism might be expected to produce translationally hot fluorine atoms, as seen in studies on Cl⁸ and O⁹, but no evidence of this was seen in the line width profiles.

As well as examining the direct component of the fluorine emission, this investigation using a series of fluorine lines, gives evidence that the fluorine atom excited state is predominantly produced from ground state fluorine atoms and CF₄ molecules. If F* were generated by electron impact of another species, such as CF_x radicals, the decay curve produced by the TRA technique would depend partly on the temporal variation of the species. The cross sections for the production of different upper states would be expected to be different from those of F atoms, as for CF₄. Thus, the lack of variation in the rise and decay curves for the different lines, combined with the low concentration of CF_x radicals, compared to F atoms (and CF₄ molecules), suggest that such a process is not significant and does not affect the measurement of F atom kinetics. A similar conclusion has been drawn from experiments by Bouchoule¹⁰.

A decay curve for fluorine atoms measured by TRA is given in figure 6.8 for 50 and 200 mTorr CF₄ plasmas. It can be seen that the decay has two regions, a rapid initial loss which decreases as a function of time after plasma extinction to a lower constant value. The two most likely loss processes for F atoms in these plasmas are gas phase three body recombination reactions with CF₃ radicals¹¹, or

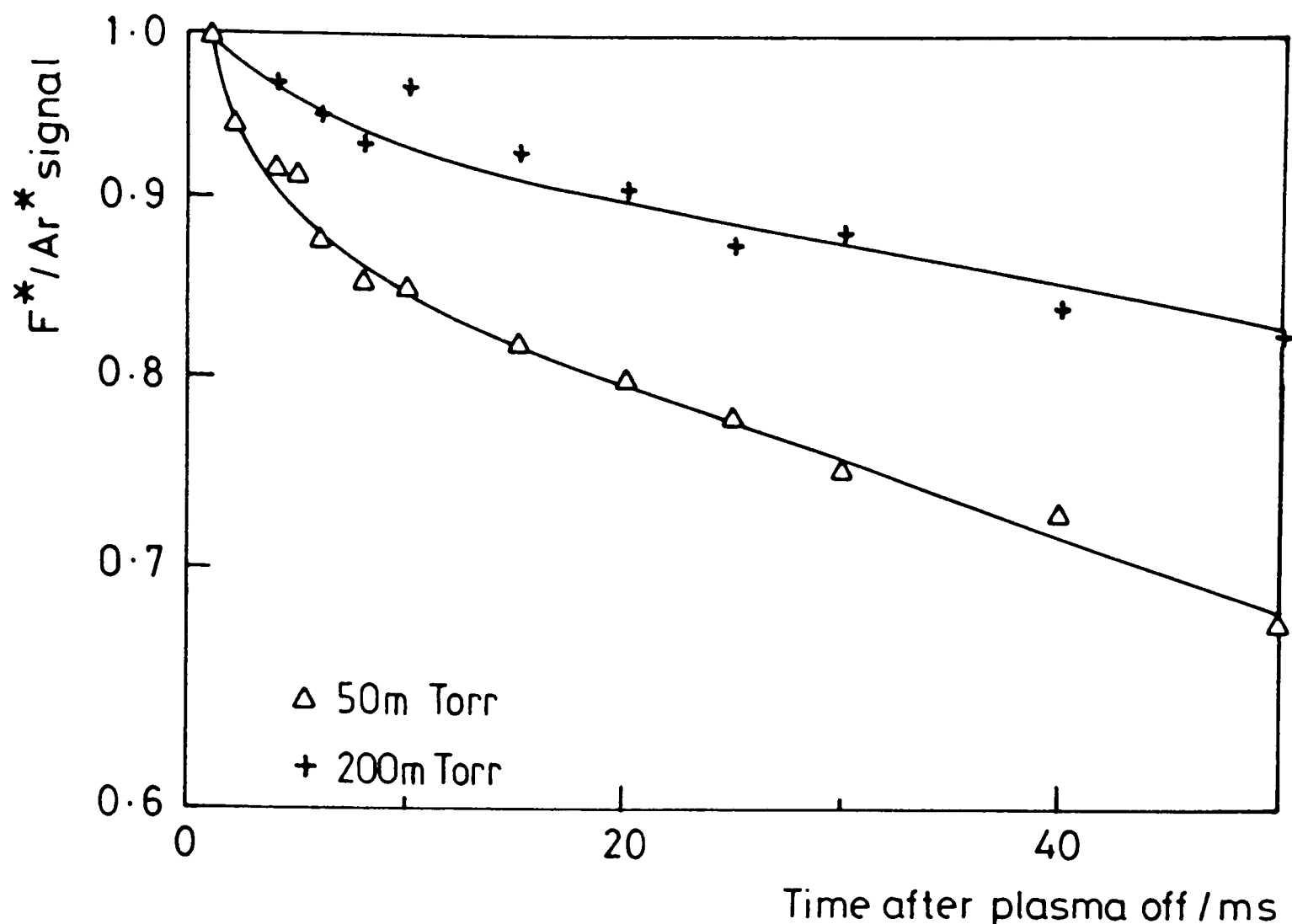


Figure 6.8 Time dependence of fluorine atom concentration measured by TRA at 50 mTorr and 200 mTorr.

diffusion to the wall followed by surface removal. At higher pressures, the concentration of reactive species in a plasma, as well as the third body concentration, increases, so the rate of gas phase recombination would be expected to rise rapidly with pressure. Diffusion rates, however, decrease with increasing pressure and so wall removal rates might be expected to fall. The decay of F atoms at 200 mTorr showed slower initial and final loss rates and thus suggests that removal at the walls is the major loss mechanism for F atoms. Wall removal will be dominated by reaction on the electrode surfaces¹, which are made of anodized aluminium. The explanation for the decrease in this rate as a function of time is not certain, (and is discussed in more detail in chapter 7), but saturation of available sites on the surface, in the absence of ion bombardment which would regenerate them, might restrict this loss mechanism and hence cause a drop in overall loss rate. A similar but less marked reduction in removal rate was also seen in LIF studies of CF₂ radicals and saturation or passivation of the surface is again thought to be the cause.

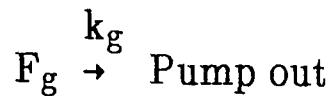
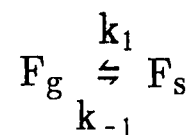
The second region shows a single exponential decay with rate constant of 3.6 s^{-1} for 50 mTorr, which approximates to the calculated pump out rate from the chamber. These rate constants were found to be dependent on gas pressure (1.4 s^{-1} for 200 mTorr), and flow rate as would be expected if pump out was the major removal process. The measured values were however slightly higher than the calculated ones, possibly due to a residual wall reaction. In order to obtain an estimate of the steady state loss rate for F atoms in a plasma, the early time limiting slope of the semi-log decay curve needs to be found. This has been done for the conditions mentioned above and the initial loss rates measured are 28 s^{-1} and 10 s^{-1} for 50 and 200 mTorr respectively.

With the above interpretation of the decay curve, an attempt was made to investigate the mechanisms responsible for the observed rise in fluorine atom concentration after plasma ignition. For an SF_6 plasma, the decay and rise curves both exhibit single exponential behaviour, with very similar time constants, but as illustrated above the CF_4 situation is less clear. Both curves show a fast initial variation in concentration followed by a slower change. An attempt to model the decay and rise curves was made using the FACSIMILE¹² numerical modelling package. A number of mechanistic models were tried based on a time dependent reduction in the overall removal rate, including one where the wall removal rate dropped as a function of time down to rate equivalent to the pump out rate and another where a second order process was used, involving the number of sites available and fluorine atoms present¹³. It was found that the decay data could easily be fitted to these types of model, but that the rise data could not.

As explained earlier in the chapter, the variation of signal on plasma ignition can also be due to slow variation in the production rate. This possibility was investigated by considering the mechanism of such a change in production rate, which requires that the concentration of one of the species involved increases at a rate of about 8 s^{-1} , (for a 50 mTorr CF_4 plasma). This suggested the influence of metastable species, particularly since previous studies have shown that helium metastables can react with CF_4 to produce F^* ¹⁴. However, the concentration of

argon was found to have no effect on the relative slow, (a), and fast, (b), components, (see figure 6.3b), and so metastables were not thought to play a major role. Molecular fluorine was also considered as a suitable production source of F (and F*), since its decay rate, (hence rise rate), is slow, being limited by pump out and electron impact dissociation. Its effect was tested by putting copper and aluminium plates on top of the driven electrode. Copper has a heterogeneous recombination rate for $2F \rightarrow F_2$ which is more than a hundred times faster than that of aluminium¹⁵, and so the $\frac{a}{b}$ ratio was expected to be smaller for the copper case. Experimentally, the effect of adding copper was to increase the wall removal process, but to show a reduction in the ratio.

One other possible source of fluorine atoms is from ion impact sputtering from the electrode surfaces, which would be expected to be particularly significant on plasma ignition, because of the covering of fluorine atoms or precursors from the previous plasma pulse, the saturation effect described above. A similar mechanism has been suggested to explain observations of spatially resolved carbon atom emission in a CF_4 plasma¹⁶. To reproduce the observed rise in the fluorine atom concentration, the extra production term not only needs to rise slowly with time, but also requires an initial burst on plasma ignition, in order to predict the fast rise component. In physical terms, this might correspond to a rapid initial clearing of the fluorine atoms from the surface to give an instant burst. Then, as the gas phase concentration increases, so the flux to the surface would rise, leading to a increase in the absorbed fluorine atom density. It is reasonable to assume that the ion sputtering mechanism is dependent on this density, and so its effect as a production term would be expected to rise with time. A model can be devised where there is exchange between the gas phase and surface fluorine atoms, together with other removal processes for the gaseous (pump out and any gas phase reactions) and the surface absorbed (formation of stable products by heterogeneous recombination) atoms.



where F_s is fluorine absorbed to the surface and F_g is gas phase fluorine.

The rate of rise of the gas phase fluorine atoms now depends on the rate of increase in the F_s density, which itself is dependent on its own removal rate, ie. k_{-1} and k_s . The best fits to the experimental data were obtained by setting k_s to 8 s^{-1} and having a relatively rapid interchange between gas and surface fluorine atoms. k_1 is the removal rate constant for fluorine atoms in the absence of ion regeneration, and so is equal to the measured fluorine decay rate, 28 s^{-1} for a 50 mTorr plasma.

The formation of products on the surface might be expected to be ion induced¹⁷ and so dependent on the ion flux to the surface. For the type of rf plasma used in this study, an ion flux of the order of $10^{15} - 10^{16} \text{ ions cm}^{-2} \text{ s}^{-1}$ would be expected¹⁸, ($\langle \epsilon \rangle \approx 4.5 \text{ eV}$, $n_e \approx 10^{10} \text{ cm}^{-3}$), and so, if an area of $(10 \text{ Å})^2$ is assumed for the interaction region for fluorine atom and other reactive species, the rate of clearing is $1 - 10 \text{ s}^{-1}$. This approximate value is at least comparable with the observed rate of 8 s^{-1} . A reduced rate of increase is observed at higher pressure, which is also consistent with this model, since the lower flux and ion energy associated with a rise in pressure, would tend to reduce the effectiveness of the ion bombardment.

The fast to slow ratios observed however suggest that the surface fluorine source accounts for approximately half the total production rate. The rate of production of fluorine atoms by CF_4 electron impact, (the other major production process), can be calculated using cross section and EEDF data, and by using calculated production rates for CF , CF_2 and CF_3 ¹⁹, It can be shown to be of the order of $5 \times 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$, and so during the initial rise which lasts about 10 ms the

number of fluorine atoms produced in the plasma volume is 10^{17} . The number of fluorine atoms that can be accommodated on the surface can be calculated by assuming the size of the absorbed fluorine site to be approximately $10 \text{ \AA}^2$. This gives a value of about 5×10^{17} fluorine atoms on the electrode surfaces. Thus, it appears that the initial rapid rise could be explained by ion clearing of fluorine atoms from the surface, if a significant proportion of the absorbed fluorine atoms are sputtered on plasma ignition. Using the ion fluxes calculated above, this would require that each ion should remove about 10 – 100 fluorine atoms, which is much higher than typical sputtering yields²⁰. After this initial burst the surface density is replenished by absorption of gas phase fluorine atoms until a steady state is reached, (the rate of this process is determined by the heterogeneous reaction rate as described above).

This model also appears to be able to model the observed behaviour over a range of under different experimental conditions, (for example see figure 6.9, where the assumed surface source term is that shown in figure 6.3e). The variation of the rise time with pressure has already been discussed, but with increasing rf power the rate of the fast component is seen to rise, which corresponds to an increase in the sputtering rate. When O_2 is added to the system, no fast component is seen and, as explained in chapter 7, this is due to a dramatic change in the nature of the surface when oxygen atoms are present. Also, when running an argon plasma after a CF_4 discharge, fluorine emission was seen to rise on initial ignition, and then fall gradually with time. The source of this emission was thought to be fluorine sputtered from the surface rather than any remaining CF_4 molecules, which supports the model proposed. However, the model does rely on a large proportion of the production rate to be due to sputtering which in turn demands an abnormally high sputtering yield for the fluorine atoms. Also in spite of the fast diffusion rates at these pressures, the mechanism might be expected to show some spatial variation of, at least, the fast component of the rise, but no such observations were seen.

A variation in the steady state concentration can also be caused by a slow change in the rate of removal, and to demonstrate a rise as observed for the fluorine atom emission, this requires that the decay rate decreases as a function of time.

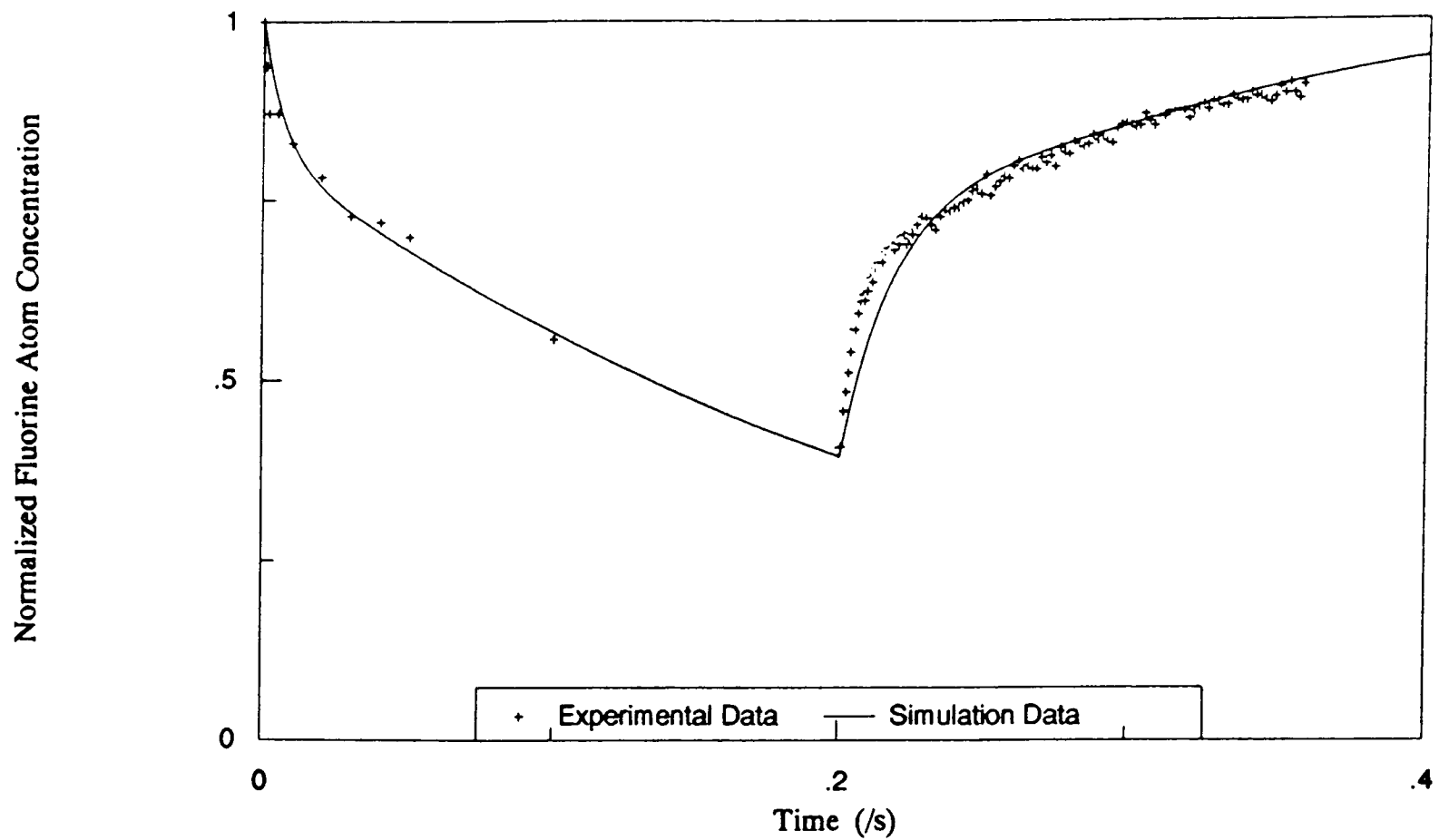


Figure 6.9 Experimental and modelled variation of fluorine concentration during the afterglow and reignition of a CF_4 plasma. The model used includes a surface production term, which has a time dependence as shown in figure 6.3e.

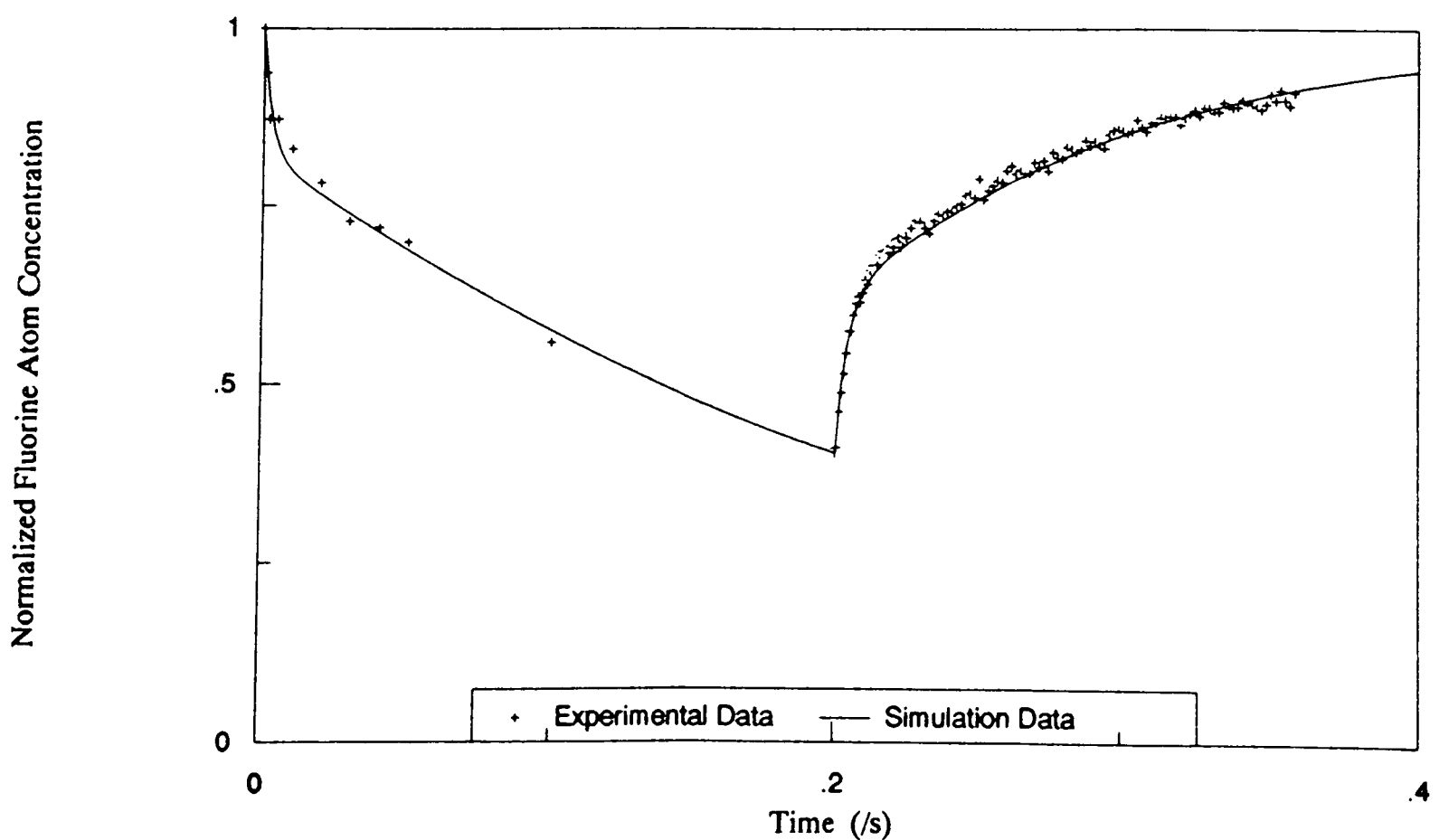


Figure 6.10 Experimental and modelled variation of fluorine concentration during the afterglow and reignition of a CF_4 plasma. The model used includes a time dependent wall loss rate, as shown in figure 6.3d.

This would then produce a total decay rate temporal profile as shown in figure 6.3d. The removal rate falls on extinction of the plasma to a very low level due to saturation of the surface, but on plasma ignition it rises rapidly as the ion bombardment is re initiated and the surfaces are cleaned. This results in a rapid initial rise in the fluorine atom concentration, towards a final steady state level. However, as the decay rate is falling with time, the steady state level, which the concentration is approaching, rises on a time scale dependent on the rate of change of the decay. The explanation for the decrease in decay rate is not certain, but heating of the surface, reducing absorption, or rearrangement and modification of the surface sites by ion bombardment are possible mechanisms. The variation of the ratio $\frac{a}{b}$ with plasma parameter and time delay were found to be consistent with such mechanisms, but can not be considered as direct evidence. Direct measurement of the decay rate at different times during the rise curve was not possible because of the nature of the technique, (the same conditions would not be present at a given point on the rise curve for all the delay times necessary). Another approach, where the plasma was off for a fixed period of time and on for a variable time, produced results that were consistent with a faster removal rate after a shorter time on, (as required by the model).

The experimental data can also be fitted well by this later model, an example of which is given in figure 6.10, where the fluorine atom concentration, measured by TRA and the rise curve, is given for a plasma off period of 200 ms. The fit assumes a time dependent wall loss as described by figure 6.3d (and in the text above). Similar fits can be made for other conditions and delay times, but to confirm the proposed variation in decay rate, direct measurements of the fluorine atom removal rates as a function of rise time are required, without the presence of extra plasma pulsing.

Time resolved actinometry has been shown to be technique, simple to apply, which is capable of studying the kinetics of plasma based species. It has been validated by comparison of LIF and TRA studies on CF_2 , and has been used for

work in this thesis, to obtain the first measurements of the important removal rates of fluorine atoms and to show that the loss process is wall removal. These are described in detail in chapter 7. The rise kinetics are less clearly understood, and models involving variation of both production rate and removal rate appear to fit the observed data. Both models require a number of assumptions and physical phenomena, which are not necessarily valid, and more work is required to ascertain the true mechanism.

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Chapter Seven

Plasma Chemistry

7.1 Introduction

The previous chapters have described the development and investigation of diagnostic techniques which can be used to measure the steady state and time dependent concentrations of radicals species in processing plasmas. With these experimental methods and from consideration of the possible reaction pathways, a mechanistic model of at least the key chemical and physical processes of the plasma can be obtained. To this end a study on oxygen and fluorine atoms has been carried out using two photon laser induced fluorescence and actinometered optical emission respectively, on CF_4 and CF_4 / O_2 rf discharges. This complements previous work on CF and CF_2 using the same experimental apparatus^{1,2,3,4}.

Before analyzing the experimental results it is of use to examine some of the plasma processes. Many of these were discussed in section 1.3, but those of particular significance to oxygen and fluorine are considered here. The production rate for O and F is predominantly controlled by the electron impact dissociation of feedstock gases, O_2 and CF_4 and is therefore dependent on the gas pressure and the electron energy distribution function, (the excitation rate). The dissociation threshold for O_2 is 5.1 eV⁵, whilst that for CF_4 is 12.5 eV⁶, although dissociative attachment⁷ can occur at lower electron energy. Electron impact on oxygen molecules can produce oxygen atoms by a variety of pathways, including atomic excitation and ionisation⁵, and so the production rate of ground state oxygen atoms is difficult to predict from electron distributions and cross sections. The fluorine production rate is also complicated, for a number of reasons. The electron attachment dissociation is found to be the major pathway at low mean electron energies, but there is a dramatic rise in the cross sections for dissociation at 12.5 eV. This energy is similar to that of the argon emission threshold, and so argon emission might be expected to give a good representation of the dissociation rate. The variation of argon emission with power, pressure and gas composition is given in

figures 5.15, 7.1 and 7.2. At 50 mTorr, the emission is seen to rise with power, and the addition of O₂ has the effect of reducing the emission. (The 200 mTorr data was discussed in chapter 5). The pressure variation results from the expected reduction in mean electron energy $\langle \epsilon \rangle$, although the effect of the transition described in section 5.3.2 can also be seen. The CF₄ molecule has many dissociation channels several of which lead to fluorine atom production, (see reactions 1.14 – 1.16). The branching ratios of these reactions have been measured under a single experimental condition^{1,8} and it is probable that these ratios will change with electron energy distribution function, (as for photon excitation of CF₄⁹), thus the argon emission may not always be a good indication of the fluorine atom production rate. Also, fluorine atoms can be produced as a result of gas phase bimolecular reactions of CF_x with O, (reactions 1.6 – 1.8). Modelling in this laboratory¹⁰ and elsewhere¹¹ has shown however that these reactions are not a major source for fluorine under the present conditions.

