

MULTIPHOTON IONISATION AND LASER-INDUCED AUTOIONISATION
IN XENON

by

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A thesis submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy
of the University of London

October 1987

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ABSTRACT

This thesis describes some experiments carried out to investigate the non-linear optical properties of Xenon under coherent optical excitation. In particular, two areas were studied

- (i) Two-photon-resonant three-photon ionisation in Xenon, with a view to understanding the mechanisms leading to saturation of such two-photon-resonant processes. The two-photon resonance was with the $6p, J = 0$ state.
- (ii) Laser-Induced Continuum Structure (LICS): the effect of a laser-induced autoionising state on the three-photon ionisation yield was studied.

These experiments were carried out using a laser system which provided two independent, high power, narrow-linewidth, tunable outputs; one in the ultra-violet at $\lambda \sim 250\text{nm}$, and one in the blue region of the visible spectrum. The system was based on excimer-pumped narrow bandwidth dye lasers and is described in detail in the thesis, together with ion detection techniques.

Saturation of two-photon-resonant three-photon ionisation at $\lambda = 249.63\text{nm}$ was investigated by measurement of the ion yield as the narrow-bandwidth laser, ($\Delta\nu \sim 1 - 2\text{ GHz}$), was tuned through the resonance. The linewidth of the resonance was measured for a range of intensities, ($10\text{ MW/cm}^2 - 3\text{ GW/cm}^2$), and was found to be substantially broadened ($\text{FWHM} \sim 100\text{ GHz}$) compared with the Doppler linewidth (2.6 GHz), indicating saturation of the process. Stimulated emission of radiation from the two-photon-resonant state was also measured.

The experimental results were compared with theoretical

predictions from rate equation analysis and consideration of a number of potential saturation mechanisms. On the basis of this analysis, we postulate that lifetime broadening, due to the stimulated emission of radiation from the two-photon-resonant state, is the mechanism most likely to be responsible for the observed saturation.

Using the second laser source at $\lambda \sim 401$ nm, we have produced a laser-induced autoionising state in Xenon, and probed the continuum structure via the two-photon-resonant three-photon ionisation process previously described. A laser-induced autoionising resonance exhibiting a Fano-like lineshape has been observed. Experimental results are presented and compared with the theory of laser-induced continuum structure.

To my parents, with love and thanks

ERRATA and CORRIGENDA

- Throughout: The symbol 'um' used to denote microns (10^{-6}m) should read μm
- page 33 line 7 '100 GHz' should read '200 GHz'
- page 41 line 14 'momentum' should read 'angular momentum'
- page 49 line 15 'ruby lasers' should read 'ruby laser'
- page 55 line 29 'Lorree' should read 'Loree'
- page 59 line 22 'range' should read 'ranges'
- page 69 line 28 'on' should read 'of'
- page 75 line 19 should read 'It can be postulated that thermal...'
- page 79 line 17 '3.1 GHz' should read '3.3 GHz'
- page 87 line 28 'truly in narrow' should read 'truly narrow'
- page 113 line 37 'Lorree' should read 'Loree'
- page 125 line 22 lifetime of state, , is missing
- page 133 Eqn 3.3 should read $\Delta_2 + \frac{1}{2\hbar^2\Delta_1} \{ |\mu_{12}|^2 \overline{E_1^2} - |\mu_{23}|^2 \overline{E_2^2} \}$
- page 135 Eqn 3.4 should read
$$\frac{\overline{E^2}}{2\hbar^2\Delta_1} \{ |\mu_{12}|^2 - |\mu_{23}|^2 \}$$
$$= \frac{\hbar}{2\epsilon_0\hbar^2\Delta_1} \{ |\mu_{12}|^2 - |\mu_{23}|^2 \}$$
- page 141 line 10 ' $1.4 \Delta \nu_0$ ' should read ' $1.2 \Delta \nu_0$ '
- page 143 line 4 ' 2×10^{17} ' should read ' 3.5×10^{16} '
- page 149 line 14 ' $r_1 = r_2 = r = 0$ ' should read ' $r_1 = r_2 = r \neq 0$ '
- page 153 line 10 'in absence' should read 'in the absence'
- page 171 line 23 ',1969]' should read ',1969))'
- page 173 line 5 'Section 3.2.3' should read 'Section 3.2.3.2'
- page 182 Fig 4.1 'Tekronix' should read 'Tektronix'
- page 193 line 22 'error the' should read 'error in the'
- page 205 line 3 'estimatations' should read 'estimations'
- page 213 line 12 $\frac{d\Omega}{4\pi}$ should read $\frac{d\Omega}{4\pi}$
- page 221 line 18 'substantiate' should read 'substantiates'
- page 231 line 3 ' $^1P^1_0$ ' should read ' $^1P^0_1$ '

page 245 line 3 'dE b_E(ξ)|E>' should read ' $\int_0^{\infty} dE b_E(\xi)|E>'$

page 245 line 18 'state k' should read 'state $|k>'$

page 259 line 14 ' $E_k - \hbar\omega_d \rightarrow 0$ ' should read ' $E_k - \hbar\omega_d - H_A \rightarrow 0$ '

page 269 line 3 'Milloni' should read 'Milonni'

page 277 line 4 'Kransnoyarsk' should read 'Krasnoyarsk'

page 295 line 2 'ensure that constant' should read 'ensure constant'

page 299 line 9 '3.5 cm' should read '3.3 cm'

page 307 line 10 '3.5 cm' should read '3.3 cm'

page 309 line 5 '499.62 nm' should read '499.26 nm'

page 319 line 29 'intensity' should read 'intensities'

page 335 line 12 '499.92nm' should read '499.26nm'

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CHAPTER 1

INTRODUCTION

1.1 Preface

The first theoretical work on multiphoton processes dates from very early in the life of quantum theory when, in 1931, Goeppert-Mayer published a theoretical paper on simultaneous two-photon absorption. The experimental realisation could not at that time be imagined, due to the lack of an intense monochromatic light source.

Since that time great progress has been made in the field of quantum optics leading to a more comprehensive understanding of the nature of light and matter and their interactions. The advent of the laser in the early 1960's precipitated the birth of experimental non-linear optics, giving researchers the tools necessary to carry out experiments previously considered only theoretically. Once started, experimental non-linear optics grew rapidly with the discovery of many new interactions and processes. Multiphoton ionisation initially attracted interest because of the challenge of predicting, isolating and observing phenomena which were highly improbable, particularly in the non-resonant case.

The work described in this thesis uses one of those once-thought improbable interactions, two-photon-resonant three-photon ionisation in Xenon, to gain a further understanding of the interaction between high intensity laser radiation and the atomic species. Relating to the resonant ionisation process itself, we have studied resonance saturation mechanisms. Using the resonant ionisation process, we have investigated

experimentally the coherent interaction of laser-induced auto-ionisation. This topic has attracted much theoretical interest in the past decade.

1.2 Background to the Work Presented in this Thesis

Presented in this thesis is a study of two-photon-resonant three-photon ionisation of Xenon, with particular emphasis on two aspects of the process. Firstly, three-photon ionisation and an associated stimulated emission process were used to investigate saturation mechanisms leading to substantial broadening of the two-photon-resonant state. Secondly, the first known experiments, in Xenon, in which the effect of a laser-induced autoionising resonance on the three-photon ionisation yield were carried out. Laser-induced autoionising resonances are also known as laser-induced continuum structure, (LICS), and these terms are used interchangeably throughout this thesis.

It is useful to describe here the background to the work to be described, as the two topics of resonance saturation mechanisms and laser-induced continuum structure both evolved from a previous non-linear optics experiment, in Xenon, carried out in our laboratory. In an experiment described by Hutchinson and Thomas, 1983, and by Thomas, 1983, a source of tunable narrow-bandwidth vacuum ultra-violet, (VUV), radiation was generated using the process of two-photon-resonant four-wave mixing, difference frequency generation, in Xenon. By achieving a two-photon resonance with the $2P^0_{3/2}$, $6p$ ($J=0$) state, at $\omega_1 = 249.63\text{nm}$, and mixing with a second wavelength of $\omega_2 \sim 630\text{nm}$, an output, $2\omega_1 - \omega_2$ was generated at a wavelength around 155nm . While a reasonably efficient VUV source was produced (maximum conversion efficiency = 0.25%), in

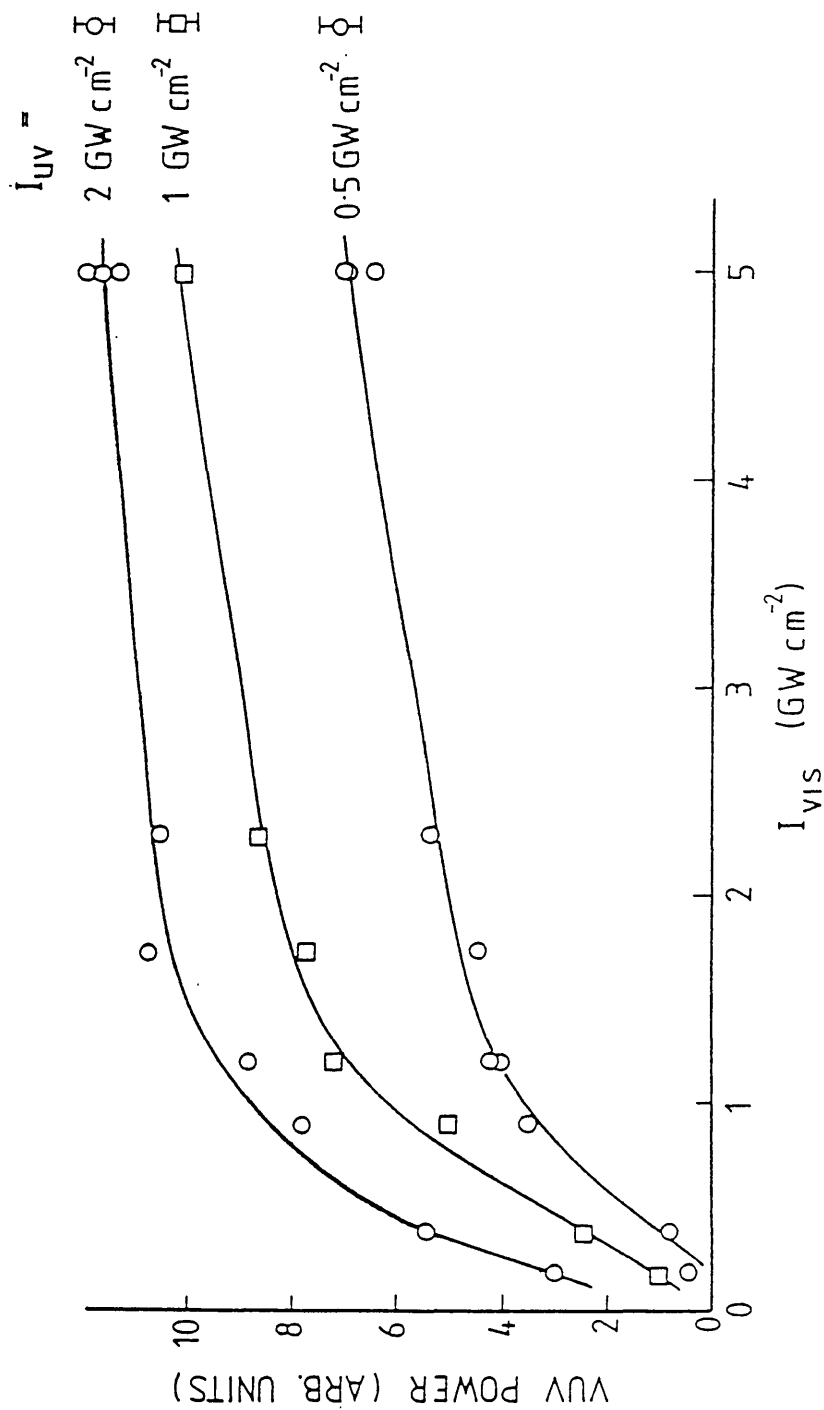


Figure 1.1 Four-wave Mixing Experiment:

Dependence of Generated Signal, ω_4 , Intensity, on Input Visible Laser, ω_2 , Intensity for a Range of Ultra-Violet (UV), ω_1 , Intensities (after Thomas, 1983)

the region of the two-photon resonance, the process was found to be very heavily saturated.

Measurements of the two-photon resonance linewidth were made by monitoring the VUV signal while tuning the two-photon-resonant frequency through the resonance. These revealed, for input intensities of around 1 GW/cm^2 , linewidths of approximately 100GHz. This is almost two orders of magnitude greater than the expected Doppler width of the resonance.

In some ways, this heavy saturation is an advantage from the point of view of producing a useful source of VUV radiation. Associated with the broadening of the resonance is a reduction in the power law dependence governing the relationship between input and output intensities. By running the process into the saturated intensity regime, one produces an output which is insensitive to input powers, as shown in Figure 1.1.

However, the physical mechanism leading to the saturation in the four-wave mixing experiment was of considerable interest in trying to gain a greater understanding of the process. At the time of the initial experiment, it was somewhat unclear which of a variety of mechanisms such as power broadening, a.c. Stark broadening or ionisation broadening, was responsible for the observed saturation. However, the large cross-section for single-photon ionisation from the two-photon-resonant state, at $\lambda = 249.63 \text{ nm}$, lead the researchers to believe that the presence of ions made an important contribution to the saturation. In addition to direct ionisation broadening, the presence of a high density of ions and photoelectrons can also lead to saturation via the d.c. Stark effect.

It is not the purpose of this introductory chapter to explain

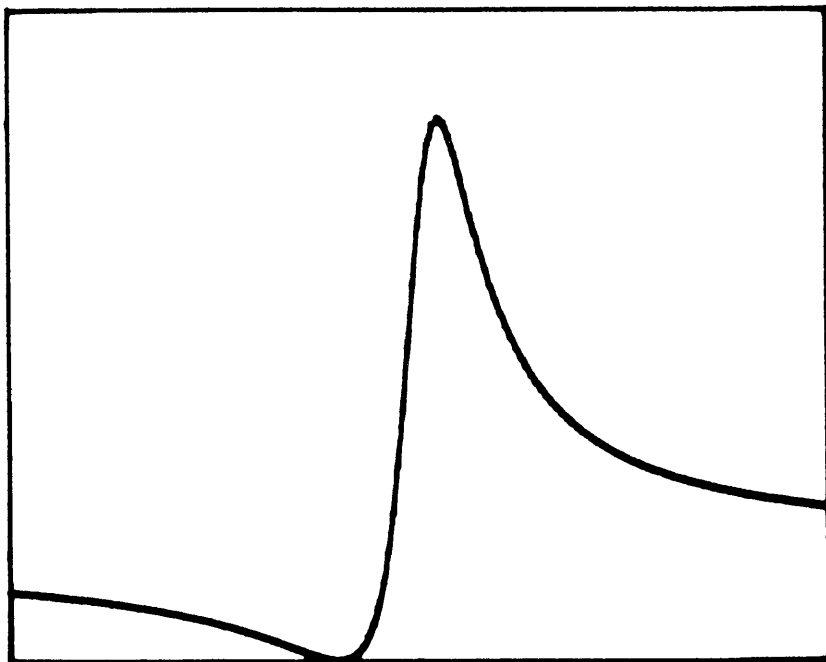


Figure 1.2 Example of a Fano Lineshape

in detail the theory relating to either of the experimental studies described in this thesis. Rather, the relevant theory is discussed as appropriate throughout the thesis. However, to fully explain the background to the work carried out requires a brief description of laser-induced continuum structure. A more detailed discussion, including references, is presented in Chapter 5.

Laser-induced autoionising resonances, which are discrete states lying above the ionisation level of an atom or molecule, are entirely analogous with real autoionising resonances, which are well known, except with respect to the form of the interaction involved in producing the continuum state. Real autoionising resonances result from the Coulomb interaction between electrons excited to multi-electron states above the ionisation limit. Laser-induced autoionising resonances, on the other hand, result from the dipole interaction between a radiation field and a bound state of the atomic or molecular species. The energy position in the continuum of a laser-induced autoionising state is controlled by the radiation field frequency, while the induced resonance width is dependent on the field intensity. This offers flexibility in the positioning and control of such states.

The feature of autoionising resonances of interest to the four-wave mixing experiment was their asymmetric lineshape, also known as the Fano lineshape. An example is shown in Figure 1.2. Physically, the significance of the Fano minimum, which is theoretically a zero, is that it offers the opportunity for an ionisation channel to be closed down in the region of the resonance. Tuning to the maximum of the resonance can result in the strengthening of a weak ionisation continuum. This can

be used in a manner analogous with resonant enhancement of non-linear processes by tuning close to a discrete energy level below the ionisation limit. However, the presence of the Fano minimum in the autoionising resonance makes possible the weakening of a strong ionisation continuum, such as that encountered in the four-wave mixing experiment in Xenon.

It was proposed to investigate the use of laser-induced continuum structure as a method of "closing down" the ionisation channel by taking advantage of the minimum in the lineshape of a continuum discrete state. It was postulated that by weakening a saturation mechanism, there would be an associated increase in the efficiency of the four-wave mixing process. Hence the proposed experiment involved using the laser-induced structure in a novel way compared with that previously described in the published literature, which describes the use of laser-induced autoionising states to produce resonant enhancement of non-linear processes (See Section 6.2).

As an associated study to the laser-induced continuum structure experiment, a further detailed study of the saturation mechanisms leading to broadening of the two-photon resonance was also undertaken. The process of two-photon-resonant three-photon ionisation was used as a probe for both this study and the LICS study.

We believe that the LICS study is the first recorded experiment of its kind in a rare gas and also the first in which weakening of a strong ionisation continuum via the Fano minimum is investigated, rather than the enhancement available from strengthening of weak ionisation continuum via such a state.

1.3 Plan of Thesis

The following section, 1.4, is a brief description of the theory of multiphoton excitation and ionisation. The remaining chapters of the thesis are arranged as follows.

In Chapter 2 the laser system used for the experiments is described in detail. The system is based on excimer-pumped dye lasers and an excimer amplifier. Development work on the laser system is described, together with diagnostics used for system monitoring and ion detection schemes.

Chapters 3 and 4 relate to the study of saturation of two-photon-resonant three-photon ionisation. In Chapter 3, we consider theoretically the saturation mechanisms involved, with some quantitative analysis of the relative importance of each to our experimental conditions. Computer modelling of the rate equation analysis used to calculate the effect of the laser excitation is also described together with results of computation for the conditions encountered experimentally. In Chapter 4, experimental details and results are presented. Conclusions are drawn about the dominant saturation mechanism on the basis of our experimental observations and theoretical considerations.

In Chapter 5, the theoretical background to the laser-induced autoionising state study is presented, concentrating on the physical interpretation of the theory and its application to experimental conditions. Chapter 6 contains a review of previous experimental work on LICS, together with experimental work, results and conclusions relating to the laser-induced autoionising state investigation.

Conclusions, applications of the studies and recommendations

for future work are presented in Chapter 7.

1.4 An Introduction to Multiphoton Absorption and Ionisation

The absorption by an atom of a single photon is easy to understand if the photon energy is equal to the energy difference between a populated state (not necessarily the ground state) and another level in the atom. The atom absorbs the photon and the electron is excited to the upper energy level. Alternatively, if the photon energy is greater than the energy required to ionise the atom, ionisation will occur. In this case the continuum of states above the ionisation limit means that all wavelengths of suitable energy will be absorbed. Hence we have line absorption spectra to energy levels below the continuum and broadband absorption above. Conservation of momentum in the interaction of photon and atom limits the range of transitions which can be accessed in this way. Once excited, the atoms or ions can return to the ground state by recombination with electrons in the case of ions, and an assortment of radiative and collisional decay channels.

In addition to single-photon transitions, it is also possible for multiphoton transitions to occur. The non-resonant N -photon absorption or ionisation rate W is given by $W = \sigma_N I^N$, where σ_N is the generalised N -photon absorption or ionisation cross-section and I is the laser intensity. W is expressed in reciprocal seconds (s^{-1}), σ_N is expressed in $cm^{2N} s^{N-1}$ units and the laser intensity in photons per cm^2 per second. It is useful to consider simple arguments leading to order of magnitude estimates of the multiphoton absorption or ionisation cross-sections. This also assists in the physical interpretation of how a multiphoton process proceeds.

Simplistically the atom must absorb all the photons involved in the multiphoton process simultaneously. If this were indeed the case, it would make the probability of multiphoton processes so small as to be almost negligible. Alternatively, one can consider the atom absorbing a single photon and being excited to some intermediate "virtual" level. Since this level is not a real level, the atom can remain in this state for a short time, τ , which is typically one cycle of the optical excitation, i.e. ω^{-1} .

Consider two-photon excitation of an atom with a laser frequency ω , and an intensity I . If an energy conserving first-order transition were possible, the single-photon transition would take place at a rate $W = \sigma_1 I$, where σ_1 , the single-photon absorption cross-section, is typically 10^{-17}cm^2 [Mainfray and Manus, 1984]. As noted, a second photon can be absorbed if it is incident within the time $\tau = \omega^{-1} \approx 10^{-15} \text{s}$. Again the rate of the second event is $\sigma_1 I$, so the overall rate for the non-resonant two-photon absorption will be

$$W \approx \sigma_1 I \omega^{-1} \sigma_1 I$$

Therefore, by comparison with $W = \sigma_2 I^2$, we find that

$$\sigma_2 \approx \sigma_1^2 \omega^{-1} \approx 10^{-49} \text{cm}^4 \text{s}$$

If there is an atomic state close to the laser-induced virtual state, then $\tau = \omega^{-1}$ must be replaced by $1/\Delta E$, where ΔE is the energy detuning between the real and virtual levels.