The key gas phase removal processes for the atomic species are three body recombination for fluorine and bimolecular reactions for oxygen, but reaction at the walls and pump out are also important loss mechanisms. The pressure dependent recombination reactions, (reactions 1.11 – 1.13), have greater importance as the pressure increases, particularly the reaction with CF₃. The dissociation branching pathways of CF₄ mean that the fluorine atom concentration is greater than that of CF₃, so recombination to generate CF₄ has a more significant effect on the concentration of CF₃ than that of fluorine. The magnitude of its effect on fluorine can only be found if the absolute CF₃ concentration is known as a function of plasma parameters. For the low pressure CF₄ /O₂ plasmas used in this study (50 – 200 mTorr), there was no evidence of the influence of this reaction on the fluorine atom concentration and modelling calculations indicate that it is not expected to be a major removal process for fluorine¹⁰ except at higher pressure. The bimolecular reactions involving oxygen and CF_x increase the loss rates of CF_x and O and hence reduce their concentrations.

Wall removal processes have been shown to be dominated by reaction at the

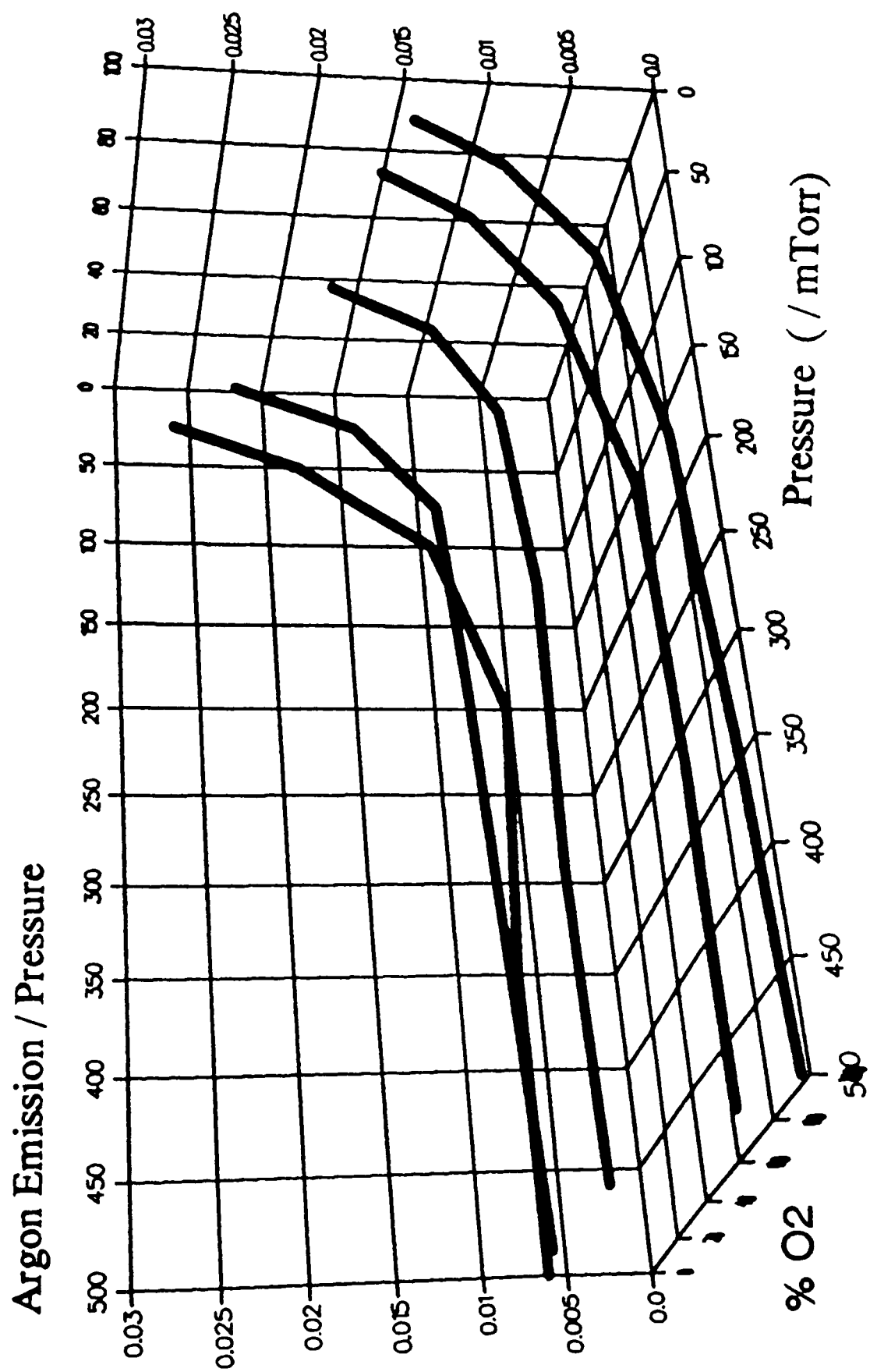


Figure 7.1 Variation of excitation rate (Ar emission/pressure), as a function of gas composition and pressure for the CF_4 / O_2 system at 200 W.

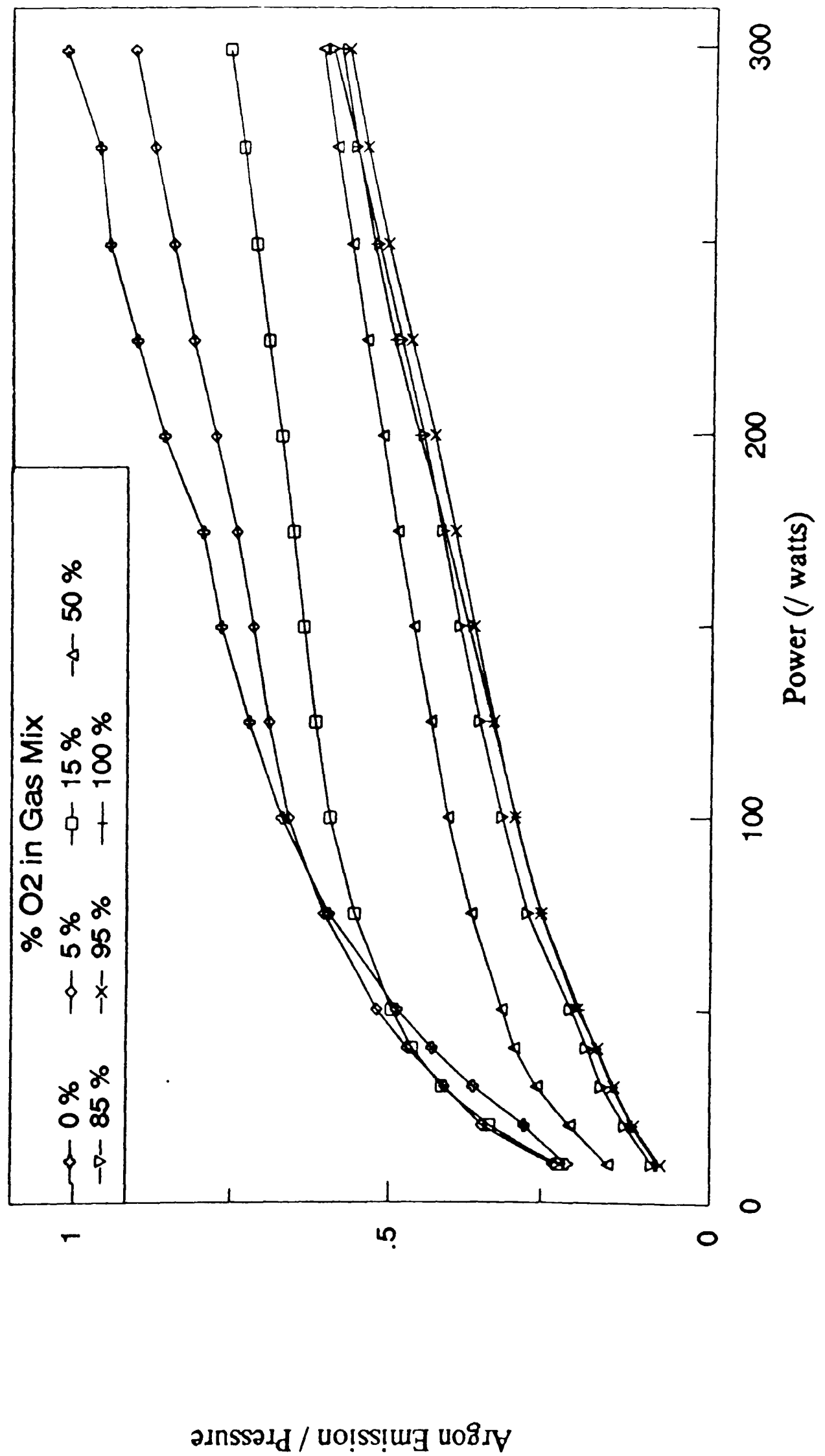


Figure 7.2 Variation of excitation rate (Ar emission/pressure), as a function of gas composition and power for the CF_4 / O_2 system at 50 mTorr.

electrode surfaces rather than the reactor walls for the chamber used in this study¹, and thus they can be influenced by ion bombardment mechanisms. The reaction involves diffusion from the bulk plasma to the electrode surface followed by an absorption mechanism. Depending on the pressure, the rate can be diffusion limited (high pressure), or wall loss limited (low pressure). The process has been modelled^{1,3} using diffusion equations and for the extreme cases, analytic solutions can be determined. For the diffusion limited case, the rate can be shown to be equal to $D \cdot (\frac{\pi}{L})^2$, and that of the wall limited case is $(\alpha \cdot \bar{c} / 4 \cdot L)$, where D is the diffusion coefficient, L is the separation between the electrodes, $\bar{c}$ is the mean velocity of the species and α is the sticking coefficient, (a factor which indicates the fraction of the impinging species which do not return to the gas phase in the same form as they are absorbed onto the surface). Between these limits, numerical solutions can be found and the results of such calculations can be seen in figure 7.3, which is shown for the fluorine atom system.

The pump out rate acts as the limiting process in the absence of chemical reaction, and the associated residence time can be calculated approximately from the pressure, chamber volume and gas flow rate¹², (for a full calculation the fluid dynamics of the system should be considered). Such calculations produce residence times of 520 ms and 2.1 s for pressures of 50 and 200 mTorr respectively, for a flow of 42 sccm. A compilation of the processes and their rates, which are of importance to oxygen and fluorine atoms in low pressure rf plasmas, is given in Appendix 2.

7.2 Chemistry of Fluorine

7.2.1 CF₄ plasma

As described in the previous chapter, in a CF₄ plasma fluorine atoms are removed predominantly by diffusion followed by wall reaction, a conclusion based on the dependence of the removal rate on the pressure, although further experimental evidence will be given here. The removal rates of fluorine atoms have been measured for a variety of plasma conditions but at high pressure and high power, the plasma breakdown process makes the TRA technique difficult to apply.

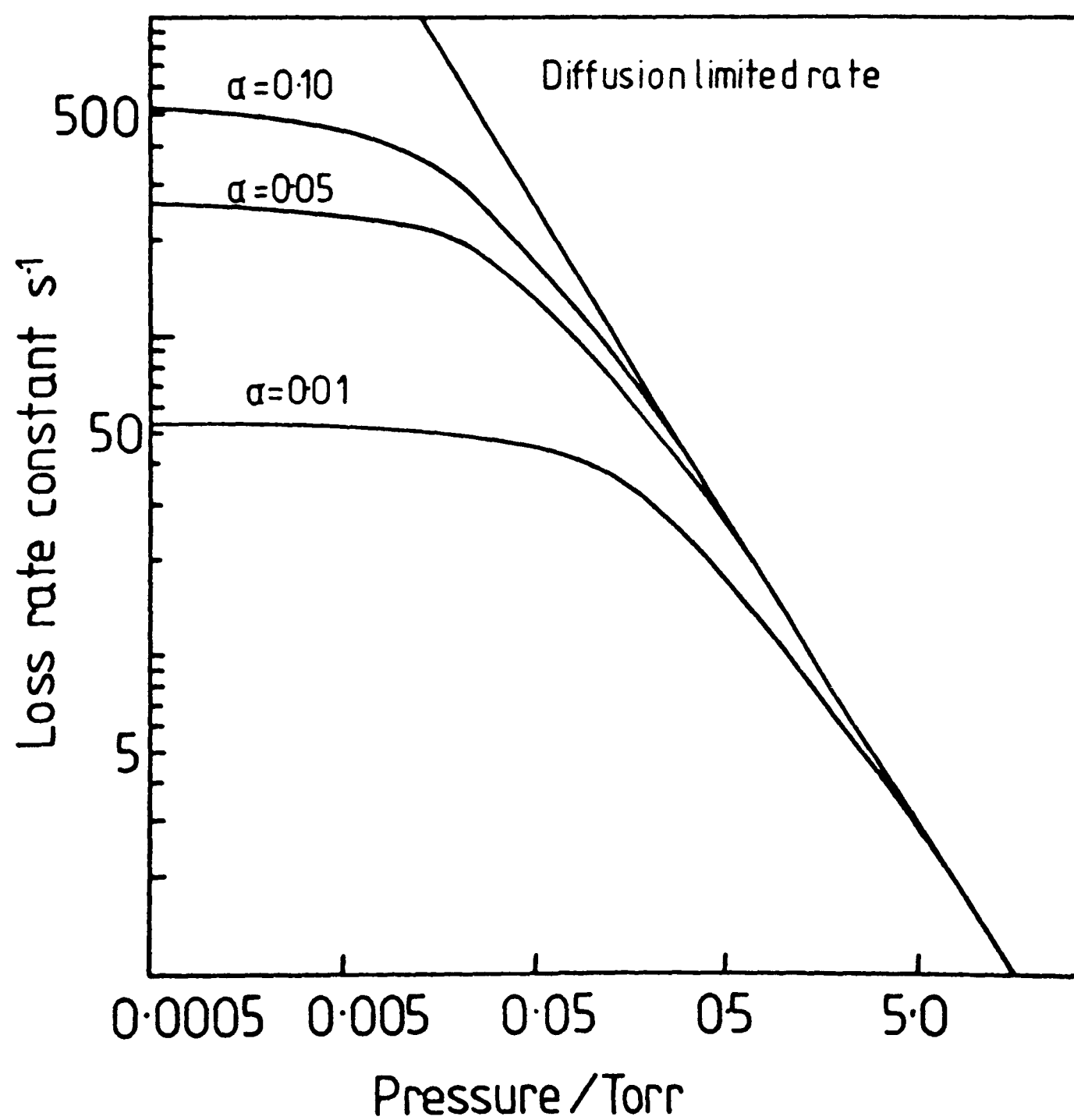


Figure 7.3 Modelled first order loss rate at the centre of the reactor using FACSIMILE, with $D = 3000 \text{ cm}^2\text{s}^{-1}$ at 50 mTorr, $L = 5.5 \text{ cm}$ and $c = 590 \text{ ms}^{-1}$.

The results are given in table 7.1.

Gas	Power (/W)	Pressure (/mTorr)	% O ₂	Initial loss rate (/s ⁻¹)	Final loss rate (/s ⁻¹)
CF ₄	100	50	0	28 ± 2	3.22 ± 0.1
	100	200	0	10.8 ± 1	1.35 ± 0.1
	100	200	0	Not measured	1.13 ± 0.1 [*]
	200	50	0	26 ± 5	4.7 ± 0.2
	50	50	0	18 ± 4	3.4 ± 0.2
	100	50	2	10.4 ± 1.7	2.7 ± 0.1
	100	50	5	8.91 ± 1.4	3.4 ± 0.2
	100	50	10	0	2.4 ± 0.2
	100	50	30	0	2.6 ± 0.2
	100	50	50	0	2.5 ± 0.2
SF ₆	200	50	0	110 ± 2.2	—
	200	50	10	12.1 ± 2.5	—

Table 7.1

^{*} data taken at the reduced flow of 11 sccm, (cf. 42 sccm).

These results are a compilation of the fluorine atom removal rates measured in an empty chamber, (see later for data taken with silicon present), and where applicable represent an average value for results obtained. The error bars are related to each individual experiment, but there were slightly larger variations seen over a series of runs, in part due to the need to obtain the initial limiting loss rates, (not for the SF₆ or CF₄ / O₂ plasmas). In an attempt to minimize the errors, a verification run was taken for each experiment, to check that the signal levels were consistent throughout the experiment, and if the values were found to vary by more than 4% the experiment was rerun.

There is some evidence that the initial fluorine atom removal rate increases

slightly with rf power, which may be due to increased ion bombardment and hence a greater number of active sites on the electrode surface. The pressure variation suggests the importance of wall removal processes, and the rates can be used to obtain approximate sticking coefficients, using the calculations illustrated in figure 7.3. This produces a value for α of 0.005 for a 50 mTorr pure CF_4 plasma, which is in reasonable agreement with in-situ measurements by Sawin¹³, and is a measure of the sticking coefficient of fluorine on the electrode surfaces in the absence of ion bombardment. As discussed in the previous chapter this may not be the same as the net loss during steady state conditions if gas phase fluorine is regenerated by ion sputtering. Part of the analysis to find the sticking coefficient requires knowledge of the spatial variation of the concentrations and loss rates, and so spatially resolved measurements of the removal and rise curves for fluorine atoms were taken, but were found to be independent of position at 50 mTorr. The sticking coefficient for fluorine on alumina, the probable material of the electrode surface has been measured¹⁴ to be 6×10^{-5} , (for a cleaned aluminium surface it is 0.002), and so it is thought that the surface processes involve reaction with the $(\text{CF}_x)_n$ based polymer formed in these discharges^{4,15}.

At both pressures studied, the removal loss rate lies between the wall and diffusion limited cases, but the decrease in loss rate with pressure is larger than that predicted by figure 7.3, and a change in α is also required to explain the observed 200 mTorr data, ($\alpha = 0.003$). The higher pressure conditions produce a thicker layer of polymer due to the increases in polymer precursor (CF_x) , and a reduction in ion energies and hence of sputtering and damage mechanisms. The chemical composition of the polymer has also been shown to be dependent on its thickness^{4,16}, with a higher concentration of fluorine being present in thicker polymers. The observation that these changes affect the sticking coefficient is not surprising but their precise influence is less predictable.

The slow removal rate is seen to be dependent on pressure and flow and has a magnitude comparable but consistently above the inverse residence time of the chamber, There is also a small variation with rf power, all of which suggest that

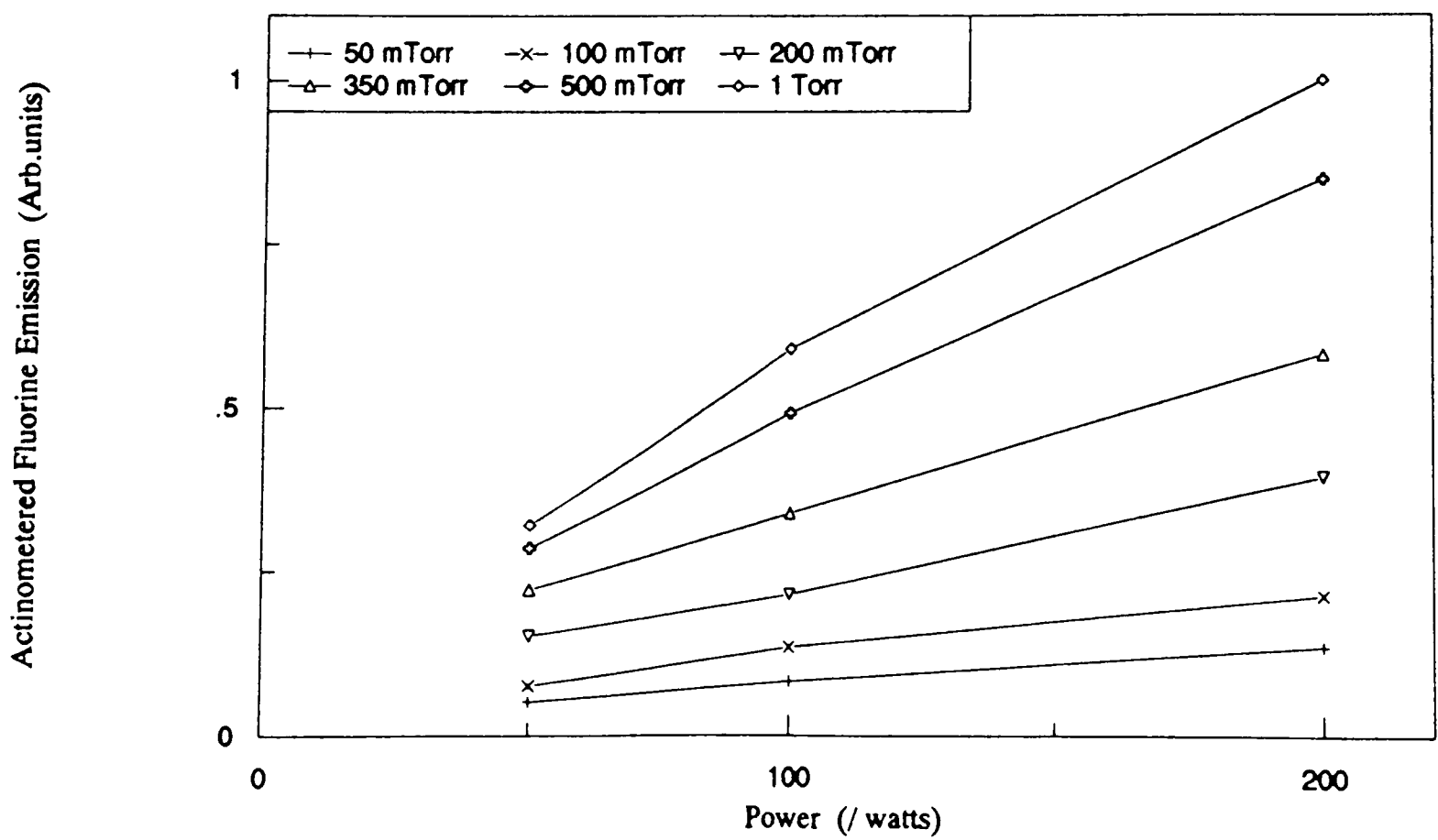
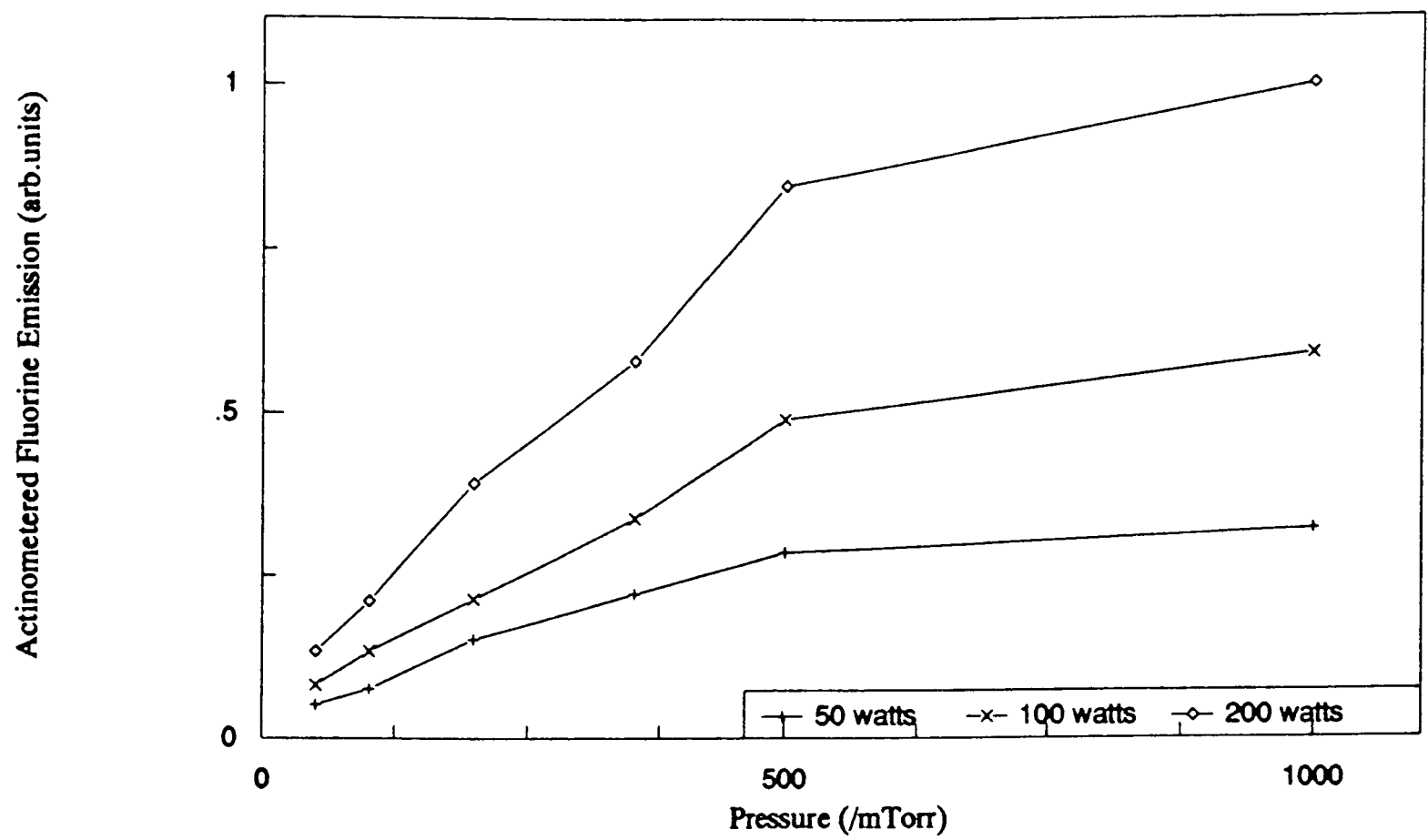


Figure 7.4 Variation of actinometered fluorine emission as a function of power and pressure in a CF_4 plasma.

there is a small wall loss component to the overall removal rate even after long delays.

The effect of the variation in the removal and production rate on the steady state levels can be seen in figure 7.4, although the near linear increase of fluorine atom concentration with rf power, suggests that the argon emission is a poor measure of the fluorine production rate, (cf. figure 7.2). The dependence on pressure is thought to be due to the variation in the removal rate, since the overall production rate is expected to be fairly constant, (a rise in CF_4 pressure but a fall in mean electron energy). At even higher pressures, the increase in the $\text{F} + \text{CF}_3$ reaction rate would tend to cause the fluorine concentration to overturn.