This crude estimate has been shown to be in good agreement with experimental and theoretical data, for example, for two-photon ionisation of Cesium [Mainfray and Manus, 1984].

The argument can be extended to higher order processes and is

generalised as

$$\sigma_N = \sigma_1^N \nu^{N-1}$$

Absorption of additional photons via virtual photons continues until the atom finally reaches a real excited state or is ionised. Of course, further step-wise absorption of photons from an excited state is possible, and recent work by Deng and Eberly, 1985, has dealt with further absorption of photons by free electrons within the continuum.

The phenomenon of resonant enhancement is universal in non-linear processes and is evident in non-parametric multiphoton excitation processes as in parametric non-linear mixing processes. By tuning close to an intermediate energy level the cross section for multiphoton absorption can be resonantly enhanced. This can be understood as an increase in the time delay available before the absorption of the next photon, due to the proximity of a real energy level.

However, if there is an exact resonance with an intermediate energy level then population of that level will occur and the overall multi-photon excitation process is replaced by two step-wise processes, with a real population in the intermediate resonant state. The total cross-section for such stepwise processes could be expected to be higher by many orders of magnitude than for the single step multi-photon process, as a virtual level is replaced by a real level and the virtual state lifetime (ω^{-1}) is replaced by a time relating to the lifetime of the real level.

Accordingly, the two-photon-resonant three-photon ionisation process investigated in the work reported in this thesis, is considered only as a two-step process i.e. two-photon

absorption followed by single-photon ionisation.

Multiphoton absorption and ionisation are interesting processes which can be used to produce sources of excited atoms or ions. However their role in many non-linear processes is that of parasitic processes. The use of resonant enhancement in non-linear processes such as four-wave mixing inevitably leads to at least some absorption to the resonant state. The use of a two-photon resonance, however, eliminates single-photon transitions back to the ground state. Such absorption to the resonant state can lead to saturation of the desired non-linear process as can subsequent processes, such as ionisation or the stimulated emission of radiation, resulting from the population of the excited state. Such was the case in the four-wave mixing experiment described briefly in Section 1.2. This leads us into the work described in this thesis.

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CHAPTER 2

LASER SYSTEM FOR NON-LINEAR OPTICS

2.1 Introduction

The first experiments in non-linear optics were carried out using available lasers and non-linear materials, in what were early days of both laser development and non-linear optics. The results were clear demonstrations of non-linear processes such as second harmonic generation [Franken et al, 1961]. However, conversion efficiencies were very low, Franken et al reporting a photon conversion efficiency of 10^{-8} for second harmonic generation of ruby laser radiation in quartz. The main reason for this was the lack of phase matching of fundamental and second harmonic beams. In addition, the limited spectral coverage of available lasers suitable for non-linear optics, namely the ruby lasers, restricted early experimenters to non-resonant processes.

Nowadays, with the wide range of lasers available, it is possible to design systems which are specifically tailored to non-linear optics, allowing both investigation of non-linear processes in atomic and molecular systems, and the production of coherent tunable radiation sources in inaccessible spectral regions. [Hutchinson and Thomas, 1983; Hellner and Lukasik, 1984; Hager and Wallace, 1982 and references therein]. Such systems can take advantage of resonant enhancement to improve conversion efficiency, as described by among others, Hutchinson and Thomas, 1983. Good frequency resolution can be achieved by using the high spectral brightness available from narrow bandwidth lasers [See for example Wallenstein and Zacharias, 1980 and Hilbig and Wallenstein, 1981, 1982].

Recently, extremely large non-linearities have been discovered in a number of classes of materials, notably photorefractive materials, liquid crystals and organic polymers. As an example, phase conjugation via real-time holography, utilising the photorefractive effect, has been observed in crystals such as Barium Titanate and Bismuth Silicon Oxide (BSO) using low power Helium-Neon and Argon ion CW lasers. [Gower, 1984 and references therein]. The photorefractive effect involves a second order non-linearity $\chi^{(2)}$, as does second harmonic generation. Large third order non-linearities have been observed via third harmonic generation, in for example, organic polymers such as polydiacetylenes [Zyss, 1985]. However, in general, high peak power lasers are required to observe non-linear effects, restricting the choice to pulsed lasers.

Additionally, a system based on tunable lasers gives the flexibility to investigate a wide range of processes and tune into resonance with suitable energy levels. It is also advantageous to use lasers of narrow spectral bandwidth so that high spectral resolution and brightness are available for the investigation of, for example, resonant non-linear processes.

The remaining sections of this chapter describe the use of Xenon as a non-linear medium and the laser system used in the study. This system, based on excimer-pumped dye lasers and using an excimer laser amplifier, was designed to give high peak powers, high spectral brightness, tunability and maximum flexibility to allow investigation of a range of non-linear processes in Xenon.

2.2 Xenon as a Non-Linear Medium

Non-linear media can be solid, liquid or gaseous.

Solids are most popularly used for second harmonic generation and other three-wave mixing processes. For these applications, the medium must be a non-centrosymmetric, crystalline material. Examples are KDP (Potassium Dihydrogen Phosphate) and ADP (Ammonium Dihydrogen Phosphate). These, together with their deuterated derivatives, are the most common crystals used, [See the review article by Franken and Ward, 1963], although organic polymers have been gaining in popularity recently as a result of the large non-linearities observed in such materials. [See for example Zyss, 1985].

Non-linear processes such as Stimulated Brillouin Scattering, (SBS), [Damzen & Hutchinson, 1983], Stimulated Raman Scattering, (SRS), and self-focusing have been observed in liquids.

Alkali metals in the vapour state have been used as non-linear media for Stimulated Electronic Raman Scattering (SERS) for both wavelength shifting of excimer lasers [Djeu & Burnham, 1977] and tunable infra-red generation [e.g. Sorokin et al, 1973]. Four-wave mixing processes in alkali metal vapours have also been extensively studied, [Miles and Harris, 1973].

Noble gases in general, and Xenon in particular, are attractive non-linear media for a variety of reasons. Firstly, gases do not suffer from permanent damage which can limit the peak power densities compatible with many crystalline non-linear media. Secondly, Noble gases are easy to handle, in contrast to the heat pipe technology necessary in experiments involving alkali metals [Vidal and Cooper, 1969 and Vidal and Haller, 1971]. Thirdly, the energy levels and ionisation potentials of noble

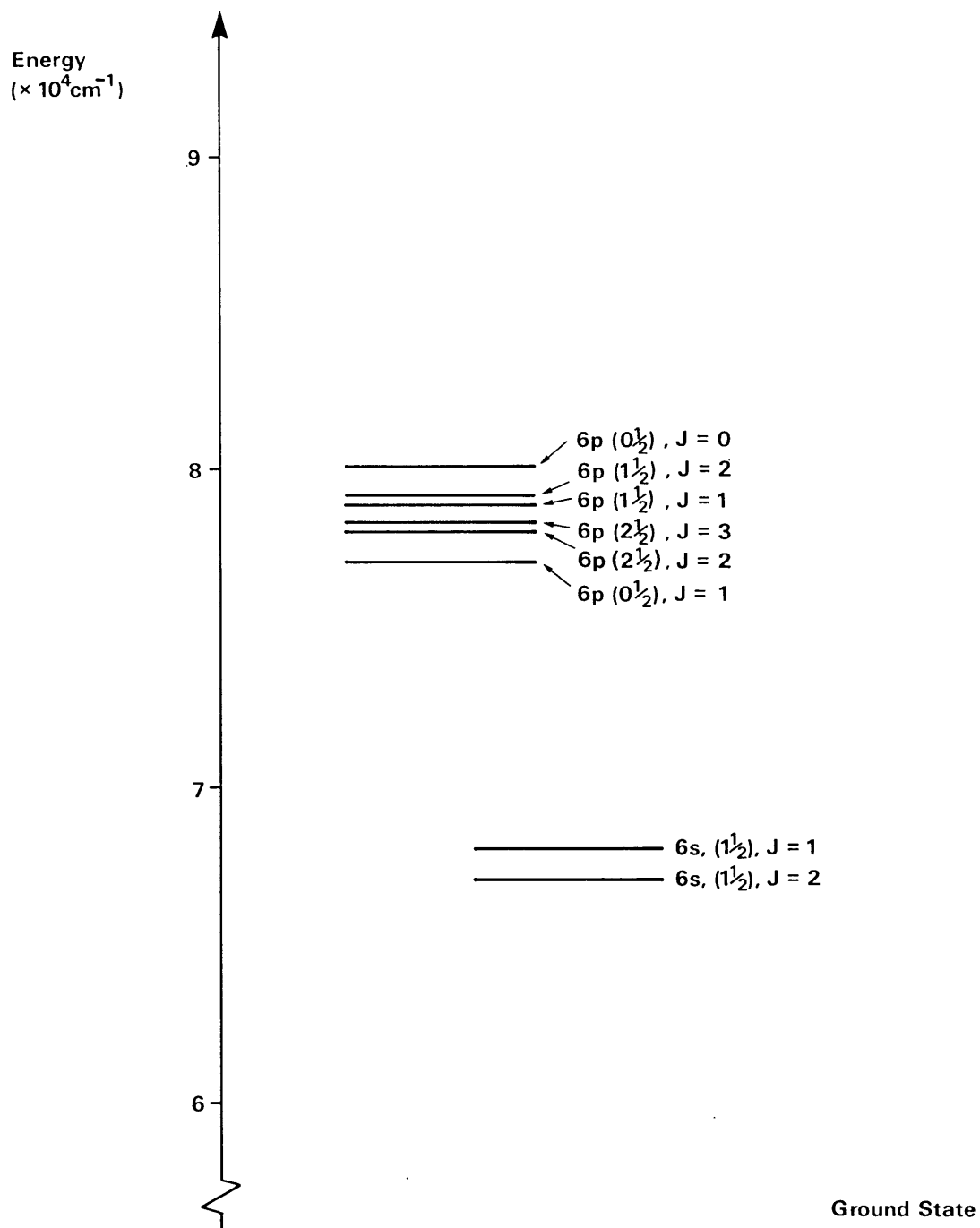


Fig 2.1 Xenon Partial Energy Level Diagram showing $5p^5(^2P^0_{3/2})$ 6p Levels

gases are high lying. This means that the non-linear susceptibility for, for example, four-wave mixing, sum frequency generation contains only bound-bound contributions even for generated wavelengths well into the vacuum ultraviolet spectral region. Consequently, large non-linear susceptibilities may be expected compared with alkali metals where, for example, the non-linear susceptibility for third harmonic generation using fundamental wavelengths in the visible usually contains a bound-free term. [Taylor, 1976].

Finally, the choice of Xenon, in particular, as a non-linear medium takes advantage of the coincidence of some Xenon energy levels with available laser sources. As shown in Figure 2.1, the $5p^5 (2P^0_{3/2}) 6p$ levels lie in the energy region 77,270-80,119 cm^{-1} . The wavelength required to reach the 6p, $J=0$ state at 80,119 cm^{-1} , via a two-photon transition, is 249.63nm. This lies within the gain bandwidth of the Krypton Fluoride excimer laser.

Hence a variety of two-photon-resonant processes can be investigated. The techniques for generating narrow bandwidth radiation at 249.63nm, required to take maximum advantage of the resonance, together with the chosen approach, are described in the next section.

2.3 Techniques for the Generation of Narrow Bandwidth Radiation at $\lambda = 249.63\text{nm}$

The requirement that the source be of narrow bandwidth and of high spectral brightness precludes the use of a spectrally un narrowed Krypton Fluoride excimer laser. Such a laser has a spectral output of bandwidth around 0.5nm peaked at 248.6nm [Lorree et al, 1978]. Thus the 6p, $J=0$ state is in the wing of

the laser line and while some resonant enhancement may be expected, detailed study of the resonant nature of non-linear processes would not be possible.

Previously, narrow bandwidth output from excimer lasers has been achieved using a narrow band excimer laser oscillator with frequency selective optics, most usually grating or prism arrangements. The output from such a laser is then injection locked into another excimer laser, usually with an unstable resonator cavity [Goldhar et al 1980]. This approach suffers from two disadvantages, namely:-

- i) The linewidth which can be achieved is limited, by the small number of round trips possible in a conventional discharge-pumped excimer laser, to around 0.1cm^{-1} (3 GHz).
- ii) The frequency selective elements are generally lossy and increase the threshold for laser oscillation. This has the effect of reducing the linewidth over which narrow bandwidth oscillation can occur so that laser action is not possible in the "wings" of the transition.

The alternative technique and that chosen for the work described in this thesis, is to use an excimer amplifier in conjunction with a frequency doubled narrow bandwidth dye laser operating in the visible region of the spectrum. This approach combines the narrow bandwidth achievable using a dye laser with the high gain of an excimer laser. In addition, since the excimer laser is used only as an amplifier, amplification right out into the "wings" of the transition is possible, albeit with reduced gain compared with that on line centre.

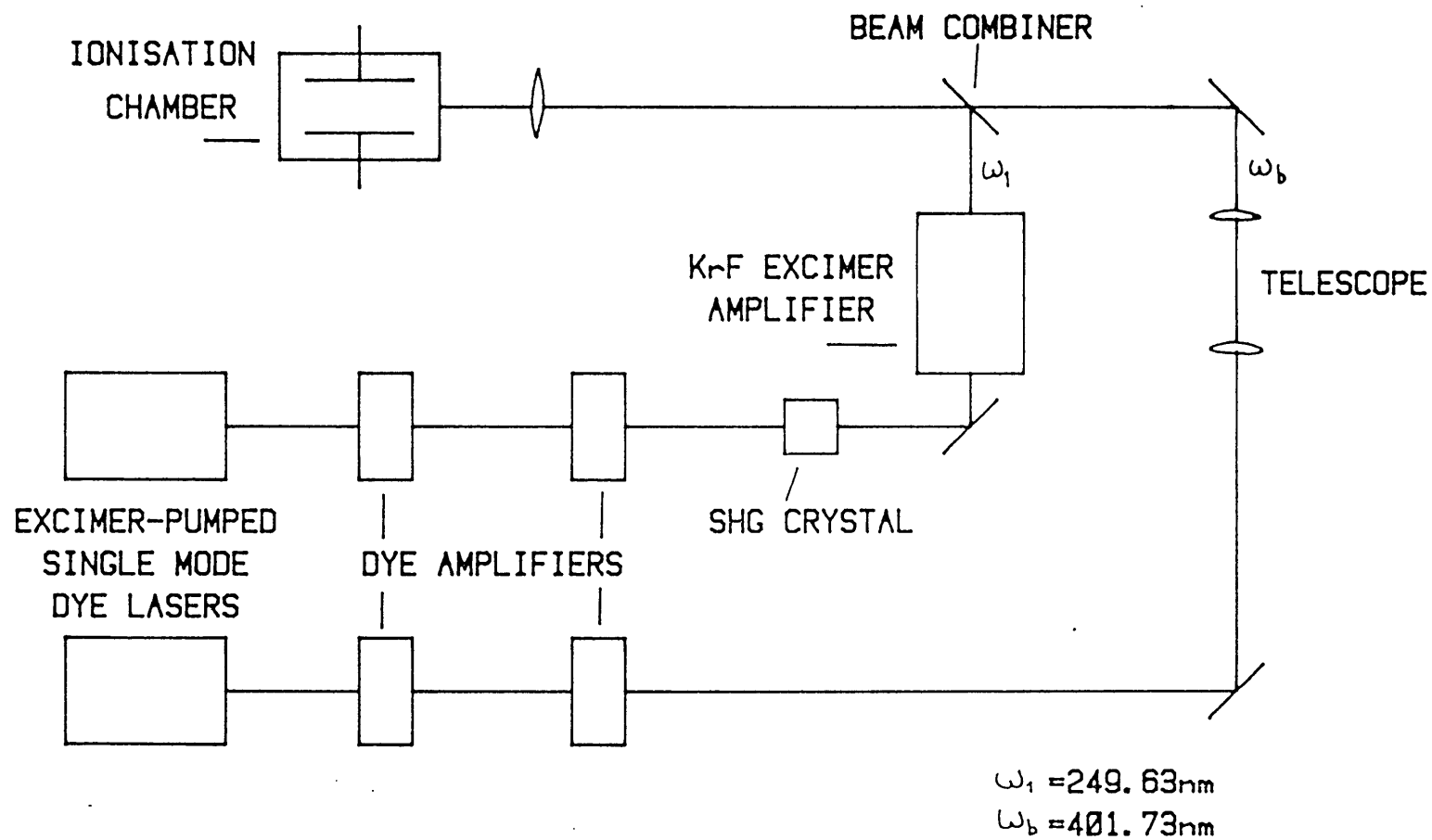


Figure 2.2 Experimental Arrangement (Schematic)

2.4 Experimental Details

A block diagram of the complete laser system is shown in Figure 2.2. The system produced two independent narrow-bandwidth pulsed laser outputs, one of restricted tunability in the region of $\lambda = 499.2\text{nm}$ ($2 \times 249.6\text{nm}$) and another tunable throughout the near ultra-violet and the visible to the near infrared spectral region. A range of laser dyes were necessary to achieve this tunability. The components of the system consisted of:

- i) Xenon Chloride excimer pump laser.
- ii) Narrow bandwidth dye laser oscillators and amplifiers.
- iii) Frequency doubling of $\lambda = 499\text{nm}$ radiation in Potassium Pentaborate (KB5) crystal.
- iv) Amplification of frequency doubled radiation in Krypton Fluoride excimer amplifier.
- v) Beam combination.

These are described in detail in sections 2.4.1 to 2.4.5.

2.4.1 Xenon Chloride Excimer Pump Laser

Commercial excimer lasers provide high power radiation at a variety of wavelengths in the ultraviolet region of the spectrum. The wavelength depends on the rare gas halide lasing medium used and range from 193nm (ArF^*) to 351nm (XeF^*). Two of these lasers are suitable for dye laser pumping, namely XeCl^* at $\lambda = 308\text{nm}$ and KrF^* at $\lambda = 248\text{nm}$. XeCl^* is the more commonly used of the two, with KrF^* only being employed for pumping of some ultra-violet dyes. In this study, two commercial excimer lasers, operating on XeCl^* , were used at different stages of the work. These were both UV preionised, discharge pumped excimer lasers. Initially a Lambda Physik EMG

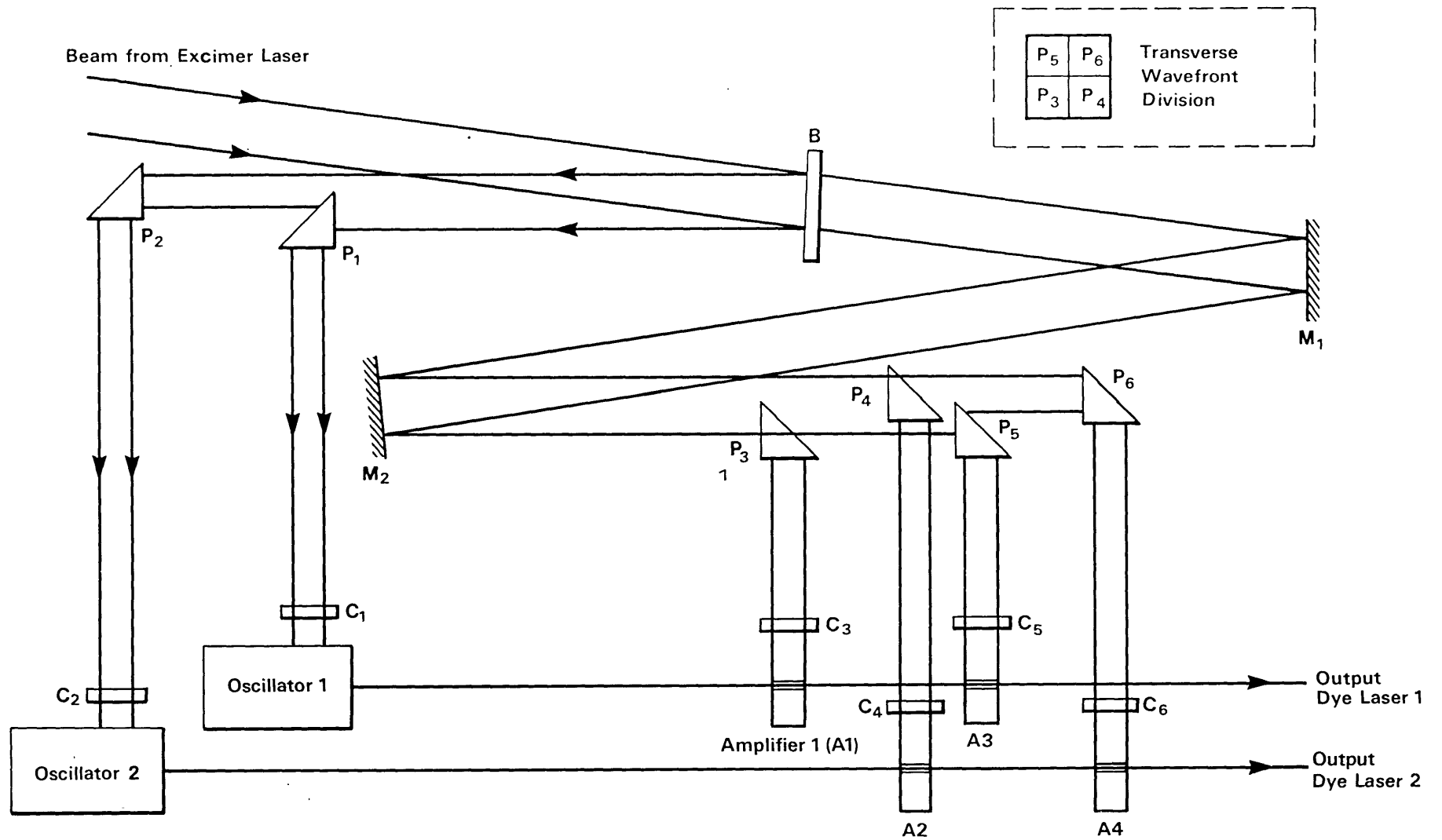


Fig 2.3 Excimer Laser Beam Division for Dye Laser Oscillator and Amplifier Pumping

101-E was used, this being replaced later by a Lumonics TE-860-4 Series laser.