7.2.2 CF_4 / O_2 Plasmas

Addition of O_2 to the CF_4 system has an important effect on the fluorine atom chemistry, as seen by the removal rates, (table 7.1 and figure 7.5), and the steady state concentration, (see figure 7.6). Even at levels of 5% O_2 addition, there is a significant rise in the fluorine atom concentration, (as has been previously observed¹⁶), and by 10% addition, the decay curves illustrate that the fast wall removal process is no longer present. Oxygen atoms are known to produce fluorine atoms by reactions with CF_x , and will also reduce the concentration of CF_3 , which at high enough pressure, can be a major removal term for F, and thus this will effectively increase the fluorine atom concentration. Such chemically based reaction schemes have been previously used to explain increases in the concentration of fluorine atoms but they related to higher pressure systems, where gas phase processes are more important and slow diffusion limits the influence of the walls^{9,17}. The magnitude of these effects on the steady state concentration under the conditions used in this study, is small compared to the change in the wall removal rate.

The fluorine atom concentration was seen to rise by a factor of six, which correlates fairly well with an 8.5 fold reduction in the removal rate. (Modelling calculations predict that the gas phase reactions cause a 40% rise in fluorine

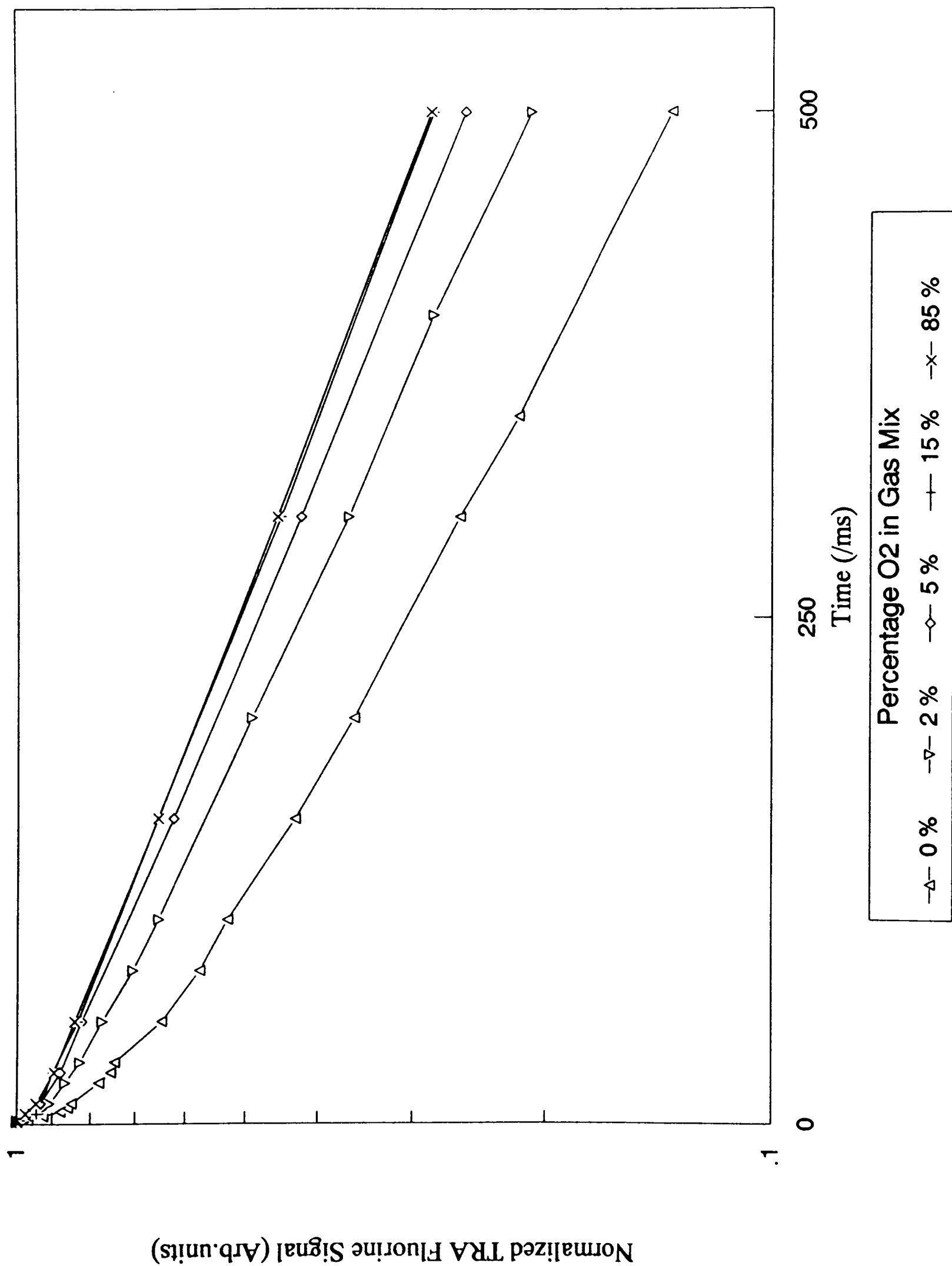


Figure 7.5 Semilogarithmic plot of the variation of actinometered fluorine emission after plasma extinction for a variety of $O_2\%$, measured by TRA.

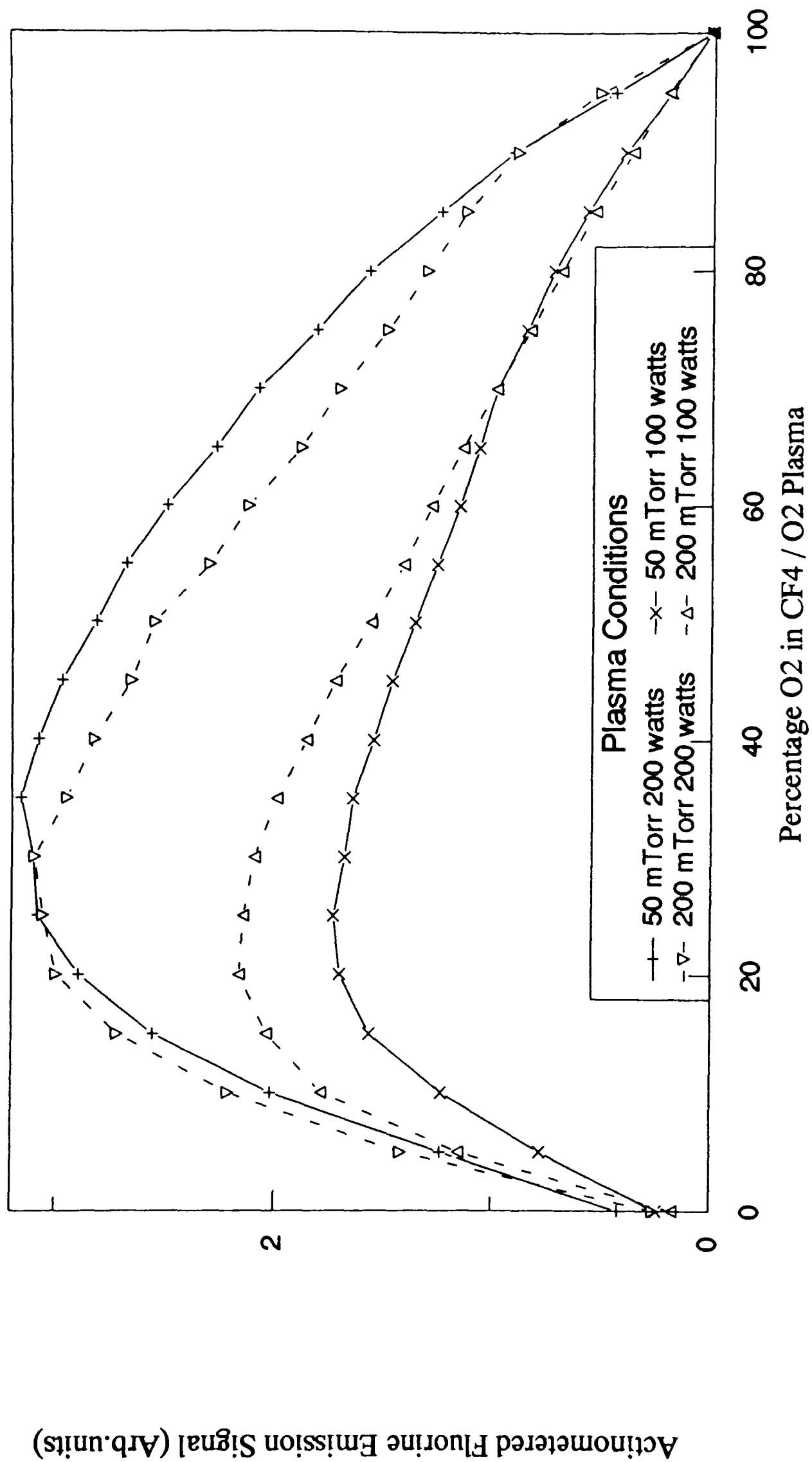


Figure 7.6 Variation of actinometered fluorine emission as a function of gas composition under a variety of plasma conditions. (Not corrected for pressure.)

concentration¹⁰.) A change in the loss rate due to direct competition between O and F for active sites, has previously been suggested to account for the variation of silicon etch rate with fluorine atom concentration, as the O₂ concentration was varied¹⁶. However, in this case consideration of the precise nature of the surface is required and the decrease in the removal rate is thought to be due to a reduction in the (CF_x)_n polymer formed on the electrodes. This may be a result of gas phase reactions, causing a reduction in polymer precursor species, or direct removal of the polymer by the etching action of oxygen atoms. As the polymer is removed more of the alumina electrode is exposed and so the observed sticking coefficient would be expected to tend towards that of alumina. This can not be tested quantitatively because the pump out rate is faster than such a wall removal rate, but the absence of any fast removal at low O₂ percentages is consistent with this explanation.

Closer examination of figure 7.6 reveals that the position of the maximum in the fluorine atom concentration is dependent on the plasma conditions, such that low pressure and high power correspond to a peak at a higher percentage of O₂. This has been investigated further over a wider range of conditions and the results are given in table 7.2. The values shown are the percentages of O₂, which relate to the maximum in the fluorine atom concentration.

		Power (/W)				
		25	50	100	200	300
Pressure (/mTorr)	50	18	20	22	25	29
	200	11	14.5	18	22	28
	500	5.5	9.5	15.5	20	27

Table 7.2

As has been seen before, low pressure and high power show comparable effects, which is because of the high ion energies and fluxes associated with these

conditions. In this situation, the ion bombardment generates active sites on the electrode surface and so the high power low pressure conditions would be expected to show a greater effect. This manifests itself in the increase in the oxygen concentration required to passivate the surface with respect to fluorine removal and is further evidence that the fluorine removal rate is dependent on the generation of active surface sites by ion induced damage. The trend may also be partly due to the variation of $\left[\frac{\text{F}}{\text{O}}\right]$ as a function of power and pressure. The ratio is seen to rise with increasing power and decreasing pressure, and so the influence of oxygen on fluorine atom concentration would be expected to be least at low pressure and high rf power, as observed. The shift in the maximum is also seen in the variation of fluorine with rf power, over a range of O₂ percentages, as shown for two pressures in figure 7.7.

7.2.3 SF₆ Plasmas

In an attempt to determine the significance of the nature of the surface on the fluorine atom removal rate, a SF₆ discharge was studied in the presence and absence of O₂. Results obtained agree with previous work on these plasmas, which revealed a dependence of steady state fluorine concentration on the O₂ percentage similar to that observed for CF₄^{18,19}, and suggests an analogous mechanism of the reduction in wall loss rate, (the chemistry of this system is however more involved²⁰). The predicted drop in removal rate was found to be observed as seen in table 7.1. The temporal profiles were markedly different from those obtained in the CF₄ based plasma systems. Both the decay and rise curves were single exponential traces with very similar time constants, as seen in figure 7.8. Also, there was no evidence of the saturation effect seen for CF₄, and although the reason for this is uncertain, for the SF₆ system, in the absence of a (CF_x)_n polymer, ion bombardment does not appear to play as an important a role in the loss of fluorine atoms. This result further suggests that it is the detailed nature of the surface which is the critical factor in determining the fluorine atom concentration.

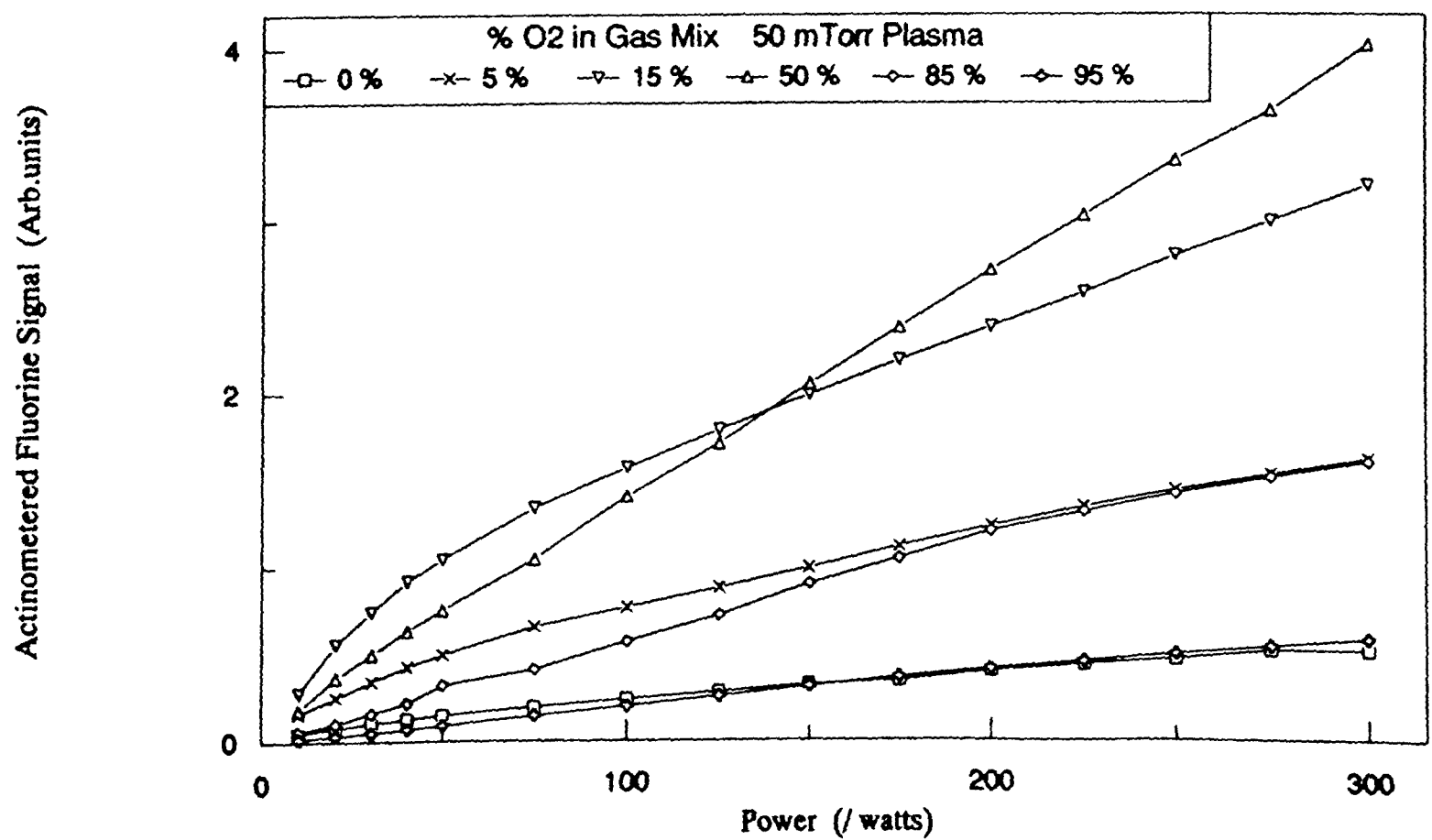
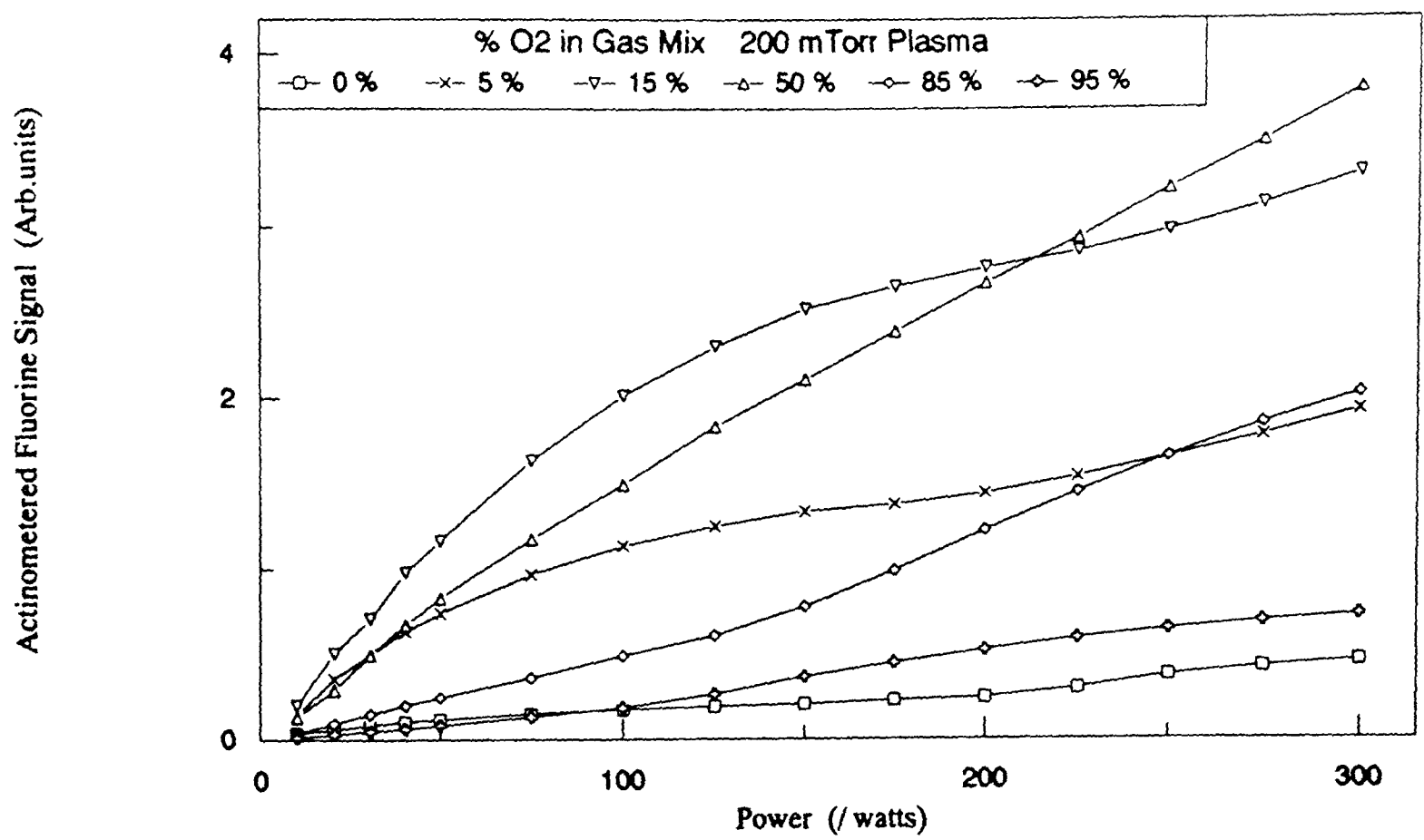


Figure 7.7 Variation of actinometered fluorine emission as a function of power over a range of O₂ % and at 50 mTorr and 200 mTorr.

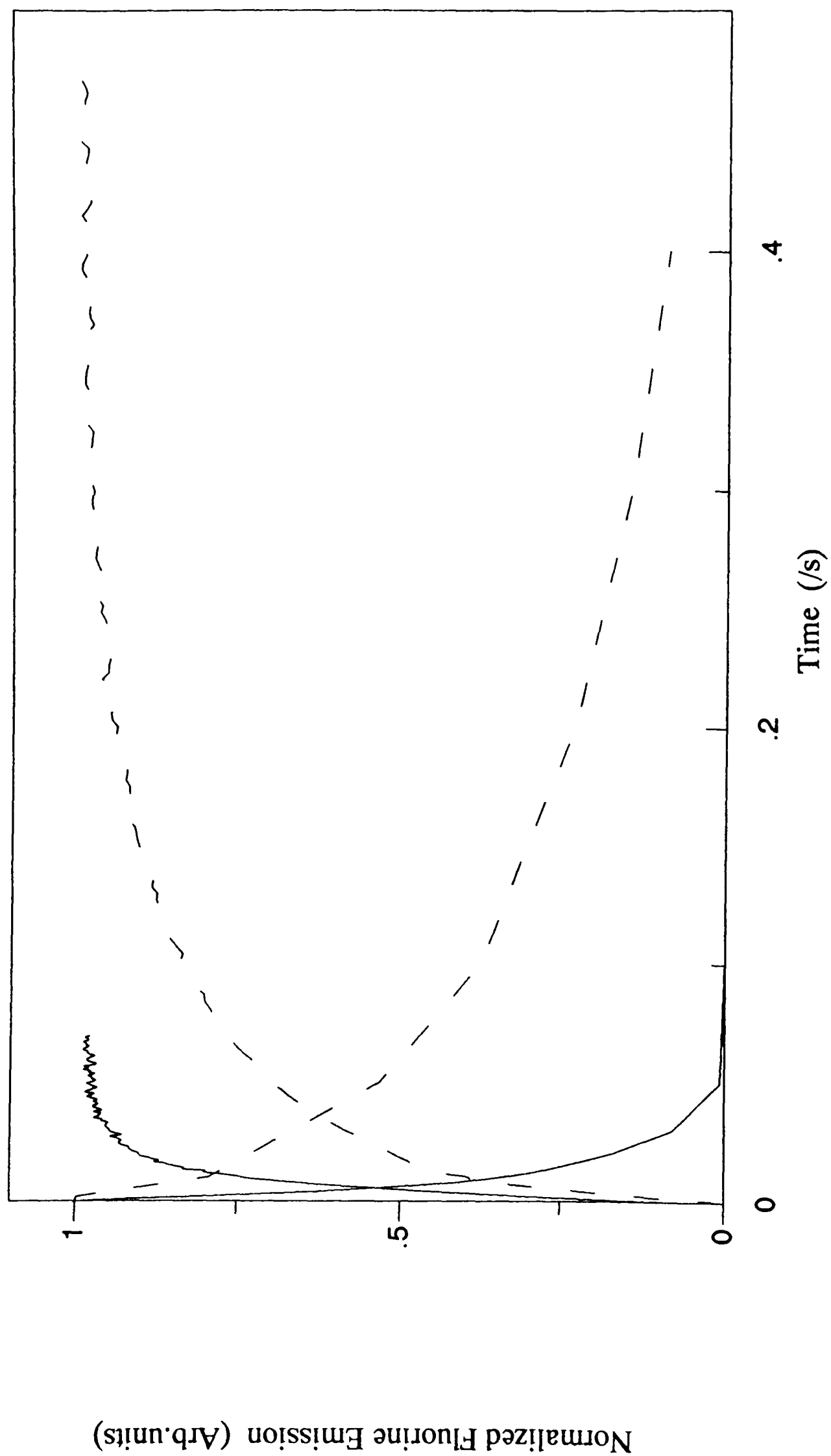


Figure 7.8 Variation of actinometered fluorine emission on plasma extinction and ignition and for SF_6 (—) and $\text{SF}_6,/, \text{O}_2$ (---), 50 mTorr, 200 W plasmas, as measured by TRA.

7.2.4 Fluorine in the Presence of a Silicon Surface

One technological application of CF_4 / O_2 plasmas is the etching of silicon and this was studied, partly to examine such a process, but also to investigate further the influence of the surface on the fluorine atom removal rates. To this end, both pure CF_4 and CF_4 / 10% O_2 plasmas were used, together with a variable number of n-doped silicon wafers which altered the surface area of the silicon exposed to the plasma. Measurements of the steady state concentration and the removal rate of fluorine atoms were taken and some of the time resolved results are shown in figure 7.9, (the rest of the data are given in table 7.3).