Output characteristics of these lasers are shown in Table 2.1.

The excimer laser output was divided both by amplitude and wavefront division to provide pump beams of appropriate energy for the dye laser oscillators and associated amplifier chains. This is shown in Figure 2.3. The pump energy for the dye oscillators was provided by 8% reflection from a quartz beam-splitter, B, which was then divided and directed to the oscillator dye cells by two quartz prisms, P_1 , P_2 . The pump radiation transmitted through the quartz flat underwent an optical delay of 5ns, formed by dielectric coated high reflectivity mirrors M_1 and M_2 . This allowed time for laser action to build up in the oscillators before pump energy reached the amplifiers. The pump energy was then split by wavefront division and directed onto the amplifier cells by an arrangement of four quartz prisms, P_3 to P_6 , also shown in plan and transverse views in Figure 2.3.

As a result of the excimer laser beam divergence, some radiation remained at the edges of the beam after prisms P_3 to P_6 . This low energy radiation was directed, at the end of the chain, by a final prism onto a photodiode to act both as an external trigger source for data collection and also as a pump power monitor.

The approximate relative division of pump energy between oscillator, first and second amplifiers for pumping of two dye lasers is shown in Table 2.2. These values were dictated by the preferred mode of operation of the dye lasers as described in the following section.

	Lambda Physik	Lumonics
	EMG 101-E	TE-860-4
Maximum Energy/Shot	150mJ	500mJ
Pulse duration	10-15ns ⁽¹⁾	30-40ns ⁽¹⁾
Beam dimensions	10 x 30mm	20 x 30mm
Beam divergence (full angle)	few mrad	few mrad
Gas fill lifetime ⁽²⁾	6 weeks	5 days

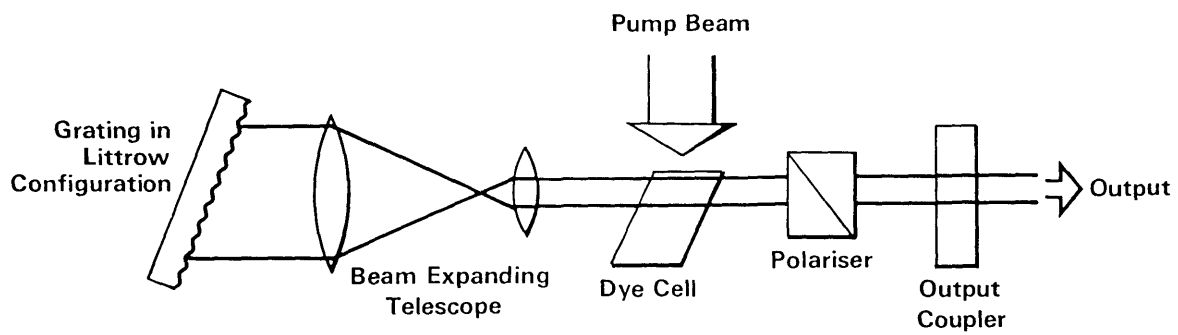
Notes

- (1) A range of pulse durations is given due its the dependence on age of gas fill.
- (2) This indicates the time to half power output for average usage of 3-5 hours per day at repetition rate of 1Hz.

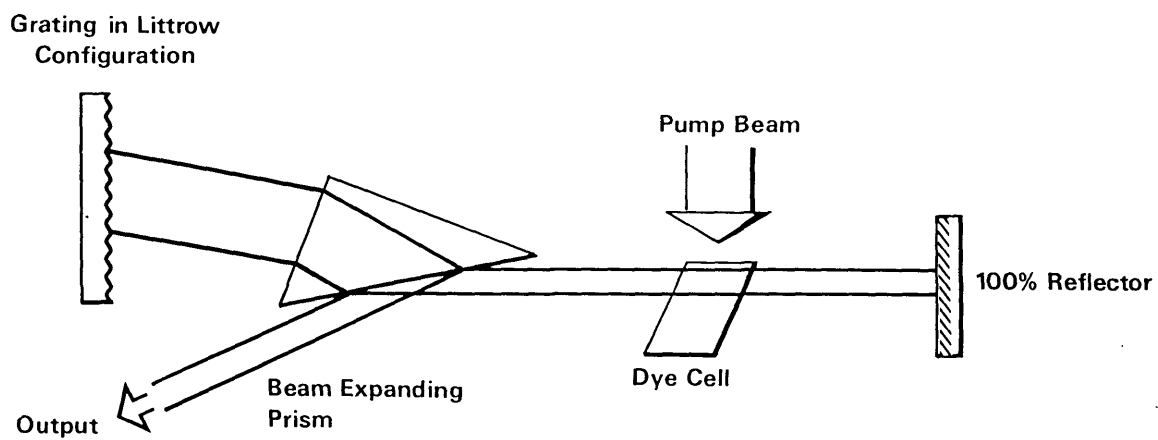
Table 2.1 Excimer Laser Performance

	Relative Pump Energy
Oscillator	2
1st Amplifier	15
2nd Amplifier	33

Table 2.2 Relative Pump Energies for Dye Laser Components



2.4(a) Hänsch Dye Oscillator (1972)



2.4(b) Hanna et al Dye Oscillator (1975)

Fig 2.4 Line - Narrowed Pulsed Dye Oscillator Configurations

2.4.2 Dye Lasers

The dye lasers each consisted of a narrow bandwidth oscillator followed by two amplifier stages, all transversely pumped by the commercial XeCl* excimer laser described in section 2.4.1. Narrow bandwidth operation is important for two reasons,

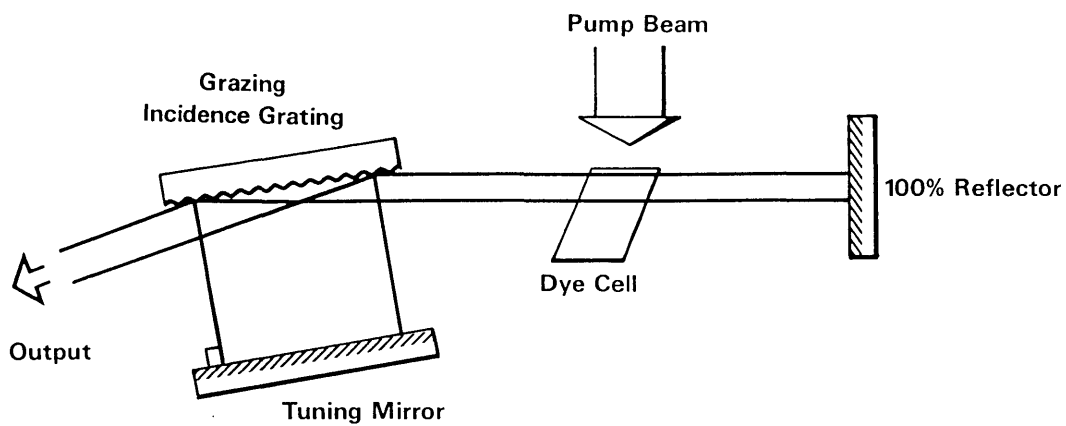
- (i) spectral selectivity,
- (ii) spectral brightness.

The second is greatly improved by single longitudinal mode operation. The transition from operation on two modes to a single mode can lead to an increase in spectral brightness of approximately an order of magnitude. The dye lasers described here were designed to operate in a single longitudinal mode.

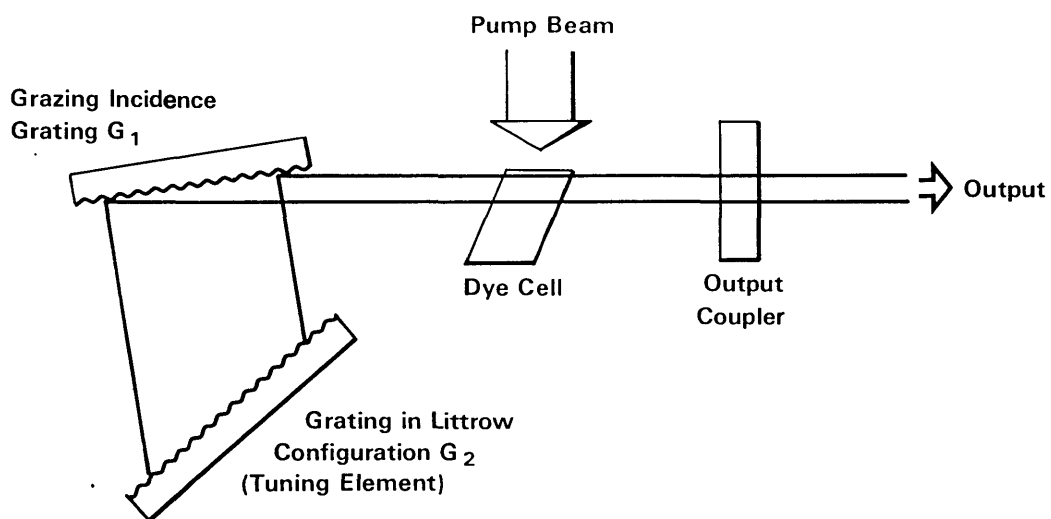
In order to achieve narrow linewidth operation of an excimer pumped dye laser the cavity must be highly dispersive, because of the limited number of cavity round trips during the duration of the pumping pulse. For a typical pumping pulse of 15ns duration and cavity length of 20cm only about 10 round trips are possible. Hence the advantages resulting from multipassing of dispersive elements such as gratings and etalons are limited.

The narrow bandwidth dye oscillator was a derivative of the design for a transversely pumped dye oscillator originally proposed by Hansch, 1972, and developed and modified by, among others, Shoshan and Oppenheim, 1978 and Littman, 1978.

In Hansch's original design, shown in Figure 2.4(a), the intra-cavity dispersive element was a grating used in the Littrow configuration which replaced the cavity end mirror. Since the resolving power of the grating, and hence its wavelength selectivity, is a function of the number of lines illuminated



2.4(c) Single Grating Shoshan et al Dye Oscillator (1975)



2.4(d) Double Grating Shoshan et al Dye Oscillator (1978)

Fig 2.4 Line - Narrowed Pulsed Dye Oscillator Configurations

[Born and Wolf, 1975], a telescope was used as an intra-cavity beam expander. Tuning was provided by the Littrow grating. Additional line narrowing was achieved by the use of an intra-cavity Fabry-Perot etalon. The pump source was a nitrogen laser.

The Hansch oscillator suffered from alignment difficulties because of the intracavity telescope. Using the fact that beam expansion is only required in the direction perpendicular to the grating grooves to achieve high dispersion, Hanna et al, 1975, worked with cavities using prisms for beam expansion, as shown in Figure 2.4(b). However, the large angles of incidence necessary to achieve adequate beam expansion meant that these nitrogen laser pumped dye cavities had extremely high losses.

A simplified cavity reported by Shoshan et al, 1975, eliminated the need for a beam expanding element by using a grating at grazing incidence for both beam expansion and dispersion. The cavity was completed by a plane mirror which also acted as the tuning element. The nitrogen-pumped Shoshan oscillator, shown in Figure 2.4(c) had the advantage of ease of alignment, compactness and hence an increased number of round trips per pulse, an advantage for line-narrowing in view of the short pulse operation of the nitrogen laser (< 10 ns). This design was used by Littman and Metcalf, 1978, and Corney, Manners and Webb, 1979, when pumping with frequency doubled Nd:YAG and XeCl* lasers respectively.

A further modification of this design resulted in the first report of such a laser operating in a single longitudinal mode by Littman, 1978. By minimising the cavity length, to gain maximum spectral separation of the longitudinal modes, Littman observed a single shot linewidth of less than 300 MHz. Narrow

Bandwidth Envelope Selected for
Oscillation by Intracavity
Dispersive Elements

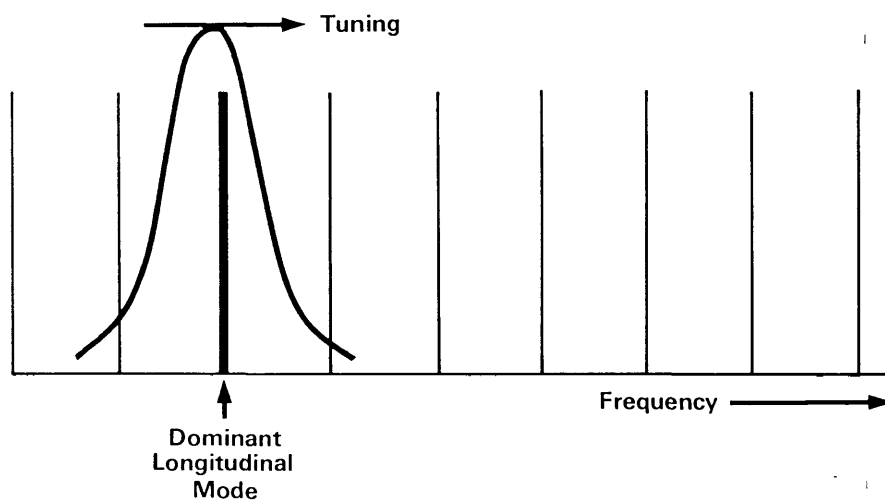
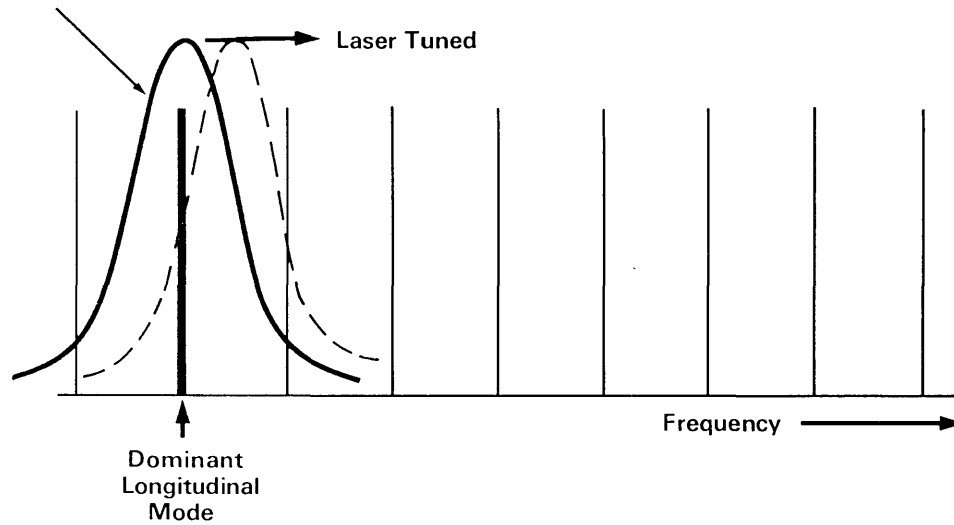


Fig 2.5 Mode - Hopping between Longitudinal Modes

linewidths were also achieved by replacing the tuning mirror with a second grating in Littrow configuration, such that the dispersions of the two gratings were additive [Shoshan and Oppenheim, 1978]. This is shown in Figure 2.4 (d).

This design suffers from two problems, one of which has been at least partially overcome by the design used in this work and one which has been the topic of other recent work.

Firstly, the losses in a cavity which includes both a grazing incidence grating and a grating in Littrow configuration are very high. This leads to low conversion efficiency, (Littman quotes 2% using Rhodamine 6G dye) and restricted dye tuning ranges. Secondly, it should be noted that the magnitude of the longitudinal mode spacing and the selected laser linewidth are usually comparable (500 MHz - 1 GHz). As the laser is tuned, discontinuities will occur in frequency as the laser jumps between longitudinal modes as shown in Figure 2.5. Unless the oscillator design is carefully chosen, the tuning and corresponding mode hopping rates are non-linear [Littman, 1984]. New designs of so-called travelling wave oscillators, however, eliminate the presence of longitudinal modes completely, allowing continuous tuning [Ewart, 1985 and Wells and Zhou, 1985].

It should be noted that some of the early dye oscillator arrangements used were what is termed as "open" cavities, i.e. the output beam was the zero order reflection from the grazing incidence grating. Duarte and Piper, 1980, point out that while good efficiencies are obtained, (8% for N_2 pumped Rhodamine 6G), a large component of non-tunable fluorescence was present. For an arrangement containing single pass amplifiers, such as the one used here, this fluorescence can be

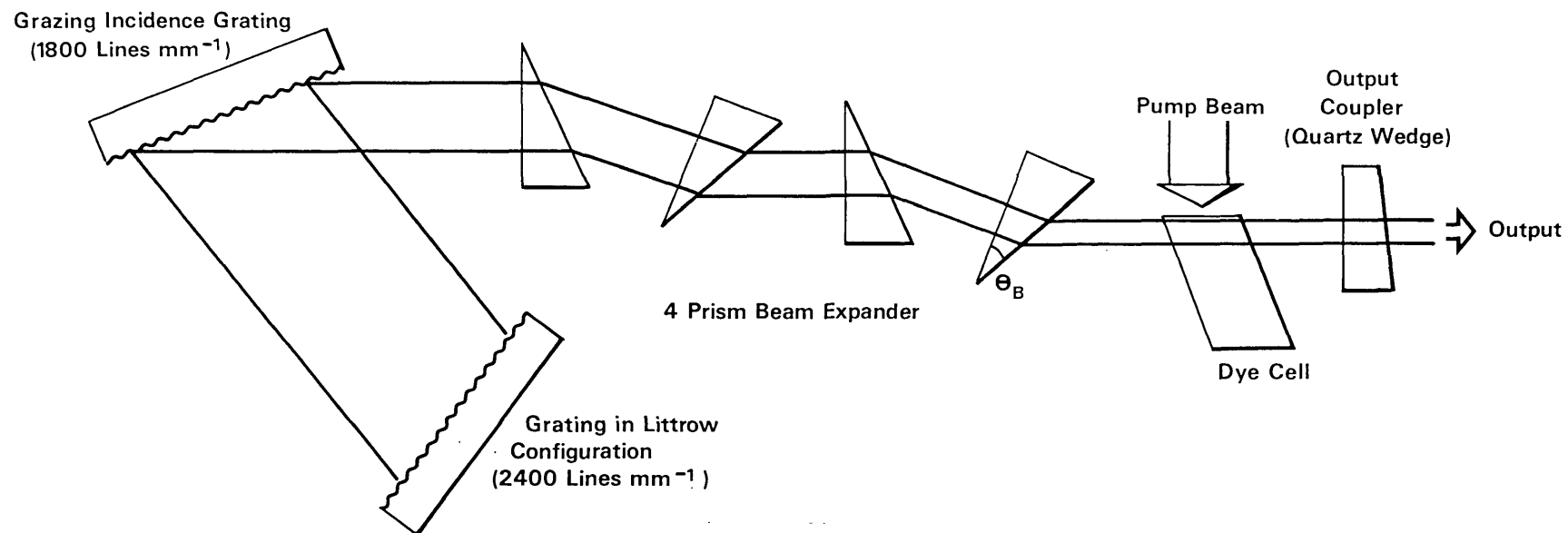


Fig 2.6 Modified Dye Oscillator Configuration

amplified at the expense of the narrow-band signal. This problem is much reduced by the use of "closed" cavities where the output is the signal transmitted through a partially reflecting output coupler which replaces the 100% reflecting end mirror of the "open" cavity. Some reduction in efficiency is experienced but can be tolerated by a saturated amplifier chain.

Cavity losses can be reduced by using the oscillator design adopted in this work and shown in Figure 2.6. This design also offers some further benefits in terms of line-narrowing as will be described. Our dye laser oscillator was a transversely pumped Littman double grating "closed" cavity with the addition of a four-prism beam expander between the dye cell and grazing incidence grating. The output coupler was an uncoated quartz wedge. The pump energy, from the XeCl* excimer pump laser, was approximately 2mJ focused to a line in the 1cm wide dye cell by a quartz cylindrical lens of 10 cm focal length. The side faces of the dye cell were angled with respect to the front face to prevent feedback between them. The dye was flowed through the cell to reduce instability in the output due to temperature dependent refractive index changes and the accumulation of ultra-violet irradiation induced decomposition products. The two gratings used were both holographic gratings, the grazing incidence grating being 1800 lines mm⁻¹ and the Littrow tuning grating being 2400 lines mm⁻¹. The cavity length was kept to a minimum to maximise the longitudinal mode spacing,

$$\Delta \nu = \frac{c}{2L}$$

where L is the cavity optical path length.

The four-prism beam expander provides some expansion of the beam in the plane perpendicular to the grating grooves and hence reduces the angle of incidence required on the grazing incidence grating to fill it with the incident beam. If the losses introduced by the cavity are less than the improvement in grating efficiency then an overall reduction in cavity losses results. This reduces the threshold for laser oscillation, and also allows laser oscillation to occur over wider tuning ranges.