% O_2	$[\text{F}]_{\text{ss}}$	Decay rate (by TRA / s^{-1})	Silicon Surface area ($/\text{cm}^2$)
0	1.0	25	0
10	6.9	2.8	0
0	0.48	16	45
10	3.2	3.0	45
0	0.2	123	180
10	1.11	7.3	180
0	0.16	200	250
10	0.8	20	250

Table 7.3

For a CF_4 plasma changing the surface to silicon had the effect of dramatically increasing the removal rate of fluorine atoms to a value of 200 s^{-1} . Furthermore, the two phase nature of the decay is no longer seen and a single exponential decay is observed. Fluorine atoms react with silicon to form volatile products such as SiF_4 , which ensures that the silicon surface maintains some free sites, and hence the saturation effects are not expected. Addition of O_2 in the presence of silicon caused a reduction in removal rate as observed for the empty

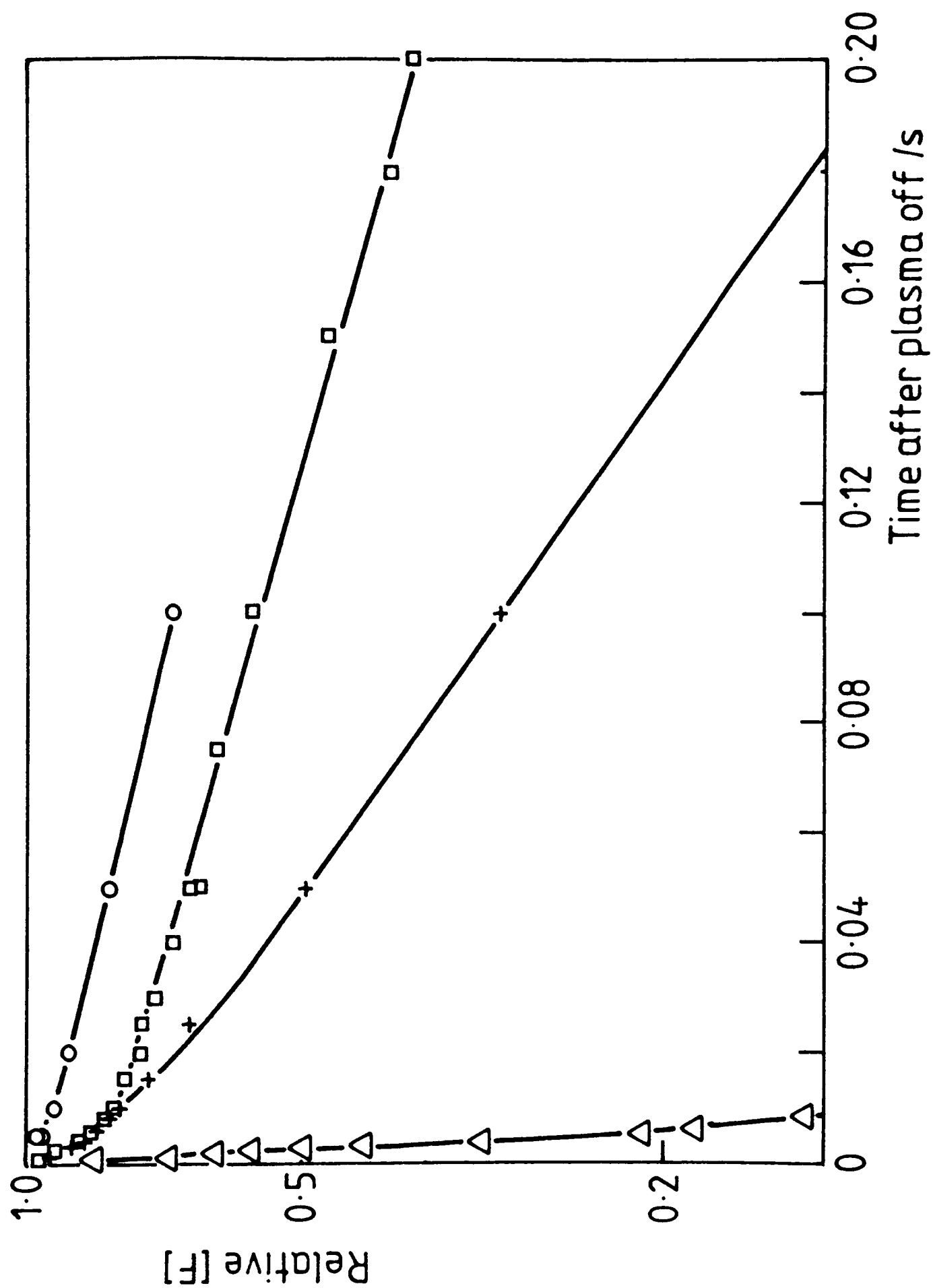


Figure 7.9 Semilogarithmic plot of the variation in the fluorine atom concentration as measured by TRA, for a CF_4 plasma in the presence ($\triangle$) and absence ($\square$) of silicon and for a CF_4 / O_2 plasma again in the presence (+) and absence ($\circ$) of silicon. The concentrations are normalized to their respective equilibrium values and are measured in a 50 mTorr 100 W plasma, with 250 cm² of silicon.

chamber. The mechanism responsible for this effect is believed to be based on the production of a passivating layer of $\text{Si-O}_x\text{-F}_y$ ^{21,22} on the silicon surface, which inhibits the formation of volatile etching products and thus reduces the fluorine removal rate and the dependence of etch rate on the fluorine atom concentration.

The effect of loading the system with silicon is seen by the increase in removal rate and decrease in the steady state concentration as the surface area of silicon was increased. This effect has technological consequences on the uniformity of the etching process over the whole silicon wafer¹². For the silicon surface area of 250 cm^2 , where the wafers completely cover one electrode, it is possible to calculate an approximate sticking coefficient for fluorine on silicon, and a value of 0.065 is obtained. A previous measurement of this value was carried out in a plasma afterglow, in the absence of ion bombardment, and produced a lower value of 0.002²³. The coefficient was shown to be dependent on the temperature of the silicon, and so, as the wafers in the experiments done for this thesis were not thermally connected to the water cooled electrodes, the higher value obtained is partly due to temperature effects, but also to the ion effects. The ion bombardment causes damage on the silicon surface and so effectively increases the silicon surface available for reaction²⁴. It should also be noted that for such a high sticking coefficient, it is probable that there is a spatial gradient in the plasma, with the fluorine atom concentration depleted near the loaded electrode. Strictly, this variation and the associated spatial variation in removal rate needs to be considered for a precise calculation of the coefficient.

Relating these results to measurable silicon etch rates demands an understanding of the etching mechanism and much work has been done in this field^{23,24,25,26}. In the reactive ion etch mode used in this study, (silicon wafer placed on the driven electrode), the fluorine atom concentration and the ion flux and energy both determine the overall etch rate. If it is assumed that all the fluorine forms the volatile SiF_4 , then an estimate of the chemical component of this rate can be gained from the product of the fluorine concentration and its removal rate. However, as the physics of the plasma is influenced by the presence of silicon on the

electrode surface, it is not possible to separate the ion and chemical effects nor to predict silicon etch rates for the conditions studied. It is interesting to note that only for the lowest silicon surface area does the concentration – removal rate product increase on addition of O_2 , despite the fact that CF_4 / O_2 mixtures are used because of the increased silicon etch rate. However this is a consequence of the formation of a $(CF_x)_n$ polymer layer on the silicon surface in the pure CF_4 case, which acts as a reactive site for fluorine atoms, but which is absent in the presence of oxygen. This effect, combined with the difficulty of separating the ion and radical etch mechanisms and contributions, removes the possibility of predicting the silicon etch rate from the fluorine atom concentration and measured removal rate.

7.3 Chemistry of Oxygen

Measurements of the steady state and time dependent concentration of oxygen atoms have been made over a wide range of experimental conditions, and by employing careful experimental practice, to avoid the complications of amplified spontaneous emission and photoionisation and to allow for quenching of the fluorescing excited state, these values can be related to the absolute concentration measurement, taken at 50 mTorr, 100 W, 85% O_2 (chapter 3). The data indicate that dissociation fractions from 1.5 – 12 % are present in the CF_4 / O_2 discharges studied. These absolute levels enable not only the variation in oxygen atom concentration to be considered, but also its influence on the concentration of other species. In practice, this concerns reactions with CF_x , since other processes, such as recombination with itself or O_2 , or reaction with CF_4 have been shown to be very slow under the conditions employed in this study^{27,28}.

The temperature studies described in chapter 3 showed the temperature to vary by only about 50K (300 – 350 K), over a wide range of plasma parameters. The effect that this variation has on the relative intensities of the three spin orbit transitions is small. In the majority of the experiments done in this work, only the most intense 3P_2 transition was measured, and taking this to be representative of the total ground state concentration, only produces a 4% error over the range of

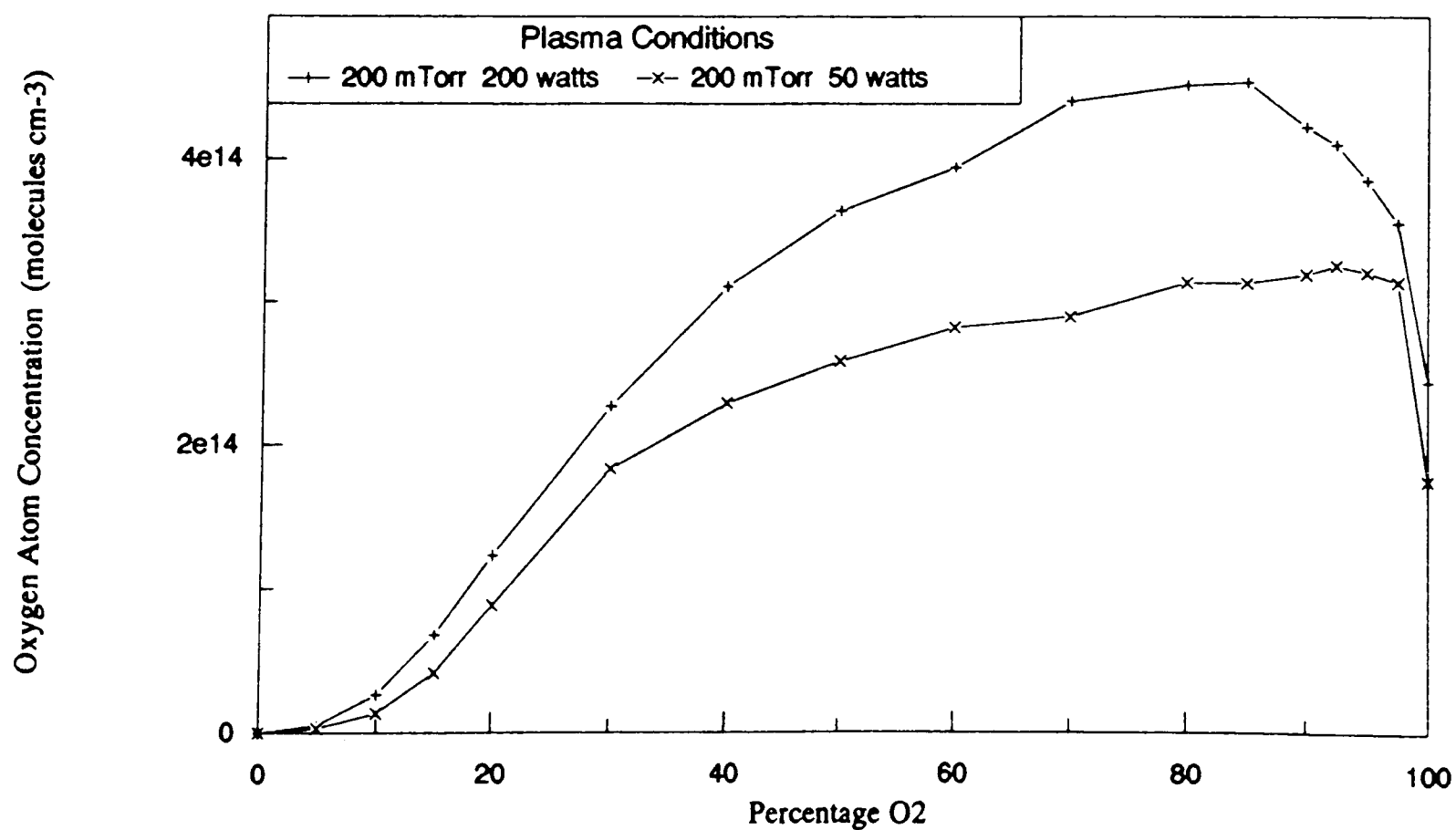
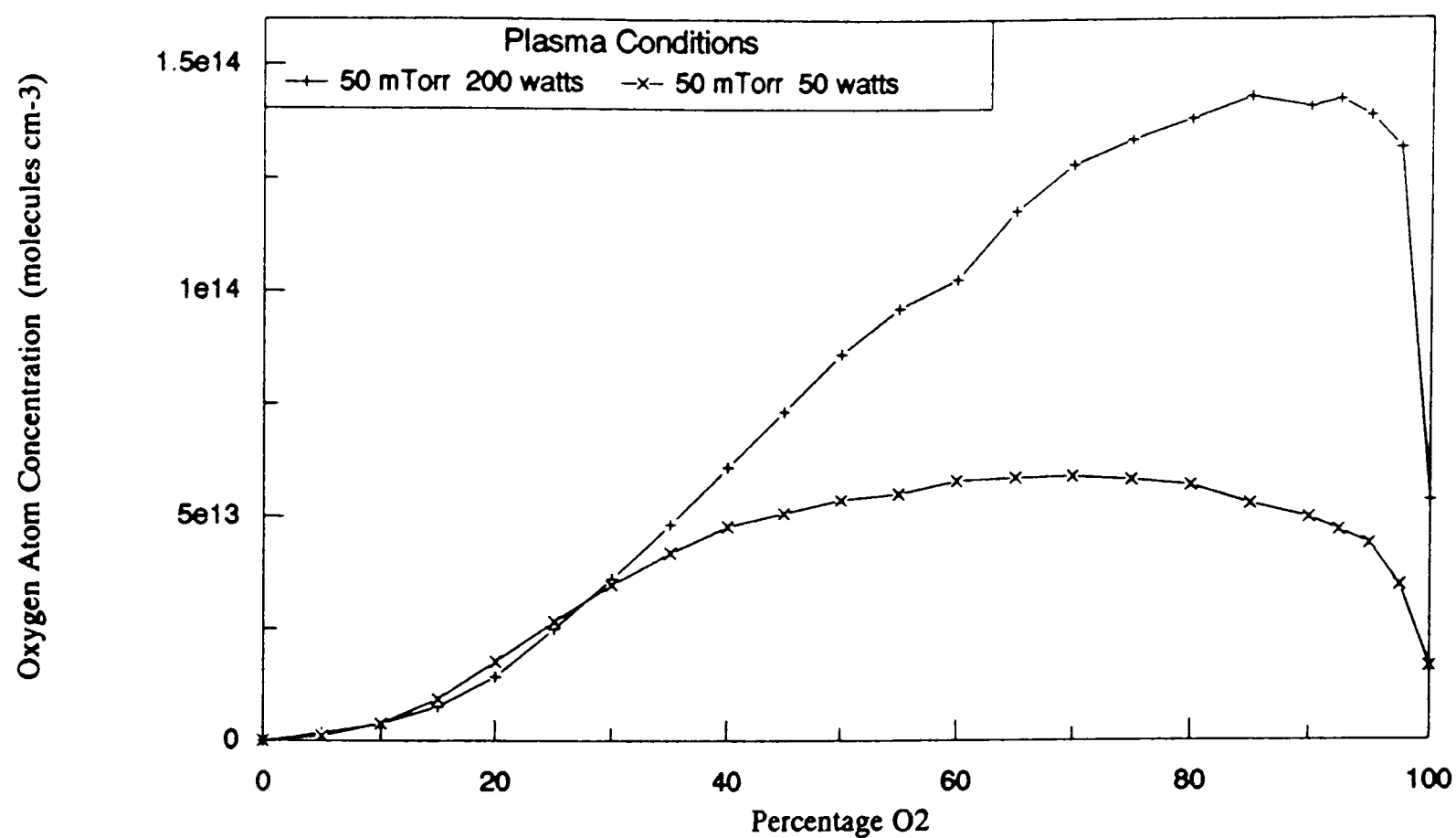


Figure 7.10 Variation of oxygen atom concentration, measured by LIF, as a function of gas composition under a variety of plasma conditions.

temperatures found.

The variation of oxygen atom concentration with gas composition is shown in figures 5.17 and 7.10, and illustrates behaviour which is analogous to that of fluorine, with an initial rise followed by a monotonic fall as CF₄ is added to an O₂ plasma, (for fluorine it is O₂ being added to CF₄). This similarity suggests that the processes taking place may correspond to the mechanisms described in section 7.2. To confirm this prediction requires measurements of the removal rates, the results of which are given in table 7.4, (and figure 7.11).

% O ₂	rf Power (/W)	50 mTorr	200 mTorr	500 mTorr
100	50	36.2 ± 2.6	13.9 ± 0.9	9.59 ± 0.6
	100	44.9 ± 4.7	14.8 ± 1.4	5.87 ± 0.8
	200	67.4 ± 5.8	16.1 ± 0.8	2.73 ± 0.5
95	50	11.2 ± 1.4	10.3 ± 0.5	
	200	30.6 ± 2.5	12.1 ± 1.1	
85	50	7.25 ± 0.4	7.47 ± 0.45	8.16 ± 0.5
	100	8.96 ± 0.65	6.56 ± 0.35	7.86 ± 0.42
	200	28.3 ± 2.1	5.98 ± 0.4	6.72 ± 0.69
50	50	6.88 ± 0.8	11.2 ± 0.4	13.8 ± 0.6
	200	14.9 ± 2.0	10.6 ± 0.3	21.2 ± 0.4
25	50	11.1 ± 2.0	19.7 ± 5.2	
	200		13.8 ± 1.3	
15	50	6.89 ± 1.21	12.9 ± 1.1	
	200		10.5 ± 1.2	
5	50		16.7 ± 1.4	

Table 7.4
Data given are the first order rate constants (/s⁻¹).

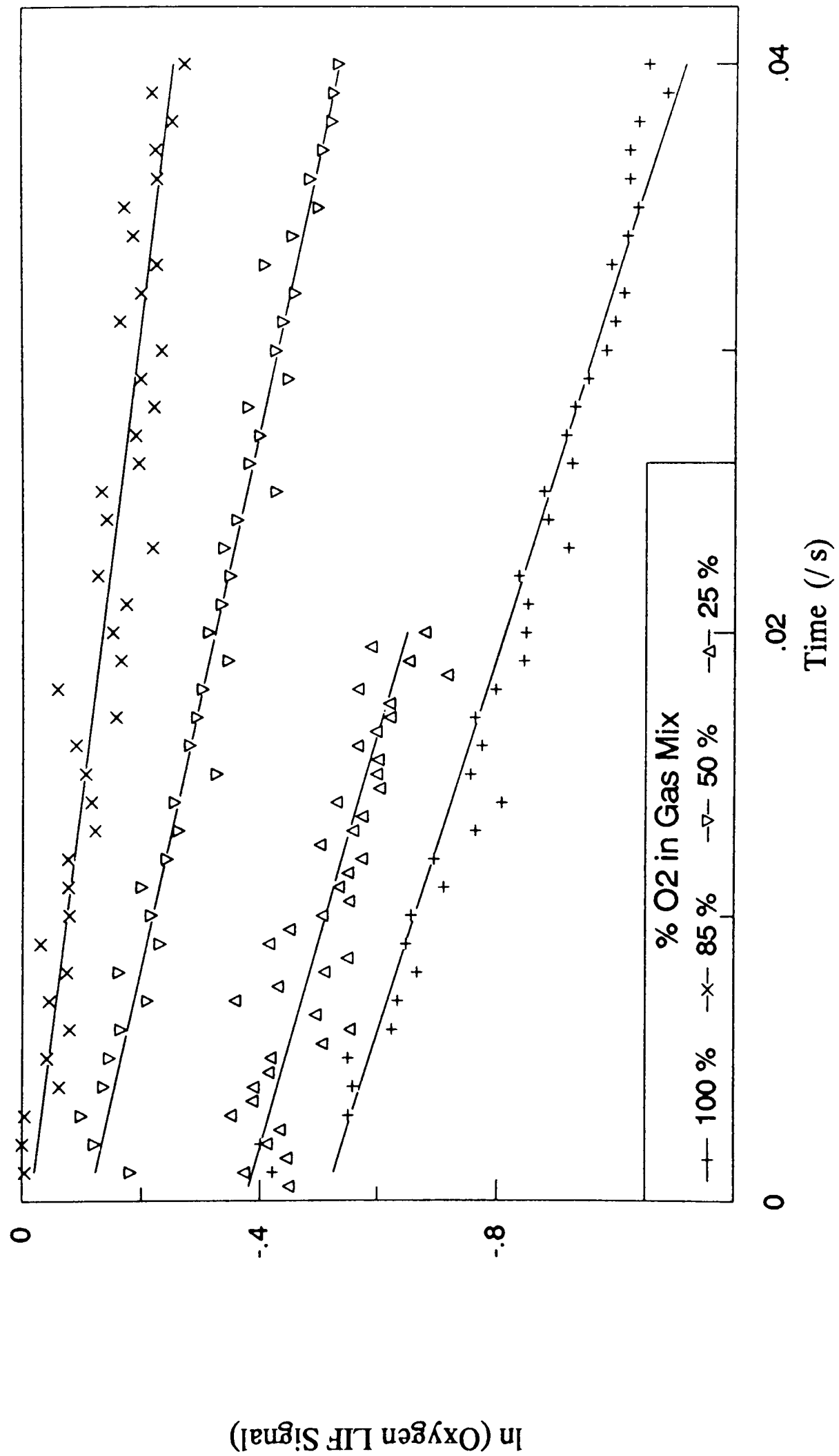


Figure 7.11 Semilogarithmic plot of the variation in oxygen atom concentration after plasma extinction, over a range of gas composition.

In oxygen rich plasmas, there was evidence of a reduction in the removal rate as a function of time after plasma extinction (possibly a saturation effect), and for all measurements the initial removal rate is the value shown. The results taken at low O₂ percentages involved very low signal levels and so have relatively large errors. Due to the intense plasma induced emission at 845 nm, measurement of rise curves was not possible except at very high pressure (1 Torr), but under these conditions the rates were found to be comparable to the decay rates.

The results show that in a pure oxygen plasma, the removal rate decreases with increasing pressure and that addition of CF₄ does significantly reduce the observed loss rate, which correlates strongly with the analogous fluorine atom results. This suggests that the general form of the variation of oxygen atom concentration with gas composition (in oxygen rich plasmas), is due to a rapid wall removal rate in pure oxygen, which is dramatically reduced by the addition of CF₄. The effect is however not as large as the influence of oxygen on fluorine atom concentration. In the fluorine case, the variation in removal rate was considered to be due to the nature and level of (CF_x)_n polymer present on the surfaces. For oxygen, the removal rate is not reduced down as low as the pump out rate, but reaction with CF_x gas phase radicals can not account for the difference, since their concentrations are expected to be too low. Therefore, it is probable that the reduction in removal rate is due to a more direct competition between fluorine and oxygen atoms, which are expected to be the most abundant reactive species present. This is consistent with the variation in the peak of the oxygen atom concentration as a function of rf power at 50 mTorr, where an observed higher $\frac{[F]}{[O]}$ ratio at high rf power, corresponds to the maximum being at a higher percentage of oxygen in the gas mixture. The 200 mTorr data is complicated by changes in the physics of the discharge, (see chapter 5).

Previous studies by Gousset *et al.*²⁹ showed the importance of wall removal for oxygen atoms in a pure O₂ dc discharge and they obtained a value for the sticking coefficient on pyrex of 0.005. Sabadil and Pfau³⁰ however reported the lower value of 0.0005 from a similar system. From the removal rates measured in pure O₂

plasmas, sticking coefficients can be calculated in the present work, although as can be seen in table 7.4, the loss rates at 50 mTorr were found to be dependent on rf power, possibly again a result of the need for ion bombardment to create sites on the surface. (This effect is less apparent at higher pressure where the ion energy is expected to be reduced.) The sticking coefficients can however be found for each condition, so for oxygen in a pure oxygen plasma, at 50 mTorr, 100 W, the value was found to be 0.008, (0.007 and 0.012 at 50 and 200 W respectively), and for a 200 mTorr plasma the slightly lower value of 0.003 was calculated. These values are in good agreement with the results of Gousset *et al.*²⁹ The variation of sticking coefficient with plasma conditions is not unexpected for species which are known to be sensitive to the nature of the surface, and thus to the effects of absorbed species and ion bombardment, (as for oxygen and fluorine). Previous studies^{1,2,3} on the sticking coefficients of CF and CF₂ have shown these values to be more constant with plasma conditions, although as described below even these values vary.

As mentioned above the spatial variation of concentration is required for full analysis to obtain an accurate sticking coefficient, but as suggested by the low values for the coefficient, no spatial variation in oxygen atoms was seen, in the pure oxygen and oxygen rich 50 mTorr plasmas probed. At 200 mTorr there was some evidence of a rise in the concentration near the plasma / sheath boundary, but the effect was small.

From table 7.4, it can also be seen that the decrease in removal rate with increasing pressure observed at high percentages of oxygen is reversed in the oxygen poor conditions, where there is evidence of the loss rate increasing with decreasing oxygen percentages. This is due to the importance of the reaction of oxygen atoms with CF_x radicals, whose concentration rises as that of oxygen falls. The influence of oxygen on the CF_x concentration is more marked than the reverse since the oxygen atoms are generally in excess, even down to gas mixtures of low percentages of O₂, as can be seen in figure 7.12³. The effect of these higher removal rates at low O₂ percentages can also be seen in the superlinear rise in steady state oxygen atom concentration as the O₂ percentage is increased. This contrasts with the linear

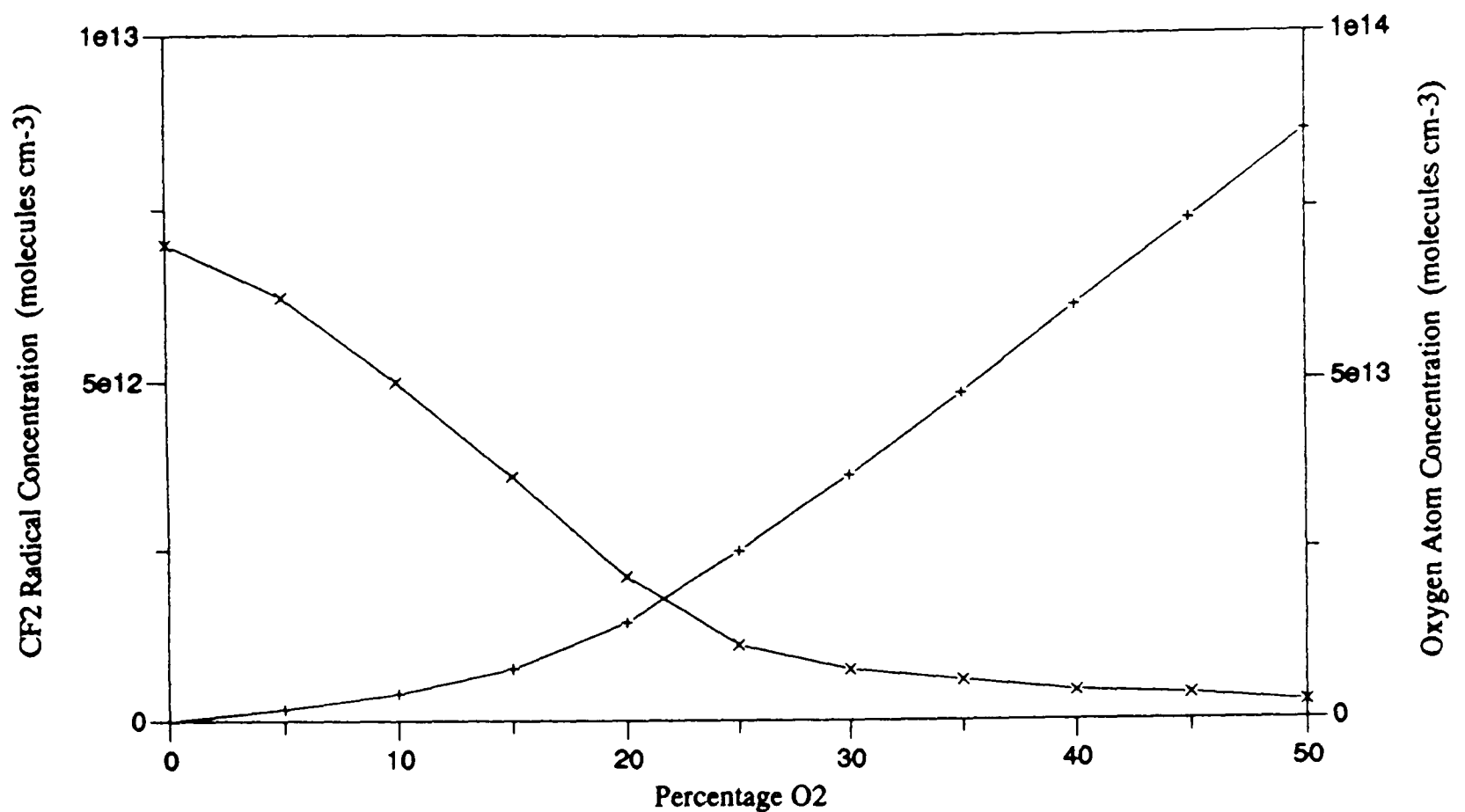


Figure 7.12 Variation in absolute concentration of atomic oxygen and CF₂ as a function of O₂ %, for oxygen poor mixtures in a 50 mTorr, 100 W CF₄ / O₂ plasma.

variation of fluorine atom concentration with CF₄ percentage (as CF₄ is added to O₂), which is a result of the constant pump out loss term, which is the only removal process for fluorine in oxygenated plasmas.