The four-prism beam expander consisted of four identical right-angle dense flint glass prisms, arranged in pairs of cancelling dispersion, as shown in Figure 2.6. Hence the net dispersion of the set is very close to zero [Duarte and Piper, 1982]. This arrangement is chosen in preference to one of additive dispersion because the small dispersion available from such an arrangement is wavelength dependent and may distort the linear tuning of the Littrow grating. Additionally, input and output beams of the prism expander are parallel for the chosen arrangement.

The prism angle, θ_B , was Brewster's angle in the material so that light entering the prism at Brewster's angle left it normally. This ensured small reflection losses for the laser radiation which was p-polarised (perpendicular to the grating lines) as a result of intracavity gratings. Anti-reflection coatings were not used. Slight misalignment was required to prevent feedback from the prism faces perpendicular to the beam leading to the formation of sub-cavities.

The expansion per prism is equal to n , the refractive index of the material; hence the choice of high refractive index glass ($n=1.61$ for dense flint glass). The expansion for four prisms

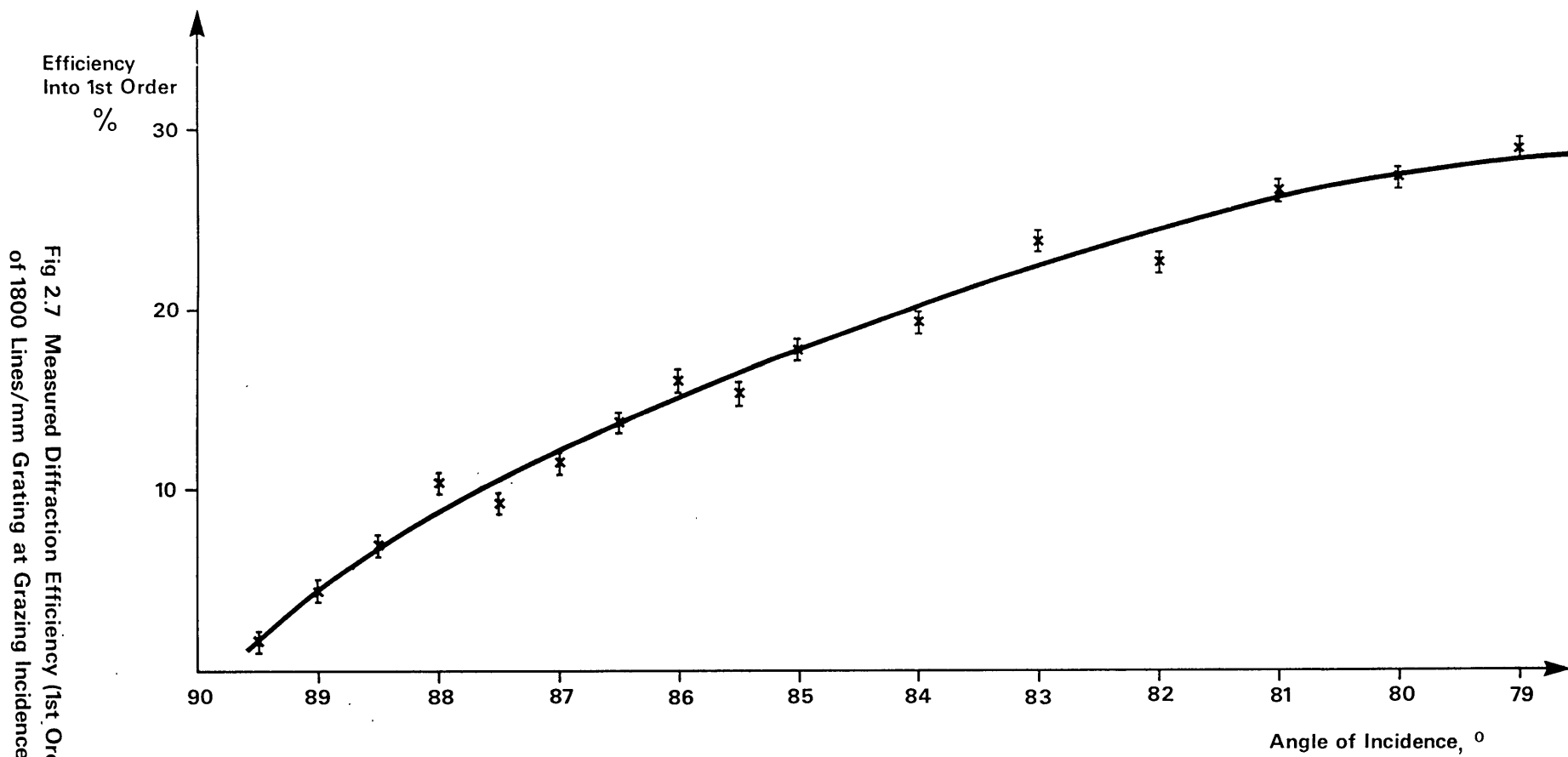


Fig 2.7 Measured Diffraction Efficiency (1st Order) of 1800 Lines/mm Grating at Grazing Incidence

is $n^4=6.7$. It can be shown, [Racz et al, 1981], that the transmission of two identical prisms with fixed overall magnification has a maximum when the partial magnifications are equal. Hence the choice of an arrangement with each prism having the same magnification.

The reflection loss at each prism was approximately 5% giving a total loss of 18.5% for a single pass through the four prisms. The increase in grating diffraction efficiency achieved by reducing the angle of incidence from 89° to 83° , as allowed by the $\times 6.7$ beam expansion of the four-prism beam expander for a 1mm diameter incident beam and 5cm long grating, is estimated to be a factor of approximately 5, from measurements of diffraction efficiency shown in Figure 2.7. This compares well with the data of Racz et al, 1981. Hence the total losses in the cavity are substantially reduced by the insertion of the four-prism beam expander, leading to a reduction in the the threshold for laser oscillation.

Reduced threshold pump power may also affect the laser oscillation bandwidth. It can be postulated that that thermal effects in the dye can cause a variation of beam propagation direction during the duration of the pumping pulse. By causing transient variation in effective laser cavity length, this can broaden the linewidth of laser oscillation. Obviously, this is a second order effect compared with the spectral selectivity of the intra-cavity dispersive elements.

Iles, 1981, considers a unified single-pass model of linewidths in the Hansch, single-, and double-grating grazing-incidence dye lasers. His treatment also allows for a beam expansion element between dye cell and grating. Assuming a Gaussian

intensity profile for the intra-cavity beam, with a beam waist 2ω in diameter in the dye cell, he shows that optimum resolution is achieved when the principal diffraction lobe of the beam just fills the grazing incidence grating. This occurs when the distance from the dye cell to the centre of the grating is equal to the Rayleigh length, L_R where

$$L_R = \frac{\pi \omega^2}{\lambda}$$

where 2ω is the beam waist in the dye
and λ is the wavelength.

For $\lambda = 500\text{nm}$ and $\omega = 0.1\text{ mm}$, $L_R \approx 6\text{cm}$. This condition is satisfied by the design employed.

For the double-grating cavity, Iles shows that the optimum single pass linewidth is given by

$$\Delta\lambda = \frac{2\sqrt{2}\lambda}{\pi L \left(\alpha + \frac{\beta \cos\phi}{2 \cos\delta'} \right)}$$

where L is the length of the grazing incidence grating,

α and β are the ratios of the diffracted order to groove spacing for the grazing incidence and Littrow gratings respectively,

ϕ is the angle of diffraction from the grazing incidence grating,

and δ' is the Littrow angle.

This can also be expressed in totally grating dependent terms by substitution using the grating equation. The elegance of the result, however, is lost by this substitution.

For $\lambda = 500\text{nm}$, an angle of incidence of 83° on the grazing

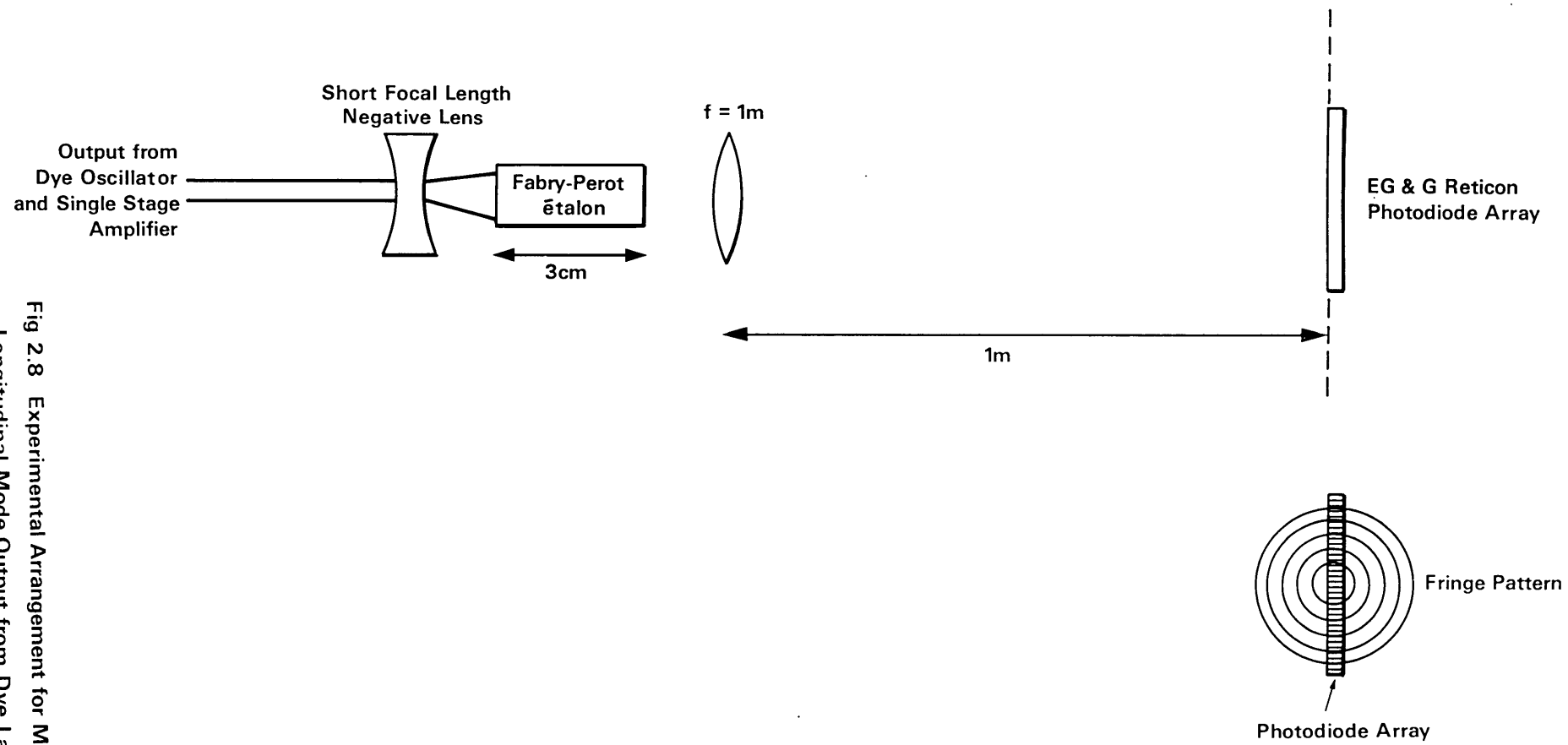


Fig 2.8 Experimental Arrangement for Monitoring Longitudinal Mode Output from Dye Laser

incidence grating, ($1800 \text{ lines mm}^{-1}$) and a Littrow grating of $2400 \text{ lines mm}^{-1}$, both used in first order, the above equation yields a predicted linewidth of 3 GHz. Multi-passing will reduce this by a further 30% to approximately 2 GHz, showing that for a cavity length of 15 cm corresponding to a mode spacing of 1 GHz, single mode operation should be possible with careful alignment.