As the absolute concentrations of O, CF and CF₂ are known^{2,3} under these oxygen poor conditions, it is theoretically possible to calculate the expected gas phase removal rates and then by subtraction the other loss processes, in particular the wall removal rates of these species. The O + CF₂ reaction has been studied³¹ and the rate constant is known, $1.8 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ and for the O + CF reaction, Peeters³² has measured the constant to be $4 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$. Previous work in this laboratory^{3,4} produced an indirect value of $7 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$, which assumed that the wall removal rate of CF was independent of gas composition, (as will be shown this is possibly not the case). A full description of the processes in the plasma which affect the CF concentration however has not been obtained³, and so only the CF₂ and oxygen atom data is given in table 7.5, which includes the calculated component of the removal rate due to the O + CF₂ reaction. At 10% O₂, for a

50 mTorr, 100 W plasma, the concentrations of O and CF₂ are such that neither is in excess, so the species should follow second order kinetics. However, the CF₂ decay exhibited pseudo first order kinetics, and the oxygen traces were also single exponential for at least the start of the decays.

Gas Mixture	Species	Conc. (/cm ⁻³)	Measured rate (/s ⁻¹)	Expected rate (/s ⁻¹)	Difference
0% O ₂	CF ₂	7.0 x 10 ¹²	134	—	—
10% O ₂	CF ₂	5.0 x 10 ¹²	254	69	186
	O	3.8 x 10 ¹²			
15% O ₂	CF ₂	3.6 x 10 ¹²	7	65	-58
	O	8.0 x 10 ¹²			

Table 7.5

For the CF₂ removal rate, it can be seen that the difference between the measured rate and the (O + CF₂) component is greater than the CF₂ loss rate in a pure CF₄ plasma. As wall removal is expected to be the only other major removal process for CF₂, (F + CF₂ is expected to produce a CF₂ loss rate of less than 5s⁻¹ in a 10% 50 mTorr, 100 W plasma)^{3,10}, these rates illustrate that the presence of oxygen does modify the CF₂ wall removal process and the sticking coefficient. In this case the coefficient changes from 0.06 to 0.08 indicating that oxygen increases the reaction rate of CF₂ on the surface, probably resulting in oxidation of the absorbing CF₂ radical.

For oxygen atoms at 15% O₂, the observed removal rate is lower than that expected from the measured concentration of CF₂. The oxygen atom signal under these conditions is very low and much averaging was required to obtain the decay data, but the measurement can not account for the higher predicted rate, particularly as reactions with CF and CF₃ would be expected to further increase the oxygen atom decay rate. The measurement of CF₂ concentration involved a

complicated calculation and analysis of the CF_2 spectrum³, and using the value obtained in modelling calculations, has shown it to predict fluorine atom concentrations in excess of levels suggested by other studies³. As well as explaining the measured oxygen removal rates, a lower CF_2 concentration would also explain the observed pseudo first order decays which were seen in this work.

Between the two extreme gas compositions, the variation of oxygen with percentage O_2 is nearly linear due to small changes in the removal and production rate, and as described in chapter 5, this is the reason for the fortuitous correlation between actinometered optical emission and ground state concentration in this middle region. The variation of oxygen with power and pressure is shown in figures 7.13 and 7.14. With increasing rf power, the oxygen atom concentration rises although not linearly which is partly due to the power dependent removal rates. Oxygen concentration increases near linearly with pressure, indicating that the change in the removal rate is matched by the variation in the O_2 dissociation rate. This behaviour is different to that of fluorine, whose production pathway has a higher energy threshold and is thus more dependent on changes in the high energy tail of the EEDF, and whose gas phase removal rate is expected to increase at high pressure.

A final observation on the CF_4 / O_2 system was that any study of the fluorine and oxygen atom concentrations, involving a change from a pure gas to a mixture, (or the reverse), produced a signal level, which required at least two minutes to settle. After a change from a 50 / 50 mixture of CF_4 and O_2 to a pure CF_4 discharge, the fluorine emission was seen to show an immediate rise followed by a slow reduction down to the new steady state level. Similar effects were observed in reverse, and for the LIF signal of oxygen. This behaviour is thought to be a result of a slow change in the surface composition. The initial rise is caused by an increase in the fluorine production term (more CF_4) without a change in the loss rate. As the surface equilibrates to the new conditions (ie. the absence of oxygen), so the removal rate increases, and the gas phase concentration of fluorine falls. The result again

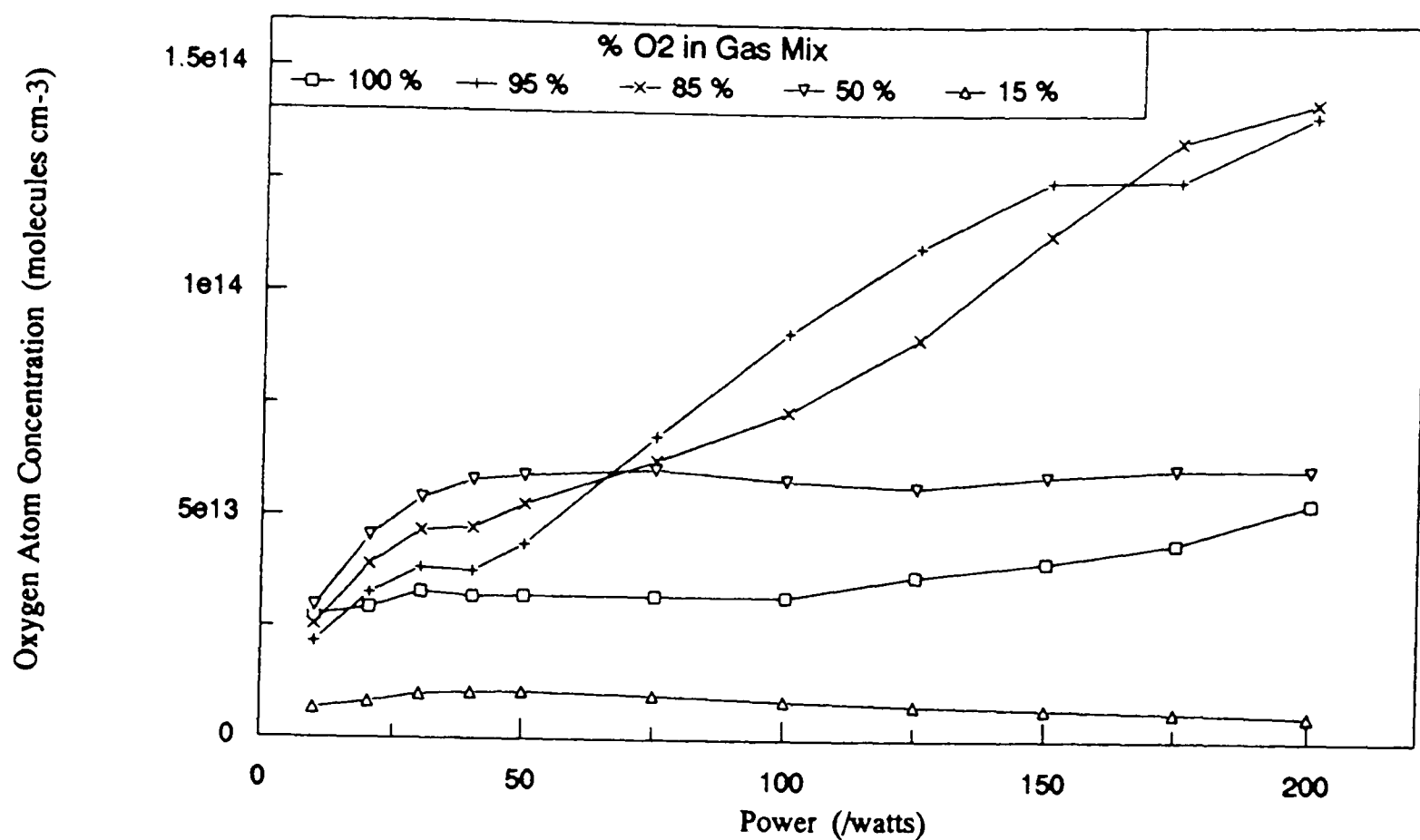


Figure 7.13 Variation of oxygen atom concentration with rf power for a variety of gas compositions at 50 mTorr.

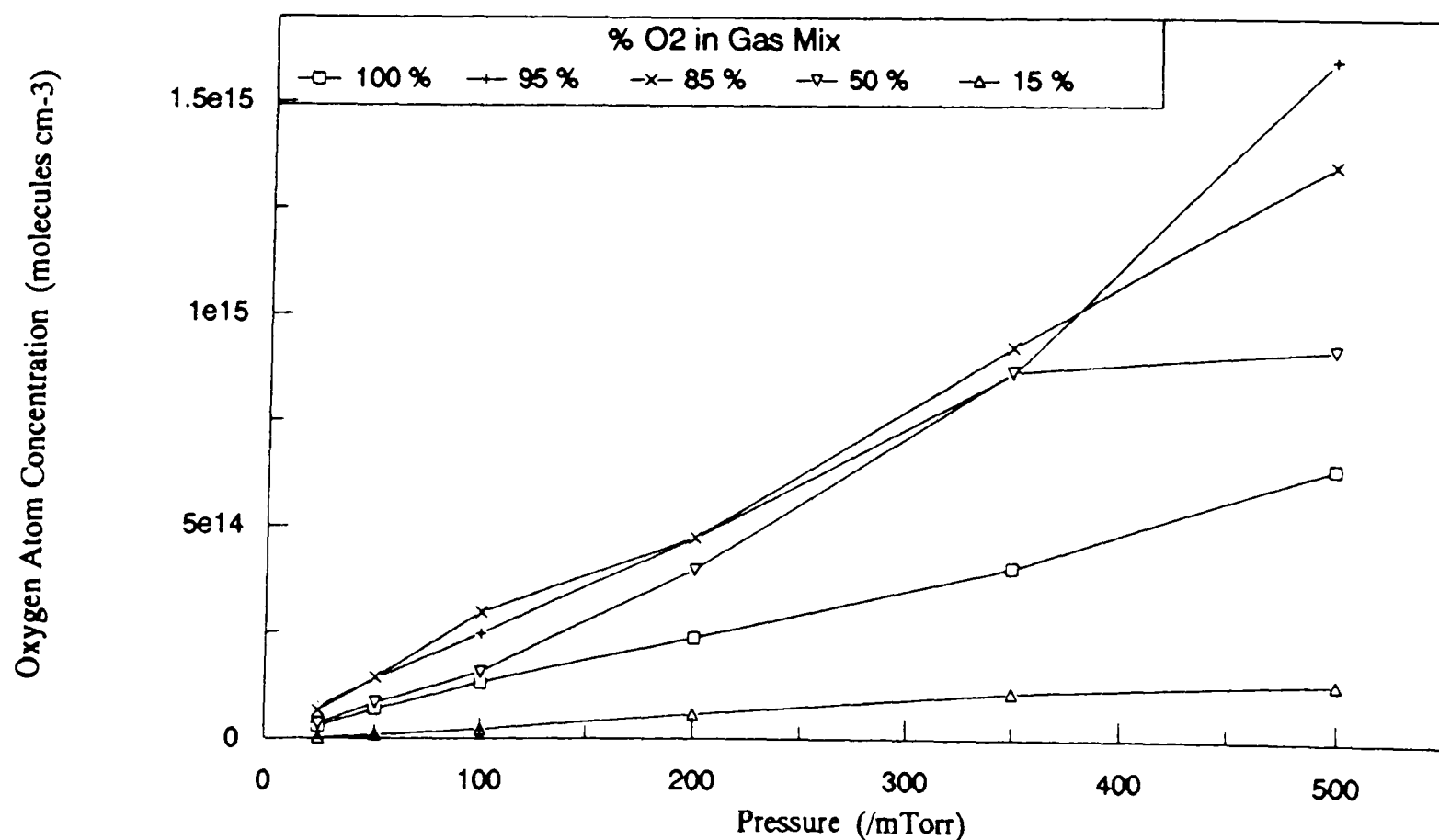


Figure 7.14 Variation of oxygen atom concentration with pressure for a variety of gas compositions at 200 watts.

illustrates the importance of the surface on the concentration of gas phase species, which has been shown in this study to be particularly true for the two species of interest, oxygen and fluorine atoms.

It can be seen that to develop a complete model of the CF_4 / O_2 system, it is necessary to obtain information on the variation of the wall removal rates, as a function of plasma parameters, particularly in the lower pressure region considered in this work. Such information requires the direct measurement of the removal rates and absolute concentrations of the key reactive species present. Development of new diagnostics and adaptation of existing techniques, which are capable of these in-situ measurements has been shown to probe and improve the understanding of the processes taking place. However, the studies need to be extended and further developed, particularly in the areas of electron and ion energy distributions, and surface reactions, on which, it has been seen, much of the plasma characteristics depend.

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Chapter Eight

Afterglow Reactor

8.1 ECR Plasma Reactor

This chapter describes a study carried out on a different basic design of reactor, an afterglow plasma chamber, where the plasma diffuses into the major chamber from an external excitation source. The work was carried out at Plasma Technology (UK) Ltd. on an ECR (electron cyclotron resonance) reactor, using optical diagnostics to study the effect of this design on chemical processes taking place inside the chamber. In particular, laser induced fluorescence of CF and CF₂ and actinometered optical emission of fluorine atoms were measured over a range of experimental conditions. This project was undertaken over a short period at Plasma Technology, with further experiments carried out in Oxford to contrast the performance of the ECR and the conventional parallel plate reactor.

The aim of the project was to ascertain if techniques developed in a conventional parallel plate plasma chamber could be used on the new reactor, and then to use these techniques to carry out a preliminary study on the relative concentrations of reactive species, principally CF, CF₂ and F atoms, to provide information on the physical and chemical processes taking place inside the chamber. However, the inability to use time dependent techniques prohibited direct measurements of these processes.

To gain information on the spatial variation of concentrations in the reactor, both the ECR source region and the region just above the substrate electrode, (downstream region), were probed. Some measurements of the rotational temperature of CF were taken to give an estimate of the bath gas temperature inside the chamber and an attempt was made to determine the absolute concentration of CF and CF₂ using the NO calibration technique. The experiments have been compared to similar studies on the Plasma Technology RIE 80 reactor, to try to identify any common characteristics.

ECR plasma chambers are a new design of reactor finding many applications

in material processing¹ in part owing to the control of ion density and energy, permitting independent determination of neutral and ion based effects. They have been used particularly for film deposition, such as C films² or ZnO layers³. The amount of diagnostic research on these plasmas is however limited. Of the work that has been done much is associated with analysis of the product, that is the etched sample or the deposited film⁴. Some measurements have been made using Langmuir probe techniques to monitor the plasma density and electron energy distribution function, and have shown the high degree of ionization attained in the ECR region⁵.

There have been some recent studies on the Doppler widths and shifts of Ar⁺ metastable, measured by laser induced fluorescence in an Ar plasma⁶. These have revealed low radial ion velocities illustrating the confining nature of the magnetic fields used in ECR plasma sources. This study reports the first measurements of reactive intermediates in ECR plasmas.

8.2 Experimental

A commercial ECR reactor (Plasma Technology) with an Astex microwave source (2.45GHz) was used with two electromagnets set up in a mirror field mode. The magnets produce the magnetic field necessary for electron cyclotron resonance, (845 Gauss), which enhances the efficiency of the applied microwave power. The field also extends into the lower chamber where it limits the motion of the charged species, to confine them away from the chamber walls. At a distance from the source, the ions and electrons follow the diverging magnetic field and this is reflected in the cone shaped emission volume seen inside the reactor.

The flanges on the reactor were adapted with optical ports and fitted with sapphire windows to allow transmission of the laser radiation and collection of the laser induced fluorescence at 90° to the laser beam, (Figure 8.1). They also allowed transmission of the plasma induced optical emission, (PIE). The ports were positioned at two heights in the chamber to allow study of the ECR region and the downstream region, (approximately 1 cm above the substrate electrode). A turbomolecular pumping system combined with a large diameter pumping port

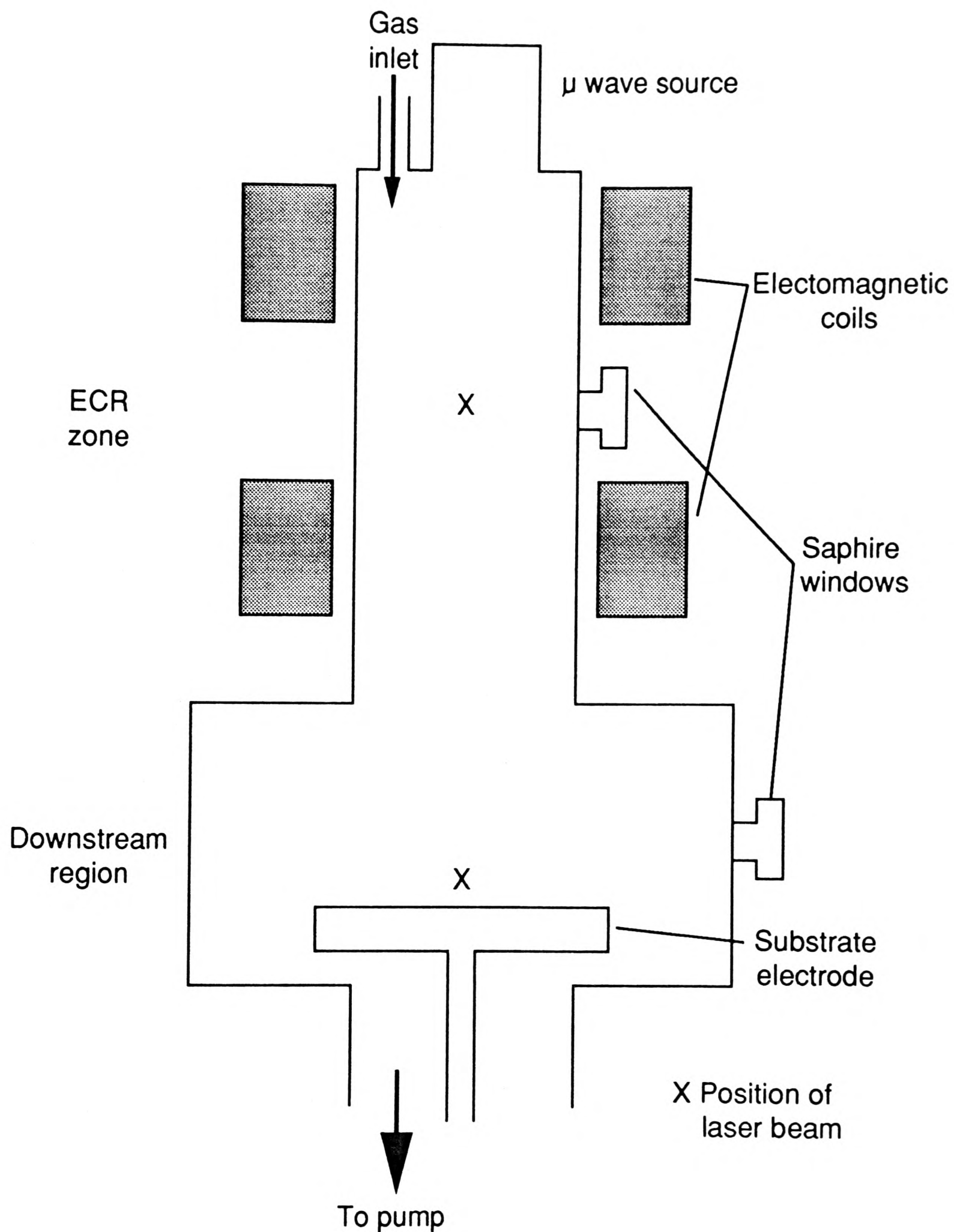


Figure 8.1 Schematic diagram of the Plasma Technology Electron Cyclotron Resonance reactor, indicating the ECR and downstream zones discussed in the text.

produced a low base pressure ($\sim 10^{-5}$ mTorr). The chamber volume was about 27 litres and the measured leak rate was typically found to be 0.008 sccm ($0.1 \text{ mTorr min}^{-1}$), which is about 0.2% of the lowest flow used in the experiments.

Throughout all the experiments the current to the magnets, and hence magnetic field, was kept constant (180 & 120 Amps to the top and bottom coils respectively), with fine tuning of the ECR discharge requiring small changes in the current supplied to the magnets, particularly as the magnet coils warmed up. There was a clear distinction in the intensity of the discharge when the electron cyclotron resonance was tuned in, showing the effect of an increase in excitation processes.

The other plasma parameters were varied to ascertain their influence on the concentration of reactive species : pressure, power, flow and gas composition were varied as follows –

Pressure	: 0.5 – 20 mTorr
Power (microwave)	: 400 – 800 watts
Flow	: 3.3 – 33 sccm
Gas composition	: Pure CF_4 or CF_4 / 8% O_2

For the excitation rate measurements at 33 sccm, 3 sccm of Ar was added to the gas mixture.

At 400 W the plasma showed some instabilities particularly at low pressure. This was a greater problem when the launch window for the microwave power input was covered by a polymer, formed from the CF_4 plasma. Much of this polymer was removed by running an O_2 rich plasma.

CF and CF_2 were detected by LIF using an excimer pumped dye laser system (Lambda Physik) on loan from the S.E.R.C laser loan facility. A BBO doubling crystal was used to generate the uv. radiation but no compensating crystal was available, so the laser beam path changed slightly with wavelength. For CF_2 , excitation of the $\tilde{\text{A}}^1\text{B}_1(0,11,0) - \tilde{\text{X}}^1\text{A}_1(0,0,0)$ band near 234.5 nm was used with observation of the fluorescence off resonance to the $\tilde{\text{X}}^1\text{A}_1(0,1,0)$ level at 237.7 nm. Two bands were studied for CF , the $\text{A} - \text{X}(0,0)$ and $(1,0)$ bands at 233 and 224 nm respectively. The $(1,0)$ was used in the parametric survey because of a better overall

signal to noise ratio and because of overlap of the (0,0) band with a CF_2 band. For the (1,0) band, the fluorescence detected was the (1,1) transition near 230 nm.

The detection equipment used was as for the parallel plate reactor and most of the details can be found in chapter 2. The Edinburgh Instruments monochromator was used with two photomultiplier tubes for LIF and emission, EMI9813QKB to detect LIF and EMI 9558b for F and Ar emission, (F emission at 703.7 nm and Ar emission at 750.4 nm).

The intricate microwave ECR plasma source was not capable of the short switching times used in the parallel plate reactor, and so interpretation of the processes taking place in the ECR plasma is based on steady state measurements.

8.3 Results

Emission spectra from the ECR zone and LIF spectra of CF and CF_2 were taken, in order to test the techniques on the ECR reactor and to compare them with previous studies on the parallel plate system. The rotational temperature of CF was measured by analyzing the CF spectra, to try to gain information on the bath gas temperature. The LIF spectra of both species were taken in an attempt to measure the absolute concentration of CF and CF_2 , using a calibration method involving the LIF signal from a known concentration of $\text{NO}^{7,8}$. Owing to the short time that the laser and ECR reactor were available, the R.S.Discover software package was used to establish a design experiment for the parametric survey. This assisted in the interpretation and modelling of the results, whilst reducing the amount of experimental data required.

8.3.1 Optical Spectroscopy from the ECR region

Optical emission was only collected from the ECR region because of the low levels of emission downstream. This was particularly true under conditions of high pressure (10 – 20 mTorr), and is a result of quenching of the electrons, leading to a large reduction in the concentration of high energy electrons in the downstream region compared to the ECR zone. At higher pressure, the probability of an electron

undergoing an inelastic collision increases, and thus the electrons lose more energy by the time they reach the lower region.

An emission spectrum from a CF_4 / 50% Ar plasma taken from the ECR region is shown in figure 8.2, where it is compared directly to that from a plasma of the same gas mixture in a parallel plate system. The spectra, which have not been corrected for instrument sensitivity, were taken using the 9813QKB PMT which has a maximum in its sensitivity at 300 nm and a poor response at wavelengths longer than 500 nm. The spectra show many of the same features, but it is the variation in the intensity of the transitions which is of interest. There are three particular differences which illustrate the highly dissociative and ionizing nature of the ECR plasma source as compared to the parallel plate chamber.

- i) The line spectra around 440 nm are predominantly due to emission from argon ions, Ar^+ , ($^4\text{P}_0 \rightarrow ^4\text{D}$ & $^4\text{D}_0 \rightarrow ^4\text{P}$) whilst those around 420 nm are due to emission from atomic argon ($5\text{p } [\frac{1}{2}, \frac{3}{2}, \frac{5}{2}] \rightarrow 4\text{s } [\frac{3}{2}]^0$ & $5\text{p}' [\frac{1}{2}, \frac{3}{2}] \rightarrow 4\text{s } [\frac{1}{2}]$). The excitation threshold for emission from Ar atoms is around 14.5eV, whereas the threshold for Ar ions is 20eV above the ionization limit (15.6eV)⁹. The ECR spectrum illustrates a higher concentration of excited ions compared to excited atoms: analysis of the peaks give a ratio of 0.6:1 (Ar:Ar⁺) for the ECR plasma and 20:1 for the parallel plate plasma. It should be remembered that the emission only gives information on the concentration of excited states, but these observations do suggest that there is a high degree of ionization, and excitation, in the ECR source region.
- ii) The broad continuum peaking around 280 – 300 nm due to dissociative excitation of CF_4 ^{10,11}, is observed from both reactors. The excitation threshold for this process is about 20eV as compared to the threshold for atomic Ar, (14.5eV), and again the relative intensities measured imply the presence of a high density of high energy electrons in the ECR source.
- iii) The structure seen on top of the continuum between 200 – 300 nm is hard to assign unambiguously because of the low resolution of the scan and because both CF and CF_2 emit in this region. The CF ($\text{B}^2\Delta - \text{X}^2\Pi$) transition emits between

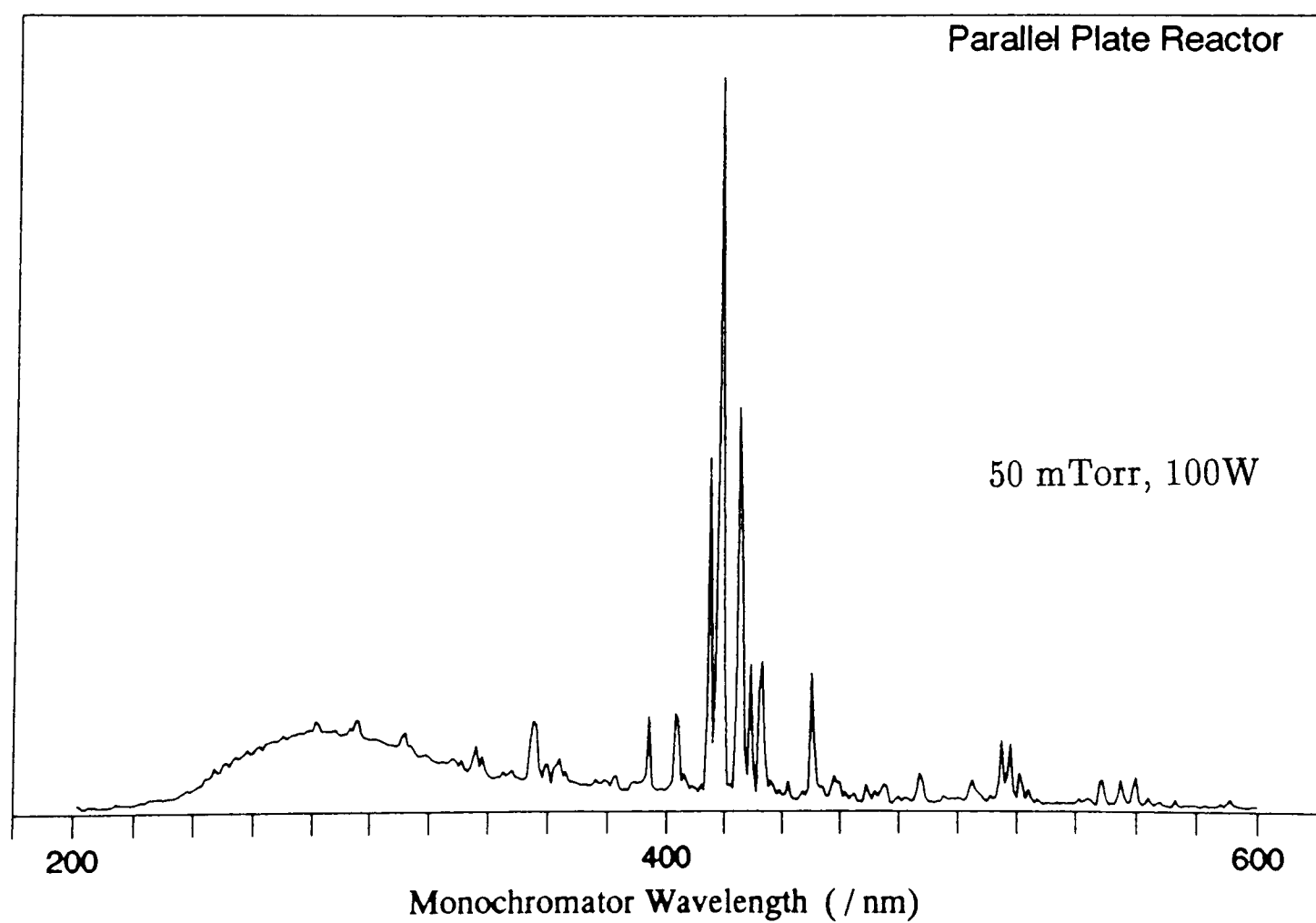
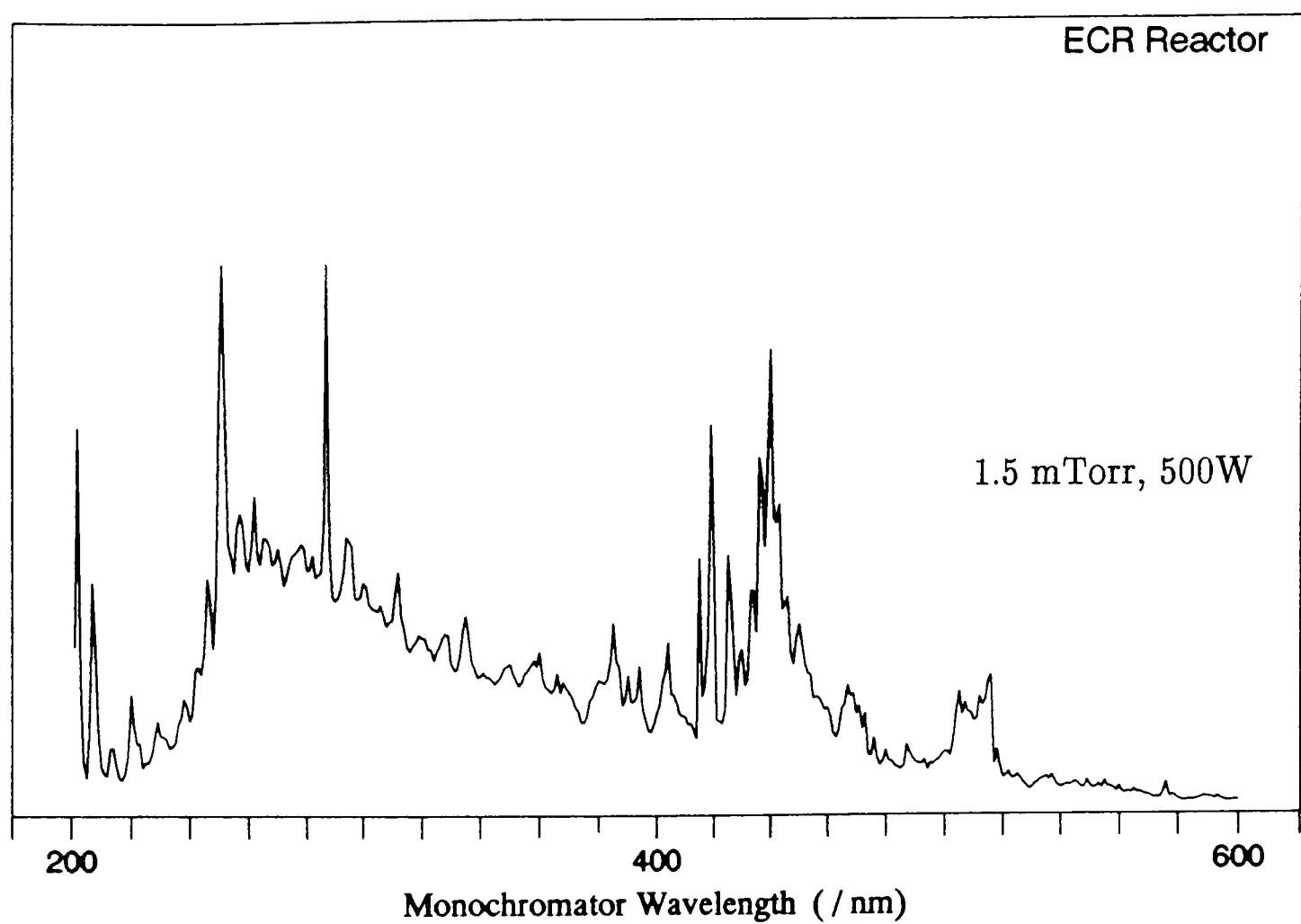


Figure 8.2 Comparison of the emission spectra from 200 – 600 nm of a 50% Ar / 50% CF₄ plasma measured from both the ECR and parallel plate reactors.

190 – 220 nm and the ($A^2\Sigma^+ - X^2\Pi$) bands lie between 220 – 300 nm, and for CF_2 , the ($\tilde{A}^1B_1 - \tilde{X}^1A_1$) transition emits between 250 – 350 nm. A high resolution scan from the parallel plate system is shown in figure 5.1 and shows that the structure can be predominantly explained by and assigned to emission from CF_2 . For the ECR spectra, the contributions of CF and CF_2 to the structure seen at wavelengths above 250 nm is not as clear, but the emission between 200 – 220 nm can be assigned to the CF ($B - X$) transition and the large peak at 248 nm is due to atomic carbon, ($^1S - ^1P_0$)⁹. The latter can also be seen in the high resolution scan from the parallel plate system. These observations are again indicative of a high level of CF_4 dissociation in the ECR source.

8.3.2 Laser Induced Fluorescence Spectra of CF and CF_2

Methods for discriminating against the intense plasma induced emission both spectrally and temporally have been described in chapter 2. However, the lack of opportunity to pulse the discharge rapidly in the ECR machine, resulted in emission being detected simultaneously with the LIF. The level of PIE from the ECR region was generally higher than that of the fluorescence signal, and the intensity varied with plasma pressure and power because of the change in density of the emitting species. This was particularly a problem for the CF_2 measurements because the monochromator had to be set at a higher wavelength, where the PIE signal was larger. In the downstream region, the problem was reduced because of quenching of the high energy electrons, but at low pressure the magnitude of the emission was still comparable with that from the ECR zone. At 0.5 mTorr, the penetration distance of electrons before they are scattered is of the order of tens of centimetres as opposed to a couple of centimetres at 20 mTorr¹². The high level of PIE compared to the fluorescence signal meant that high laser pulse energies had to be used to increase the fluorescence signal level. Typically the data was taken with pulse energies of 0.4 – 1 mJ with a beam size of about 1 mm². At these intensities, there is saturation of the CF transition and so the fluorescence signal was corrected using a saturation plot, for laser energy variation.

The LIF spectrum of CF₂ (A (0,11,0) – X (0,0,0)), and part of the LIF spectrum of CF (A(ν' = 1) – X(ν'' = 0)) are shown in figures 8.3 & 8.4. These enable identification of the species being probed and also allow determination of the rotational temperature of CF. The intensity of each rotational line, I_{cf} , depends on the rotational line strength and the population of the rotational level, which itself is dependent on the rotational temperature.

Thus,

$$I_{cf} \propto S_J \cdot \exp(-E_J / k \cdot T_r)$$

$$\ln(I_{cf} / S_J) = -(1 / k \cdot T_r) \cdot E_J + C$$

where S_J is the Honl London line strength factor, E_J is the energy of the J th rotational level, k is the Boltzmann constant and T_r is the rotational temperature. T_r is found by plotting $\ln$ [intensity / line strength] against the energy of the level, for a series of rotational lines. For a Boltzmann distribution of levels such a plot yields a straight line with a gradient directly related to T_r .

The Boltzmann plot for the CF spectrum in figure 8.3 is shown in figure 8.5 and produces a rotational temperature of 355 ± 30 K for CF in the downstream region of a 20 mTorr plasma. T_r was also measured under conditions of lower pressure (1.5 mTorr) in both the ECR and downstream regions giving values of 980 ± 100 K and 450 ± 40 K respectively. These values can be compared with a measurement of 311 ± 15 K from a CF₄, 50 mTorr 100 W parallel plate discharge, where translational – rotational equilibrium for neutral species is expected.

Rotationally hot CF radicals are produced by electron impact in the severe environment of the ECR source region. They are not in thermal equilibrium with the chamber walls and so quenching will take place at the walls. Outside the production volume, the radicals will be partially quenched before they reach the downstream region. Also, it is possible at this low pressure, that the rotational energy transfer rate is not sufficient to thermalise the CF radicals which will be rotationally excited by electron impact. Thus, the rotational and translational temperatures may not be at thermal equilibrium and this again illustrates the high level of internal excitation.

The technique of using LIF to measure the relative ground state

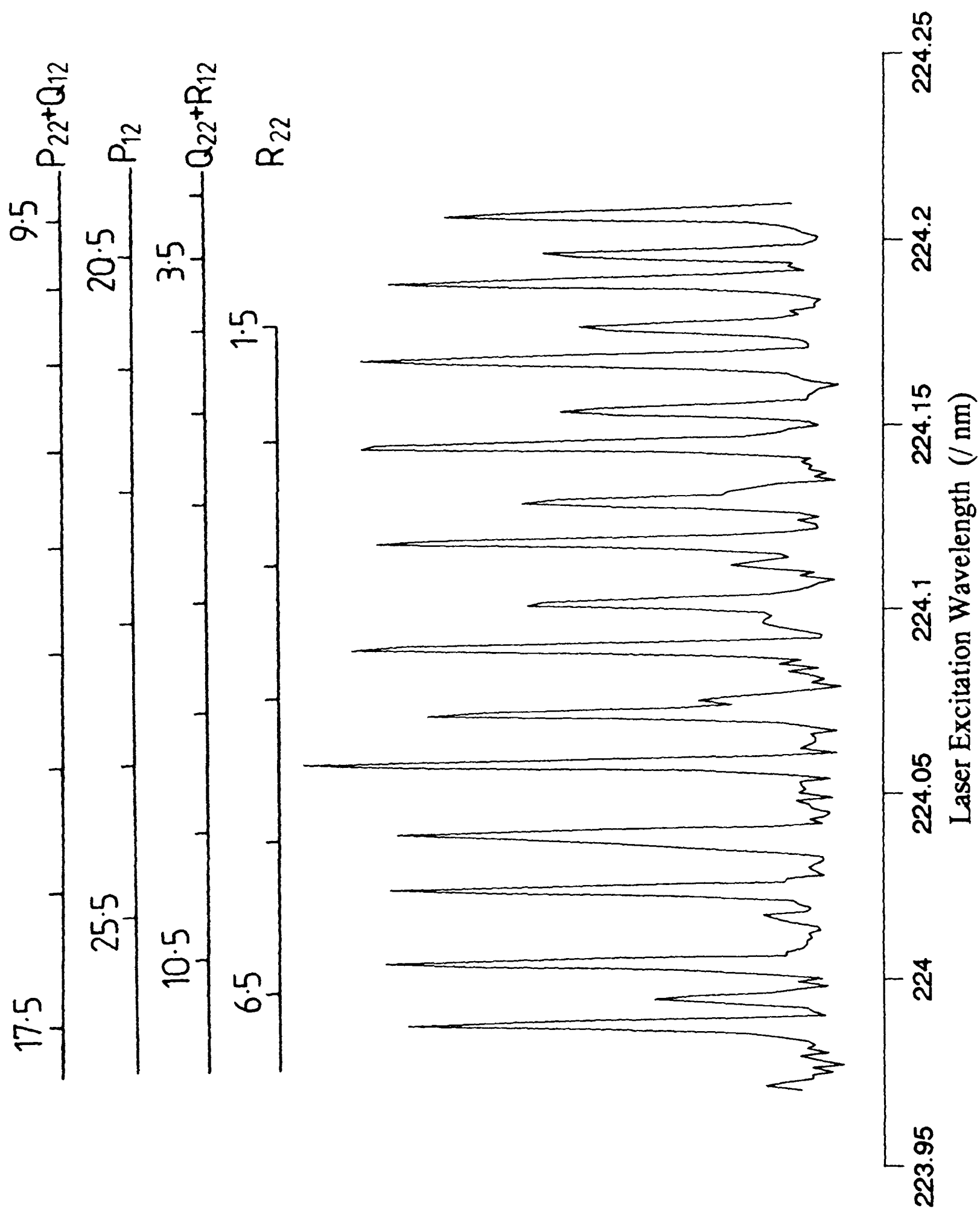


Figure 8.3 Part of the LIF excitation spectrum of the (1,0) band of the CF (A - X) transition taken from the downstream region of the ECR reactor.

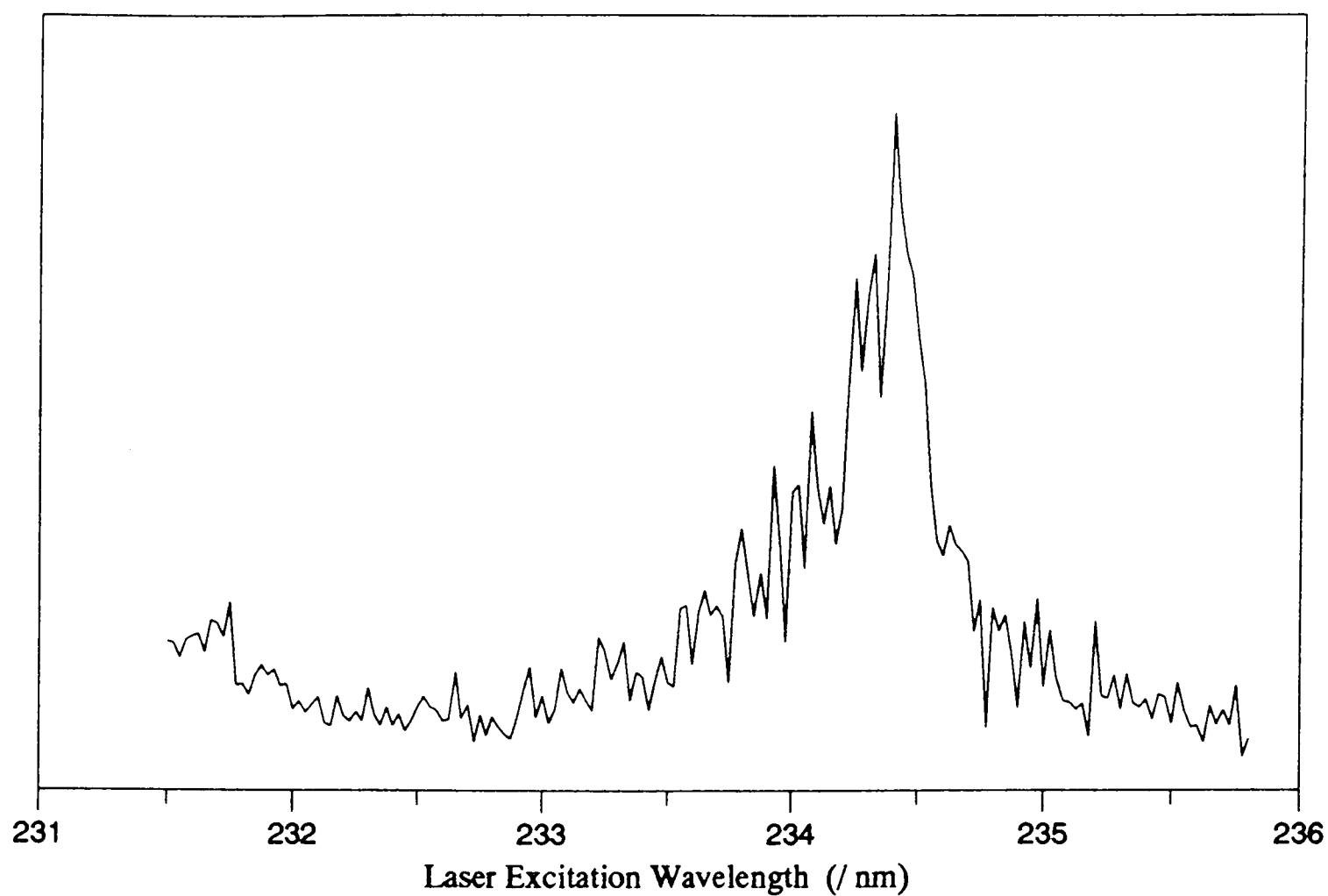


Figure 8.4 LIF excitation spectrum of the (11,0) band of the $\text{CF}_2 \tilde{\text{A}}^1\text{B}_1 - \tilde{\text{X}}^1\text{A}_1$ transition taken from the downstream region of the ECR reactor.

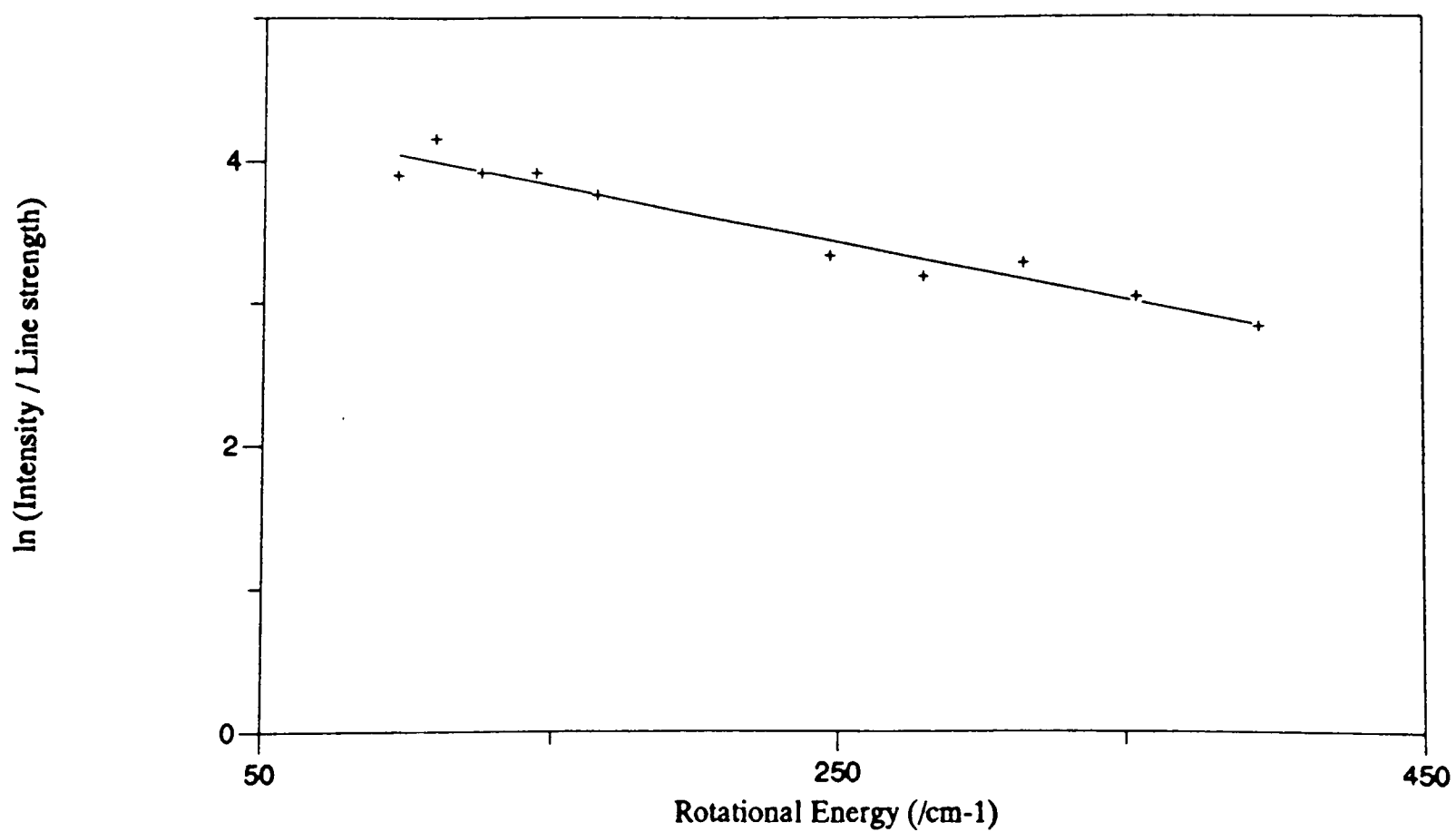


Figure 8.5 Boltzman plot from the LIF spectrum of CF (figure 8.3), for a 20 mTorr, 600 W CF_4 discharge.

concentration of a particular species is usually done by tuning the laser to a single ro-vibrational transition and monitoring the fluorescence as the conditions are varied. However, the ro-vibrational population distribution of a species can vary as a function of plasma conditions. Compensating for such changes requires a full analysis of the rotational and vibrational distributions, so that a true representation of the total electronic ground state concentration can be gained. For small changes in temperature, careful selection of a single transition can minimize the effect of the shift in distribution on the measurements made. However in this study, the large variation in rotational temperature will affect the population distribution of CF to such an extent that the measurement of a single rotational transition is not really sufficient. Unfortunately, in the parametric study there was only time for this type of measurement and this needs to be considered when reviewing the data. For the particular transition used ($P_{22} + Q_{21}$ ($J = 11.5$)), the shift in distribution can result in an underestimation of 34% at 1000 K compared with 350 K, (only 2.5% between 350 and 450 K), if the single signal is assumed to be proportional to the total ground state concentration.

The vibrational temperature of species in these low pressure plasmas are generally found to be much higher than the rotational and translational temperatures,¹³ because of the relative rates of relaxation of vibrational and rotational energy. Population of the higher vibrational levels may also be significant, and for CF, with a separation in vibrational levels of 1280 cm^{-1} , nearly 20% of the radicals will be in the first excited vibrational level, and thus not probed by the laser, at a vibrational temperature of 1000 K.

8.3.3 The Parametric Study

The range of parameters outlined in the experimental section were fed into the R.S.Discover program which then produced a limiting series of experimental conditions to study. (Some of the combinations were not possible, such as high flow with low pressure, and were excluded from the model). LIF and OE measurements were taken under these conditions and the results were entered into the program

together with linear and quadratic combinations of plasma parameters, which it was thought would effect the experimental variations seen. The data is then analyzed to show correlations between these plasma parameter terms and the measured signal.

The analysis produces a mathematical best fit of the measured data to linear and quadratic terms involving flow rate (FL), pressure (PR), microwave power (PO) and percentage of O₂ in the flow (O2). It provides no direct information on the influence of these parameters on the mechanisms in the plasma, but merely an empirical mathematical relationship. This type of experimental analysis is widely used in industrial research and development, where empirical results are sufficient and where time is a major limiting factor. In this study, an attempt has been made to relate the observations to known chemical and physical phenomena.

The CF concentration was monitored using the P₂₂ + Q₂₁ (J = 11.5) line mentioned above and for CF₂ the laser was tuned to the central maximum of the transition. Measurement of the absolute concentrations of CF and CF₂ proved to be difficult because of the high levels of PIE and the absence of a compensator for the doubling crystal so that as the laser wavelength varied the path of the beam moved. However, values were obtained using the calibration technique and then scaled using the parametric survey over the full range of conditions, (see Appendix 3 for table of data). It should be remembered that the variation in rotational temperature can cause a 34% error in the value obtained and this combined with the high levels of PIE leads to some uncertainty in the data. In all the parametric studies, repeat measurements showed good reproducibility and ensured consistency throughout the experimental run, leading to results from which some general principles can be drawn. However, the designed experiment was poor owing to the limited region of the parameter space realizable and so models obtained should be treated with care.

i. CF₂

For CF₂ in the ECR region the analysis produced the following model –

$$\begin{aligned} \text{CF}_2 \text{ ECR signal} = & 4.42\{\text{PR}\} + .0023\{\text{FL.PO}\} - 1.55\{\text{FL}\} - .121\{\text{PR}^2\} \\ & - .0022\{\text{PO.O2}\} + 3.22 \end{aligned}$$

$$\text{adj.-R}^2 = 83\%$$

The influence of each term can be judged by considering the maximum value it can take, for example, at the highest pressure used the first term in the equation will be equal to 60. For the above and all following analyses the terms are arranged in descending order of the modulus of this maximum value. A negative coefficient indicates that an increase in the parameters involved in the term will cause a decrease in the CF₂ signal measured and the reverse occurs for a positive coefficient. Terms involving two parameters imply that there is a combined effect, for example a FL.PO term would suggest that power and flow have the greatest influence at high levels of the other parameter. The adj.-R² value is a measure of the completeness of the fit, relating to the percentage of experimental points which are fitted by the mathematical model, and so 83% is a reasonable fit. A low value indicates that the terms put into the model are insufficient to match all the experimental data. The limitation of the model should be realized and the evaluations of each term should not be taken in isolation, but considered together with all the data available.

Rationalizing the data for CF₂ in the ECR zone shows that the concentration increases with microwave power, particularly at high flow rates, and also with pressure. The addition of O₂ causes a decrease in the concentration, an effect which is enhanced at high levels of power and pressure.

Analysis for the CF₂ data from the downstream region produces :

$$\begin{aligned} \text{CF}_2 \text{ downstream signal} = & .0028\{\text{FL.PO}\} - .029\{\text{FL}^2\} - .045\{\text{PR}^2\} \\ & - .0017\{\text{PO.O2}\} + 16.32 \end{aligned}$$

$$\text{adj.-R}^2 = 87\%$$

The adj.-R² value again shows reasonable agreement between experimental results and model predictions.

The influence of power and oxygen on the CF₂ concentration is much the same as in the ECR region, but the pressure variation produces a different response, as can be seen by comparing figures 8.6 and 8.7. In the downstream region, an

increase in pressure produces a marked decrease in the measured CF₂ signal in contrast to the rise seen in the ECR zone. The CF₂ concentration tends to increase with flow rate.

Another method of studying these changes is to examine the variation in the ratio of the downstream concentration to the ECR concentration, R_{cf2}, as a function of the plasma parameters, (see Appendix 3 for table of data). A complete analysis has not been done for this input data, but several points can be made. R_{cf2} increases with power, particularly at high pressure, and with flow rate. Addition of O₂ generally causes a reduction in the ratio, but pressure variation has the largest impact on R_{cf2}, such that as the pressure is increased there is a marked decrease in R_{cf2}.

ii. CF

The analyses of CF in the ECR and downstream regions are shown below. For the ECR region two different models were used, one based on flow and the other on pressure. They all have rather low adj.-R² values indicating a poor fitting model.

$$\text{CF ECR (flow model)} = 0.0023\{\text{FL.PO}\} - 1.17\{\text{FL}\} + 1.8\{\text{PR}\} + 6.45$$

$$\text{adj.-R}^2 = 70\%$$

$$\text{CF ECR (pressure model)} = 2.7\{\text{PR}\} + 0.0028\{\text{PR.PO}\} - 0.11\{\text{PR}^2\} + 2.0$$

$$\text{adj.-R}^2 = 67\%$$

$$\text{CF downstm.} = 0.33\{\text{FL}\} - 0.0076\{\text{FL}^2\} + 0.00001\{\text{PO}^2\} - 0.00033\{\text{PR.PO}\} - 0.8$$

$$\text{adj.-R}^2 = 59\%$$

In both regions, the CF concentration increases with microwave power, particularly at high flow rates. and the presence of O₂ reduces the CF concentration, an effect which tends to be greater at high power and pressure. The CF concentration increases with flow particularly in the downstream region. The impact of pressure is similar to the behaviour observed for CF₂, with contrary dependencies

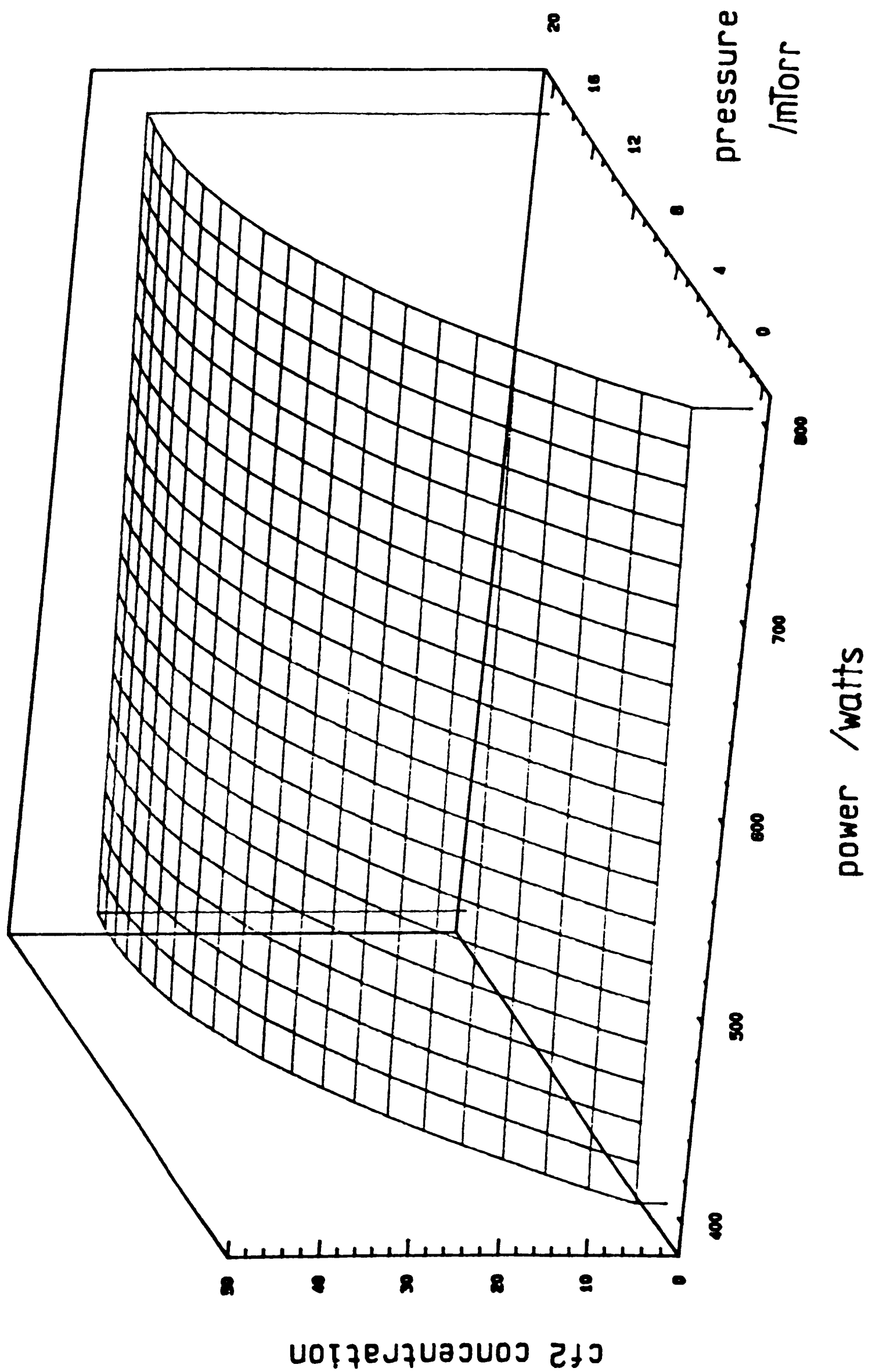


Figure 8.6 R.S.Discover simulation of the variation in CF_2 concentration for the ECR region of the reactor, as a function of pressure and microwave power.

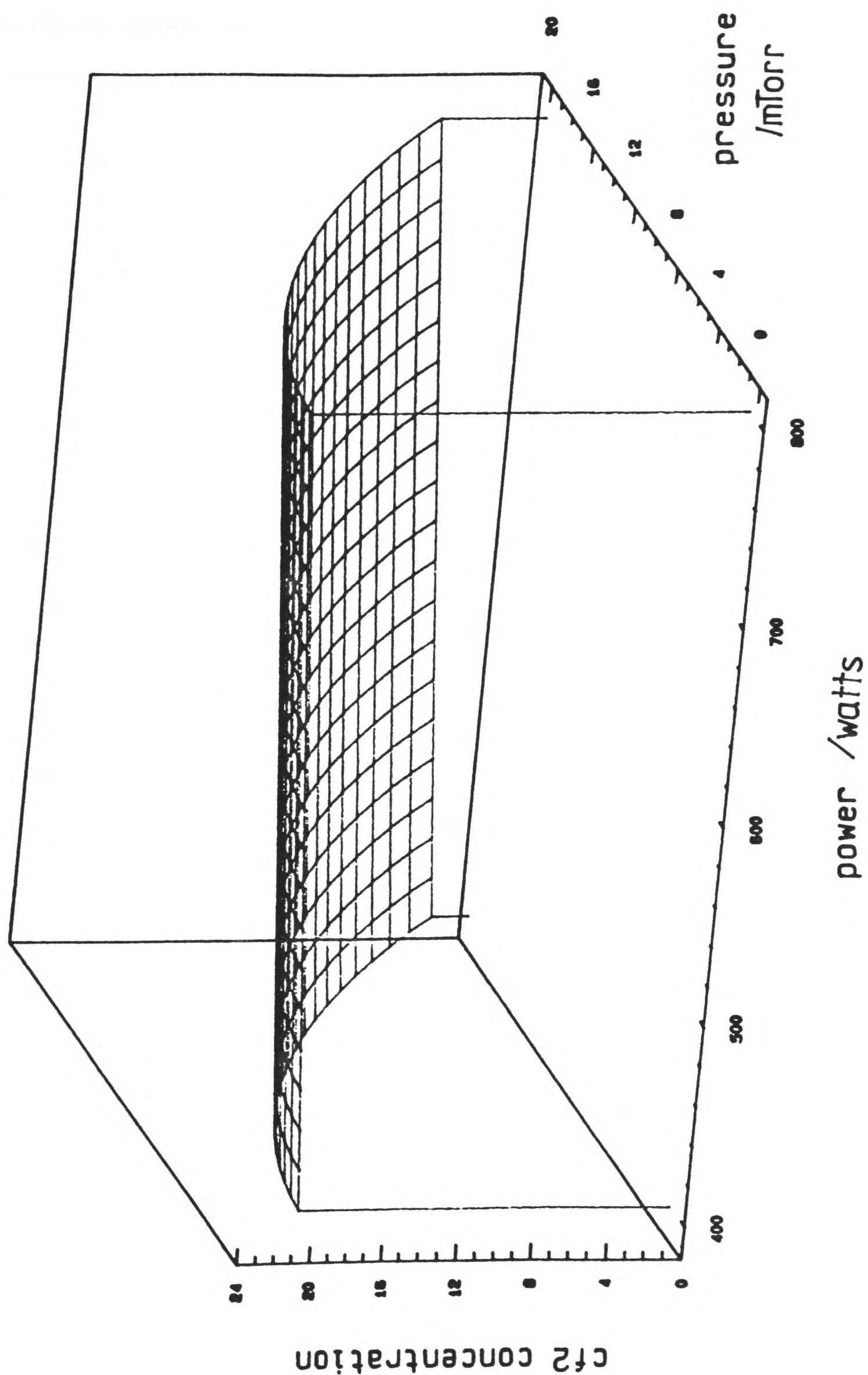


Figure 8.7 R.S.Discover simulation of the variation in CF_2 concentration for the downstream region of the reactor, as a function of pressure and microwave power.

in the two regions. One further point is that at low flow rates, the CF concentration goes through a maximum as the pressure is raised, as seen in figure 8.8.

As for CF₂, the ratio of signal measured downstream to that measured in the ECR zone, R_{cf}, can be used to assist analysis of the data. R_{cf} is seen to increase with power, although the higher rotational temperatures associated with high microwave power will tend to enhance this effect. Addition of O₂ causes a reduction in R_{cf}, particularly at high pressure and power. Pressure has the most dominant influence on R_{cf} as seen for CF₂, but with CF the overall variation is even larger.

The ratio of CF to CF₂ concentration, CF/CF₂, is also given in Appendix 3 (see table 1), and this highlights the differences between the two radicals. In absolute terms, CF/CF₂ in the ECR region varies from 0.2 – 0.9 whereas downstream the values range from 0.04 – 0.27, and this can be compared with a ratio of 0.14 found in the parallel plate system for a 50mTorr, 100W, 42sccm, CF₄/5% Ar plasma. In the ECR region, the flow rate has the most dramatic effect on CF/CF₂, an increase in flow resulting in a rise in the ratio, whilst downstream pressure has the major influence with an increase in pressure causing a marked decrease in CF/CF₂.

iii. Optical Emission

F atom Concentration

The actinometered F atom emission, representative of the ground state F atom concentration, has also been analyzed by R.S.Discover. (see Appendix 3 table 2 for full list of data).

$$\begin{aligned} \text{Actinometered F emission} &= .0014\{\text{PR.PO}\} + .064\{\text{PR.O2}\} - .020\{\text{PR}^2\} \\ &+ .00001\{\text{PO}^2\} + .29\{\text{PR}\} - 1.12 \end{aligned}$$

$$\text{adj.-R}^2 = 99\%$$

The high adj.-R² value shows the excellent fit of the model to the experimental data, but the absence of any flow rate term simplifies the analysis.

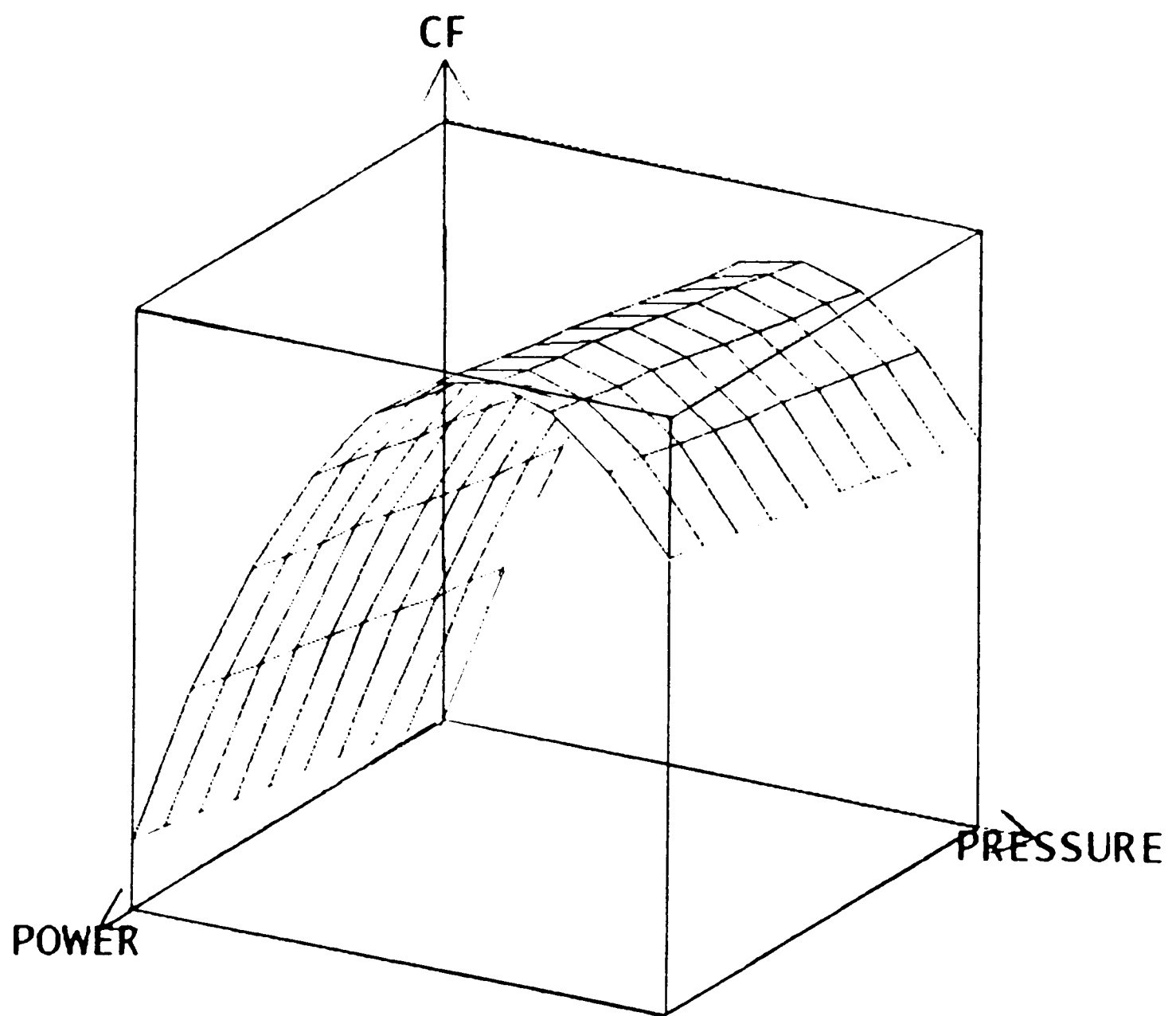


Figure 8.8 R.S.Discover simulation of the variation in CF concentration for the ECR region of the reactor, at a flow rate of 5 sccm.

The concentration increases monotonically with both power and pressure as shown in figure 8.9. The figure also illustrates how addition of 8% O₂ increases the F atom concentration, particularly at high pressure.

Excitation Rate

The Ar emission intensity when divided by the pressure, can be used as a relative measure of the high energy electrons in the plasma, that is as a rough guide to the excitation rates (E_r) in the plasma.

$$\begin{aligned} \text{Excitation Rate} = & -0.038\{\text{PR}\} + 0.0019\{\text{PR}^2\} + 0.0008\{\text{PO}\} \\ & - 0.00004\{\text{PR.PO}\} + 0.03 \end{aligned}$$

$$\text{adj.-R}^2 = 98\%$$

Variation of E_r with plasma parameters is shown in figure 8.10 and shows that an increase in microwave power produces a near linear increase in E_r , whilst increase in pressure reduces the excitation rate. Addition of O₂ has little effect but tends to slightly decrease the value.

High values for E_r would be expected to correlate with high degrees of dissociation of CF₄. An indication of the latter can be found by considering the ratio of radical concentration to the initial concentration of CF₄. This has been done and the results for F are shown in figure 8.11, (see Appendix 3 for CF and CF₂). The "degree of dissociation" factor has the same qualitative dependence on microwave power and pressure as E_r . (This is also seen in the CF and CF₂ data).

8.4 Discussion

To explain the observed behaviour, it is necessary to ascertain the relative importance of the processes taking place in the plasma chamber. At the pressures used in these plasmas, the major production pathway for neutral radicals is by collisions between electrons and the feedstock molecules, since chemical gas phase production terms are generally small. A possible exception to this is the reaction of

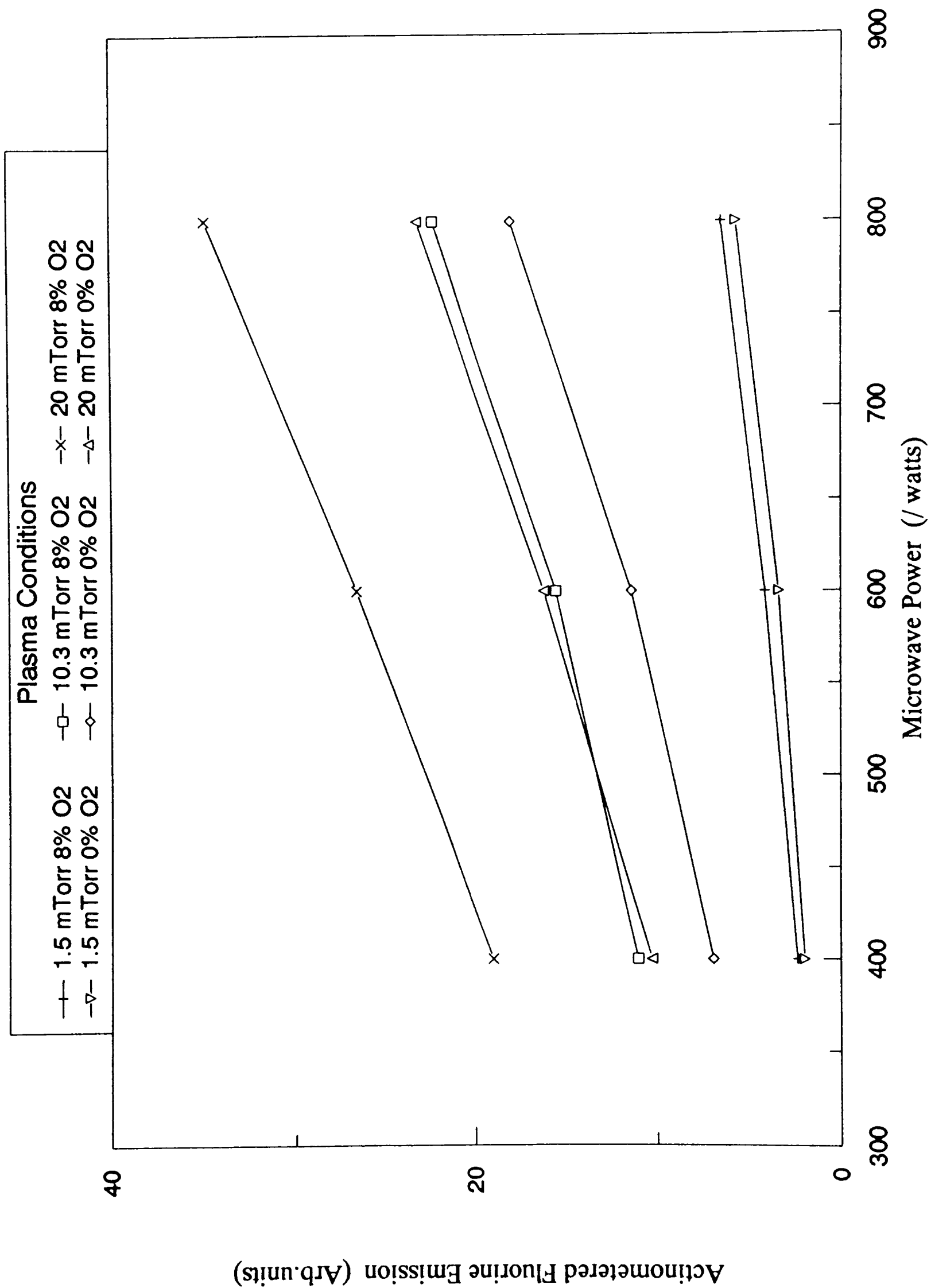


Figure 8.9 Variation of actinometered fluorine emission with microwave power, pressure and gas composition measured from the ECR region.

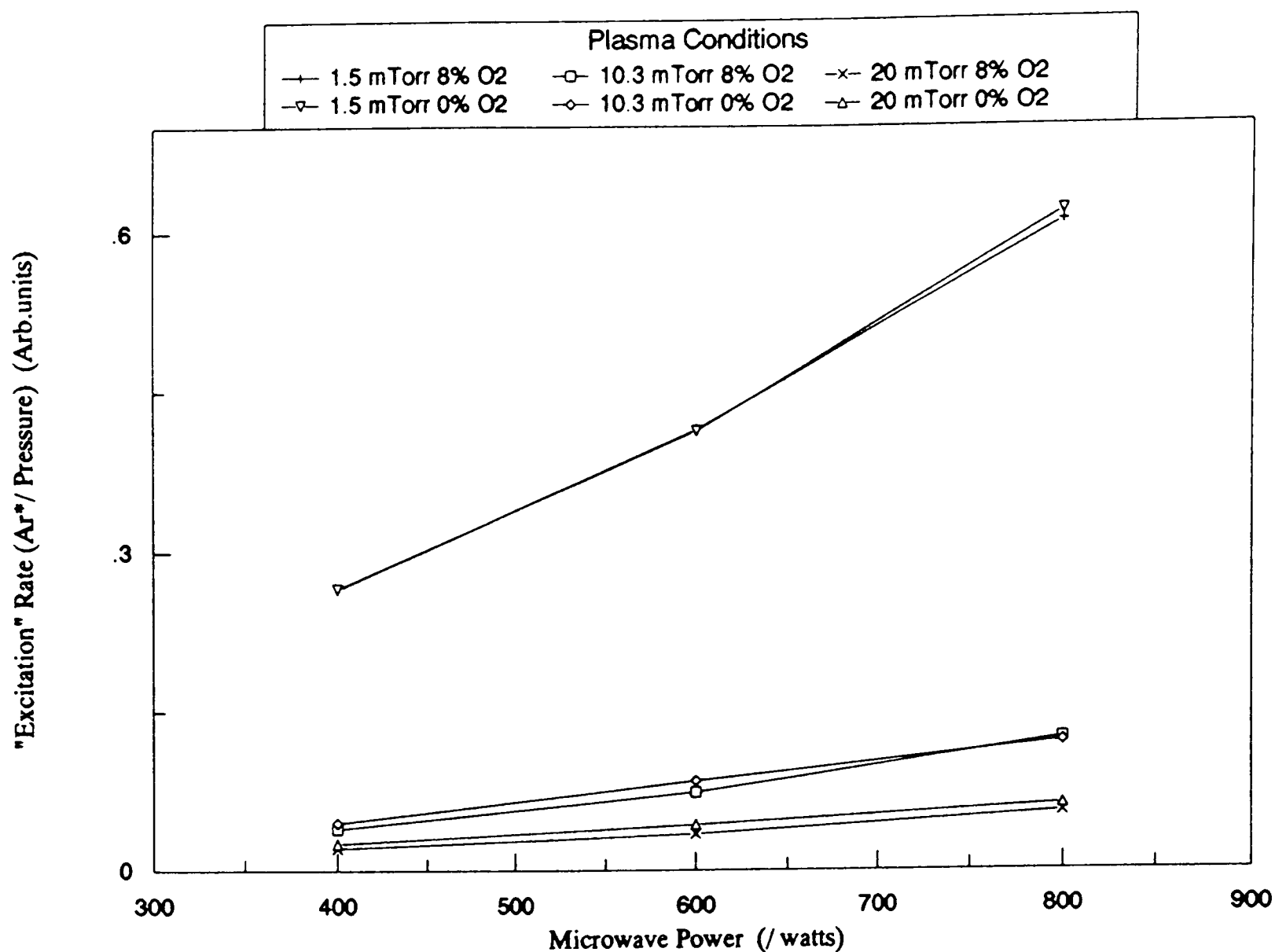


Figure 8.10 Variation of "excitation" rate (see text), with microwave power, pressure and gas composition measured from the ECR region.

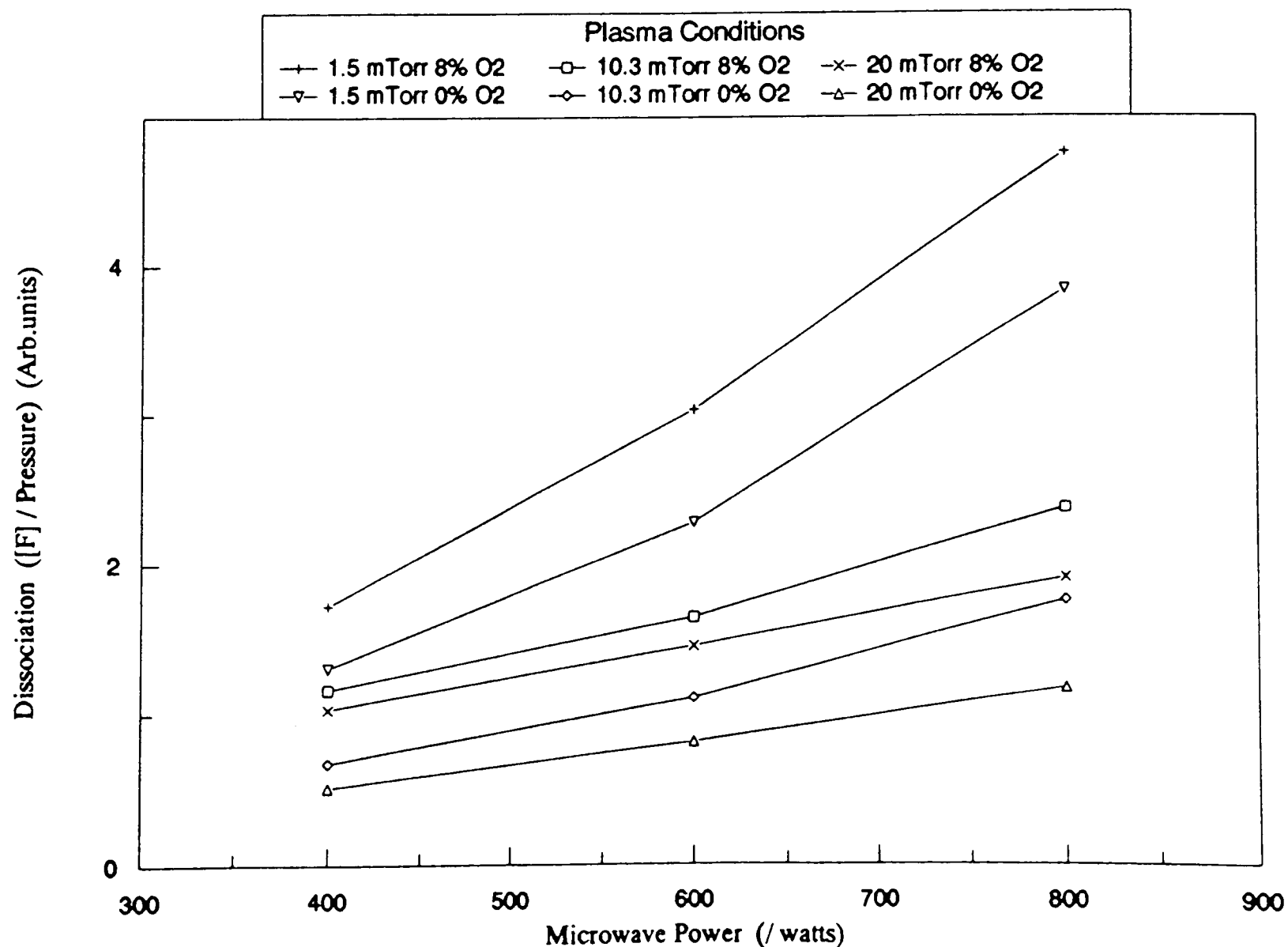


Figure 8.11 Ratio of actinometered fluorine emission to the CF₄ pressure as a function of power and pressure, as a measure of dissociation of the parent molecule.

O atoms with CF_x radicals in CF_4 / O_2 plasmas, acting as a source of F atoms.

The removal processes are likewise dominated by fast diffusion to the walls followed by the rate limiting reaction at the surface, and not by gas phase chemical reaction. As discussed elsewhere in this thesis, CF_2 , CF and F are all lost predominantly by reaction at the wall, with sticking probabilities of 0.04, 0.2 and 0.005 respectively. These values were obtained from the parallel plate reactor where the surfaces of interest were the electrodes themselves, and so subject to ion bombardment. The wall reaction of F was found to be dependent on the presence of ions, which are thought to generate new potential reaction sites at the surface. In the ECR reactor, where high energy ions and electrons are confined predominantly to the centre of the chamber, this regeneration effect may not be present and so removal of F atoms by surface reaction may not be so significant.

The loss processes can be compared with the pump out rate of the system and the transit time from ECR to downstream region (see table 8.1). To calculate the residence time of each species requires a detailed model of the flow dynamics inside the chamber, however a crude approximation based on the flow rate, pressure and chamber volume can be used¹², which yields a time of 1.3 s at 20 mTorr and 33 sccm. This time is also approximately equal to the time taken for a species to travel from the ECR region to the downstream region. The theoretical number of collisions undergone by the species during transit is given in table 8.1 and illustrates the large influence of pressure on the results. Most of the gas phase collisions will be with feedstock molecules, which despite relatively high levels of dissociation, are probably the major species present, and so will not result in any chemical reactions but merely act to cool and relax the CF_x radicals. Collisions with the walls will also result in cooling, but they will react and so the concentration will fall.

The optical emission results and the intense nature of the plasma along with the elevated rotational temperatures measured in the ECR zone show the high level of excitation in the plasma source. Langmuir probe measurements in ECR reactors suggest that the maximum in the electron energy distribution occurs at energies around 20eV, contrasting values of 2 – 5 eV found in parallel plate systems.⁵

Conditions flow /sccm	Residence press. /mTorr	Time /s	Pump out Rate /s ⁻¹	Wall Lmtd. CF /s ⁻¹	Diffusion Lmtd. CF /s ⁻¹	Wall Lmtd. CF ₂ /s ⁻¹	Diffusion Lmtd. CF ₂ /s ⁻¹	No.of Collisions
33.0	20.0	1.31	0.76	615	790	100	535	2x10 ⁵
33.0	10.3	0.67	1.48	615	1530	100	1040	5x10 ⁴
18.2	20.0	2.37	0.42	615	790	100	535	4x10 ⁵
18.2	10.3	1.22	0.82	615	1530	100	1040	9x10 ⁴
3.3	20.0	13.1	0.076	615	790	100	535	2x10 ⁵
3.3	0.5	0.3	3.1	615	31600	100	21400	1200

Table 8.1

The absolute concentration measurements produce dissociation percentages relative to CF₄ feedstock concentration of 0.085 – 0.4 % for CF and 0.2 – 1.7 % for CF₂ as compared to 0.06 % for CF and 0.3 % for CF₂ in the parallel plate system. The ECR values, whilst higher than the parallel plate system, do suggest that the concentration of CF₄ is only slightly depleted. The parametric study however demonstrates that the flow rate, hence availability of new feedstock gases, can affect the steady state concentration. For a given pressure, the higher the flow rate is the greater the impact of an increase in power, which is consistent with a flow limited regime. Such a regime tends to be associated with a level of dissociation where there is a significant reduction in the concentration of CF₄, which is not indicated by the absolute values obtained in this study. As mentioned above, there is a degree of uncertainty in the absolute value measured and it is also possible that CF₄ is dissociated completely to atomic C. For the latter to be true however, the expected increase in pressure on plasma ignition would be for factors in excess of 100% as compared to the observed 10 – 20 %.

8.4.1 The ECR Region

The major removal mechanism for both CF and CF₂ in a CF₄ plasma is wall reaction, which in this study is independent of flow rate, pressure and microwave power. Changes in the measured steady state concentration in the ECR source region will thus tend to reflect changes in the production term. This term is a product of the excitation rate and the feedstock concentration, and so at constant pressure it increases with power, as indicated by the concentration measurements, particularly at high flow rates. With pressure, the feedstock concentration increases but the excitation rate falls so the overall production term will rise sub-linearly and may even turn over at high pressure, as seen in the concentration of CF at low flow rates.

Addition of O₂ introduces a further removal mechanism for CF and CF₂ by the reactions with O atoms. The surface reaction rate may also change because of the presence of O atoms on the surface. These changes modify the steady state concentration compared to the O₂ free system, due to the weak dependence of excitation rate on the presence of O₂. The greater influence of O₂ at higher pressure and power is a result of the higher concentration of O atoms under these conditions. In the parallel plate system addition of 10 % O₂ to a CF₄ plasma, causes a 50% reduction in the concentration of both CF and CF₂ which is higher than the values obtained in the ECR region and reflects the lower absolute concentration of O atoms due to the lower pressures used.

8.4.2 The Downstream Region

The quenching of high energy electrons by collisions with molecular species and the absence of any excitation source outside the ECR region, results in a much reduced production rate in the bulk of the chamber, particularly at the higher pressures where the penetration of fast electrons is limited. The "effective" loss term for the downstream region is a combination of the transit rate of the species down the chamber and the gas phase and gas-surface reaction rates, that is physical transport and chemical reactions. The surface reaction rates are constant with

pressure, but the transit rate varies inversely, so that at high pressure the net observed loss during transit is much larger than at low pressure. An increase in flow rate shortens the transit time without influencing the chemical reaction processes, so it enhances the probability of CF and CF₂ reaching the downstream region and decreases the "effective" loss rate. The concentration measured downstream depends on the initial level formed in the ECR production zone and on some evaluation of the "effective" loss rate during the transit time. Due to the higher reaction probability of CF, the reduction in CF concentration for a given variation in transit time is more marked for CF than for CF₂.

The concentration of CF and CF₂ downstream is reduced by the presence of O₂ in a similar manner, but to a larger extent, than in the ECR region. This decrease is enhanced at higher pressure and is again a consequence of the "effective" loss term for the downstream region and explains the variation in R_{cf} and R_{cf2} as a function of pressure and %O₂.

A rise in power tends to increase the concentration of all reactive species, which would be expected to increase the rate of gas phase reactions and so reduce the ratios of steady state concentrations, R_{cf} and R_{cf2}. These ratios increased as a function of microwave power, illustrating that gas phase chemistry does not play a major role in determining the concentration of CF and CF₂ in a CF₄ ECR plasma. This observed increase may be due in part to changes in the temperature of the radicals and possibly due to an extension of the production zone down into the chamber.

8.4.3 Fluorine Atom Concentration

The data on F is more limited, but the dependence on power and pressure in the pure CF₄ plasma can be attributed to changes in its production rate, that is the rate of electron impact on CF₄. Addition of O₂ causes an increase in the F atom concentration but at most by a factor of 2 as compared to factors of 5 – 10 seen in the parallel plate reactor. An explanation for the large rise in concentration for the parallel plate system, is an observed dramatic reduction in the surface loss rate of

the F atoms as a result of surface modification by the O atoms, (see chapter 7). As mentioned earlier, the lack of ion bombardment at the surfaces may reduce the influence of wall reactions on the F atom concentration in the ECR region. Thus the observed increase in F atoms in this study may be a result of the extra production terms of the reactions of oxygen atoms with CF_x radicals, and not dominated by modification of the surface reaction rate as it is in the parallel plate reactor. The enhancement of the F atom concentration on addition of O_2 at high pressure is consistent with this interpretation.

8.4.4 The Excitation Rate

The correlation between percentage dissociation and the measured excitation rate is as expected. Their variation with pressure is most probably due to a combination of changes in the plasma density and the electron energy distribution function. It is generally found that an increase in pressure results in a decrease in mean electron energy and so will tend to reduce the concentration of high energy electrons and the excitation rate. It is interesting to note that the CF/CF_2 ratio is not affected by pressure. Power usually affects the plasma density only and often shows a near linear relationship between E_r and power¹⁴.

8.4.5 Conclusion

It should be remembered that the data was taken over a very short period of time and so all the usual practices were not always possible. This was certainly the case in the parametric survey where the influence of high rotational temperatures and high levels of PIE should have been investigated further. Also lack of any time dependent studies limits the understanding of the mechanisms to indirect measurements of the steady state concentrations. In spite of this some interpretation of the results in terms of chemical and physical processes has been possible and the conclusions are comparable to the parallel plate system. The major differences can be attributed to the source – afterglow nature of discharge and the high levels of excitation and dissociation present in ECR reactors.

Finally, from an empirical point of view and in connection with the processing of semiconductor materials in an ECR reactor on the downstream substrate electrode, conditions of high pressure and low power in the presence of O_2 , produce high levels of F atoms and low levels of CF_x radicals which should be ideal for the etching of Si selectively with respect to SiO_2 . However the high pressure may result in the formation of a polymer in the ECR source and ultimately may create problems with contamination and even ignition of the plasma. Moving to lower pressure will enhance the concentration of CF_x downstream whilst maintaining the F atom concentration and so might be suitable for SiO_2 etching.

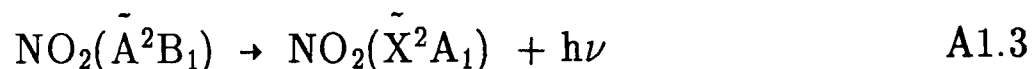
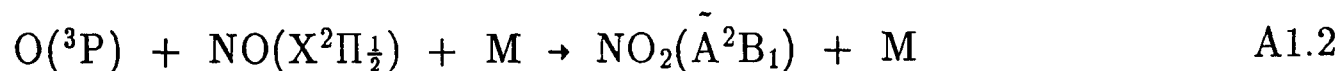
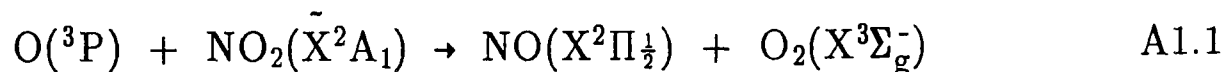
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Appendix One

Oxygen Atom Titration

The reaction scheme behind the oxygen atom titration technique used in this study, known as the "air – afterglow" method, is outlined below¹ :—



The radiation emitted in process A1.3 extends from 400 nm to the infrared and in this study was detected by RCA 1P28 photomultiplier tubes, equipped with Schott OG 515 filters. Reaction A1.2 is the rate limiting step in the scheme, and so the emission is proportional to $[\text{NO}][\text{O}]$.

Using NO_2 as the titrant, the end point (where $[\text{O}] = 0$), occurs when the emission disappears, and $[\text{NO}_2] = [\text{O}]_0$. However, mass flow controllers have been found to be unreliable at passing NO_2 and so the improvement suggested by Reeves *et al.*² was used. Initially, NO_2 was added through a stainless steel needle valve until the afterglow intensity reached a maximum. At this point $[\text{NO}] = [\text{O}] = \frac{[\text{O}]_0}{2}$ and the intensity is proportional to $\frac{[\text{O}]_0^2}{4}$. Then NO was flowed through the mass flow controller until the equivalent intensity was observed. In this case, $[\text{NO}]$ is half that of the previous step, since oxygen atoms are now not consumed to form NO . Thus, $[\text{NO}]$ added in the second step = $\frac{[\text{O}]_0}{4}$ and so knowing the flow of NO , the concentration of oxygen atoms can be found. In practice, the NO and NO_2 were diluted in argon because of the low concentration of oxygen being studied.

This procedure was carried out at two titration points, one either side of the LIF collection zone, which allowed measurement of the oxygen atom removal rate down the flow cell, and hence interpolation to the region of interest. Under the conditions used, heterogeneous wall removal is expected to be the major loss process, which is first order in oxygen concentration. This was investigated by

varying the oxygen atom concentration and comparing the reduction in concentration between the upstream and downstream titration points. This indeed indicated that oxygen was being removed by a first order process and therefore, that complications with $O_2\ ^1\Delta_g$ (formed in large concentrations in these discharges) were not present.

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Appendix Two

Reactions of importance to oxygen and fluorine atoms in CF₄ / O₂ plasmas.

<u>Reaction</u>	<u>Rate Constant</u>	<u>Reference</u>	
e + CF ₄ → CF ₃ + F + e	5.0 x 10 ⁻¹¹	1	
→ CF ₂ + 2F + e	1.3 x 10 ⁻¹⁰	2	
→ CF + 3F + e	6.0 x 10 ⁻¹¹	3	
→ CF ₃ + F ⁻ + e	3.1 x 10 ⁻¹¹	4	
→ CF ₃ ⁻ + F + e	1.9 x 10 ⁻¹¹	5	
e + F ₂ → 2F + e	4.2 x 10 ⁻¹⁰	6	
→ F + F ⁻	5.6 x 10 ⁻¹¹	7	
e + O ₂ → 2O + e	3.4 x 10 ⁻¹¹	8	
e + O ₂ → 2O + e	1.7 x 10 ⁻⁹	9	
→ O + O ⁻	4.4 x 10 ⁻¹¹	10	
	<u>@ 50 mTorr</u>	<u>@ 500 mTorr</u>	
F + CF ₃ → CF ₄	5.2 x 10 ⁻¹²	1.3 x 10 ⁻¹¹	11
F + CF ₂ → CF ₃	5.0 x 10 ⁻¹⁴	4.2 x 10 ⁻¹³	11
F + CF → CF ₂	5.6 x 10 ⁻¹⁶	5.0 x 10 ⁻¹⁵	2
2CF ₃ → C ₂ F ₆	7.7 x 10 ⁻¹²	8.0 x 10 ⁻¹²	2
2CF ₂ → C ₂ F ₄	3.7 x 10 ⁻¹⁴	5.0 x 10 ⁻¹⁴	12
CF ₂ + CF ₃ → C ₂ F ₅	7.5 x 10 ⁻¹³	8.8 x 10 ⁻¹³	2
2F → F ₂	8.6 x 10 ⁻¹⁹	8.6 x 10 ⁻¹⁸	13
2O → O ₂	1.3 x 10 ⁻¹⁷	1.3 x 10 ⁻¹⁶	14
F + COF → COF ₂	1.1 x 10 ⁻¹⁶	8.0 x 10 ⁻¹³	2
F + CO → COF	1.4 x 10 ⁻¹⁶	1.3 x 10 ⁻¹⁵	2
F + C ₂ F ₄ → CF ₂ + CF ₃	4.0 x 10 ⁻¹¹		2
F + C ₂ F ₅ → 2CF ₃	1.0 x 10 ⁻¹¹		2
O + CF ₃ → COF ₂ + F	3.1 x 10 ⁻¹¹		15
O + CF ₂ → COF + F	1.4 x 10 ⁻¹¹		16
→ CO + 2F	4.0 x 10 ⁻¹²		16
O + CF → CO + F	7.0 x 10 ⁻¹¹		16
O + COF → CO ₂ + F	9.3 x 10 ⁻¹¹		16
F → Walls	Variable (see text)		
O → Walls	Variable (see text)		
O or F → Pump Out	2 s ⁻¹	0.2 s ⁻¹	

Values given are the second order rate constants in cm^3s^{-1} except where indicated.
Electron impact rates are based on a Druyvesteyn function with mean energy 5.5eV.

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Appendix Three

Data from ECR plasma reactor for CF₂, CF, F atoms and Ar, (chapter 8).

Run No.	Flow	Pres	Power	% O2	ECR Region		Downstream Region				DOWN/ECR		% OF CF ₄		CF ₂ ECR
					[CF]	[CF ₂]	[CF]/[CF ₂]	[CF]	[CF ₂]	[CF]/[CF ₂]	Ref	Ref2	CF ECR		
3	33	10.3	400	8	3.0E+11	5.9E+11	6.2E+09	8.9E+10	0.069575	0.069575	0.020357	0.151155	0.098585	0.190834	
9	33	10.3	800	8	3.5E+11	7.0E+11	2.2E+10	2.5E+11	0.088532	0.088532	0.062378	0.349509	0.113291	0.228387	
8	33	10.3	800	8	6.4E+11	1.9E+12	7.8E+10	4.7E+11	0.166310	0.166310	0.122526	0.249774	0.207156	0.611026	
21	33	20	400	8	4.7E+11	1.2E+12	2.8E+09	2.9E+10	0.093745	0.093745	0.005866	0.025209	0.078684	0.195321	
18	33	20	600	8	6.1E+11	1.1E+12	4.9E+09	7.6E+10	0.064833	0.064833	0.008143	0.068163	0.101858	0.187703	
7	33	20	800	8	1.3E+12	1.4E+12	1.0E+10	1.9E+11	0.052650	0.052650	0.007976	0.136833	0.215790	0.238923	
5	33	10.3	400		3.9E+11	7.2E+11	1.6E+10	1.6E+11	0.099204	0.099204	0.039512	0.217257	0.117792	0.215949	
1	33	10.3	800		1.1E+12	2.1E+12	1.1E+11	4.8E+11	0.239649	0.239649	0.107877	0.222505	0.316293	0.639886	
16	33	20	400		6.6E+11	1.2E+12	3.9E+09	6.9E+10	0.056564	0.056564	0.005891	0.055635	0.101923	0.190815	
24	33	20	600		8.6E+11	1.3E+12	1.2E+10	2.0E+11	0.058131	0.058131	0.013496	0.148662	0.132948	0.207630	
4	33	20	800		1.8E+12	3.1E+12	2.9E+10	3.1E+11	0.090783	0.090783	0.015484	0.102314	0.284510	0.474289	
23	18.2	10.3	400		4.2E+11	7.4E+11	1.4E+10	1.4E+11	0.094719	0.094719	0.032816	0.194331	0.125077	0.222988	
17	18.2	10.3	800		6.0E+11	1.9E+12	1.1E+11	5.2E+11	0.202456	0.202456	0.174299	0.280621	0.180997	0.555287	
22	18.2	20	400		6.6E+11	1.4E+12	2.4E+09	6.5E+10	0.037115	0.037115	0.003672	0.044865	0.101182	0.223159	
14	18.2	20	600		8.2E+11	1.6E+12	1.0E+10	1.5E+11	0.067691	0.067691	0.012427	0.093894	0.126353	0.247064	
13	3.3	0.5	400		5.4E+10	2.7E+11	3.2E+10	1.3E+11	0.236639	0.236639	0.585263	0.497965	0.334341	1.660566	
20	3.3	0.5	400		6.0E+10	2.7E+11	3.2E+10	1.3E+11	0.236639	0.236639	0.528810	0.497965	0.370034	1.660566	
15	3.3	0.5	800		5.7E+10	2.1E+11	5.7E+10	2.1E+11	0.274839	0.274839	0.995113	0.999219	0.352044	1.275643	
19	3.3	0.5	800		5.7E+10	2.1E+11	5.7E+10	2.1E+11	0.274839	0.274839	0.999301	0.999219	0.350568	1.275643	
10	3.3	10.3	600		1.0E+12	1.9E+12	2.2E+10	1.4E+11	0.160234	0.160234	0.021102	0.070629	0.307844	0.574006	
6	3.3	20	400		6.2E+11	1.8E+12	1.4E+09	1.9E+10	0.072350	0.072350	0.002242	0.010701	0.095825	0.277497	
12	3.3	20	400		5.4E+11	1.8E+12	1.4E+09	1.9E+10	0.072350	0.072350	0.002601	0.010701	0.082574	0.277497	
2	3.3	20	800		7.8E+11	2.5E+12	6.5E+09	9.3E+10	0.069724	0.069724	0.008313	0.036771	0.119912	0.388810	
11	3.3	20	800		6.7E+11	2.5E+12	6.5E+09	9.3E+10	0.069724	0.069724	0.009653	0.036771	0.103264	0.388810	

Table 1

					Actinometered F	[F]/[CF ₄]	Ar	Ar/Pressure
1	33	1.5	400	8	2.375501	1.721377	0.3992	0.266133
2	33	1.5	600	8	4.181586	3.030134	0.6256	0.417066
3	33	1.5	800	8	6.563317	4.756026	0.9176	0.611733
4	33	10.3	400	8	11.01209	1.162103	0.4079	0.039601
5	33	10.3	600	8	15.53874	1.639799	0.7603	0.073815
6	33	10.3	800	8	22.41389	2.365332	1.289	0.125145
7	33	20	400	8	19.00048	1.032634	0.4202	0.02101
8	33	20	600	8	26.66081	1.448957	0.6834	0.03417
9	33	20	800	8	34.91833	1.897735	1.102	0.0551
10	33	1.5	400		1.957157	1.304771	0.4003	0.266866
11	33	1.5	600		3.410293	2.273528	0.6237	0.4158
12	33	1.5	800		5.747558	3.831705	0.9317	0.67588
13	33	10.3	400		6.961564	0.67588	0.4631	0.044961
14	33	10.3	600		11.37117	1.103997	0.8731	0.084766
15	33	10.3	800		18.0086	1.748407	1.256	0.121941
16	33	20	400		10.27931	0.513965	0.5084	0.02542
17	33	20	600		16.20862	0.810431	0.8609	0.043045
18	33	20	800		23.28502	1.164251	1.242	0.0621

Table 2