The linewidth of the dye laser output was measured using a 3cm solid Fabry-Perot etalon and an EG & G Reticon photodiode array as shown in Figure 2.8. The oscillator was operated just above threshold by aperturing the pump beam, and a single amplifier stage was used to increase intensity to a level such that the Fabry-Perot fringes could be detected by the photodiode array. The Reticon was a 1024 element linear array with a pixel size of 25um, and was positioned to sample across a diameter of the fringe pattern. The free spectral range of the etalon was

$$\text{FSR} = \frac{c}{2nL} = 3.1 \text{ GHz}$$

and the finesse was approximately 10, giving a resolution limit of around 300MHz. The laser cavity length was approximately 15 cm giving a longitudinal mode spacing of 1 GHz. The measurements were taken with the dye laser operating in the red region of the spectrum, $\lambda = 630 \text{ nm}$ (Rhodamine 101).

It was found that with careful alignment, the oscillator operated reliably in a single longitudinal mode, as shown by the Reticon scan in Figure 2.9. In this case the measured linewidth was detector limited and was less than or equal to 300MHz. However, when pumped above threshold, oscillation occurred on two longitudinal modes, as shown in Figure 2.10,

incidence grating, ($1800 \text{ lines mm}^{-1}$) and a Littrow grating of $2400 \text{ lines mm}^{-1}$, both used in first order, the above equation yields a predicted linewidth of 3 GHz. Multi-passing will reduce this by a further 30% to approximately 2 GHz, showing that for a cavity length of 15 cm corresponding to a mode spacing of 1 GHz, single mode operation should be possible with careful alignment.

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It was found that with careful alignment, the oscillator operated reliably in a single longitudinal mode, as shown by the Reticon scan in Figure 2.9. In this case the measured linewidth was detector limited and was less than or equal to

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For close-to-threshold pumping and careful alignment, approximately 90% of the shots showed single longitudinal mode oscillation. Shot-to-shot fluctuations were greater for above threshold pumping, with two modes being most commonly present.

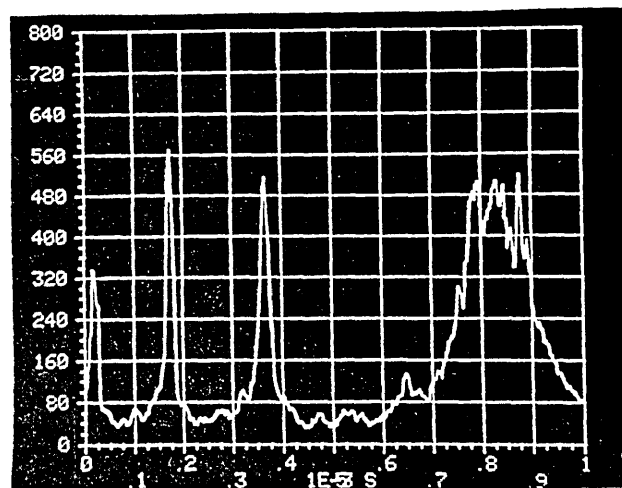


Figure 2.9 Fabry-Perot Fringes showing
Single Longitudinal Mode Operation of Dye Laser

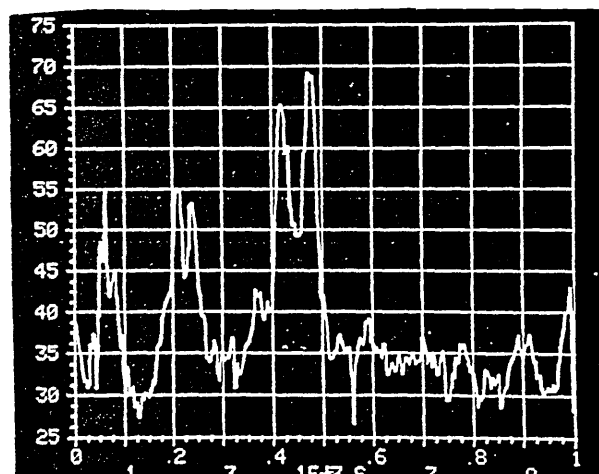


Figure 2.10 Fabry-Perot Fringes showing
Operation of Dye Laser in Two Longitudinal Modes

with the occasional trace of a third mode. For operation on two modes, the envelope linewidth (full width, half maximum) was about 1GHz.

Each oscillator was followed by a polariser to remove 50% of the unpolarised amplified spontaneous emission (ASE), a half-wave plate positioned so as to rotate the laser polarisation by 90° , so that the radiation was p-polarised with respect to the dye amplifier cells. This ensured small reflection losses at the Brewster angled, (θ), amplifier dye cells. Finally, a lens and pinhole arrangement was used to approximately collimate the laser beam and to eliminate ASE. These are shown in Figure 2.11 which is a side view of oscillator and amplifiers.

The laser beam was arranged to enter each amplifier dye cell close to the front face and to travel through the cell parallel to this face. Pump beams, directed onto each amplifier by the prism arrangement described in section 2.4.1, were focused by cylindrical lenses of focal length 10-15cm. The amplifying region in each amplifier was 1 cm long, limited by the size of the dye cell. The direction of the transverse pump line focus in the dye cell was tilted relative to the laser beam by a small angle, α , shown in Figure 2.11, which was typically around 5° . This ensured that the amplified laser signal and ASE from the amplifier were spatially separated so that ASE from amplifier 1 was not coincident with the gain region of amplifier 2. This was useful in ensuring a spectrally pure laser output from the amplifier chain. To ensure maximum pump power on the second amplifiers, additional cylindrical lenses with their axes perpendicular to the main focusing lenses were sometimes used in the second amplifier pump beams.

The division of pump power between the amplifiers is shown in

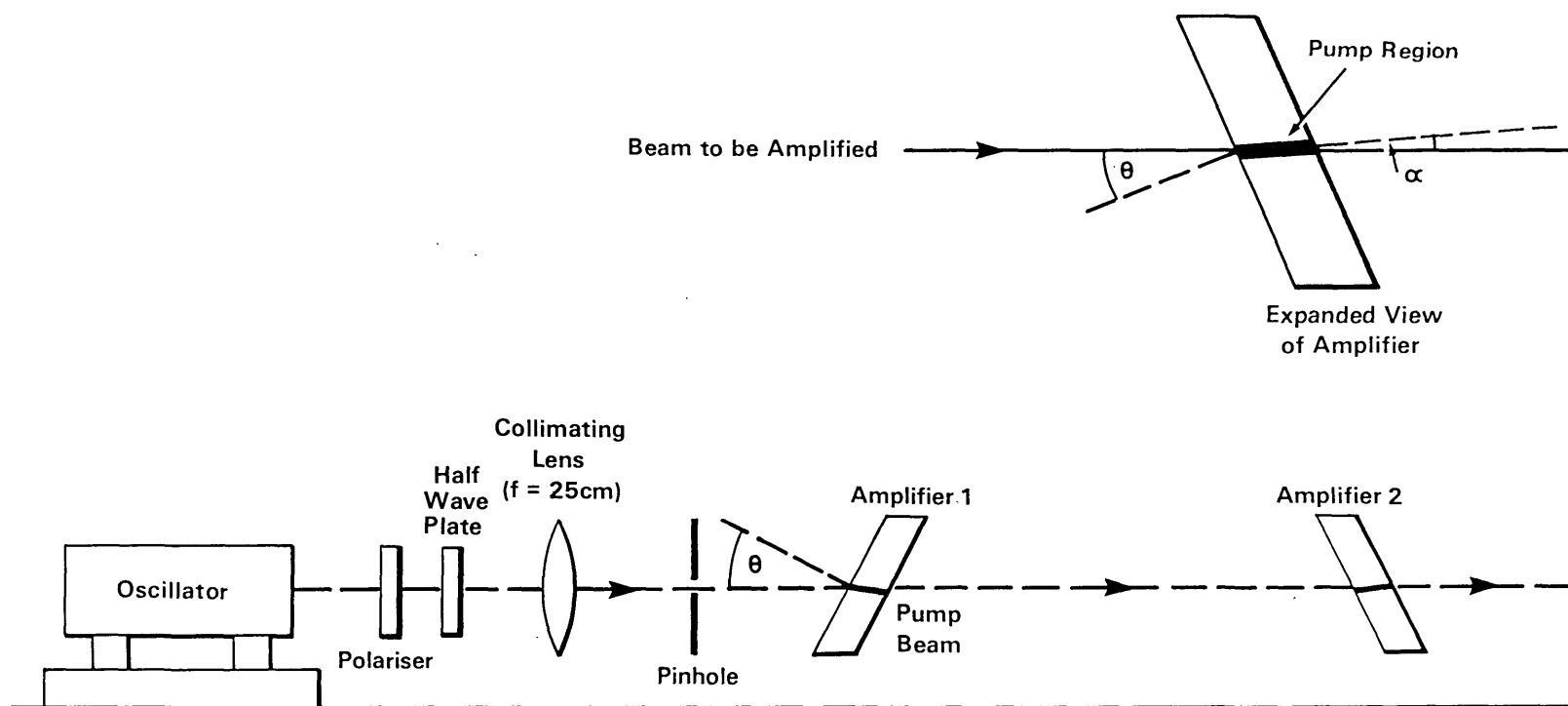


Fig 2.11 Side View of Dye Oscillator and Amplifiers

Table 2.2. These ratios could be altered to increase the pump energy available for pumping the second amplifier. This was the case when only one dye laser was being pumped for the two-photon-resonant three-photon ionisation experiments described in Chapter 4 to be carried out. Only the green ($\lambda = 499\text{nm}$) dye laser was used.

The dye concentrations for oscillators and amplifiers were chosen to give pump absorption depths which lead to laser output with as circular an output beam as possible. It should be noted, however, that TEM_{00} mode operation was not achieved in this transverse pumping arrangement. Accordingly, for focusing of the dye laser radiation, focal spot sizes cannot be calculated using Gaussian beam expressions. Each dye laser had two separate dye circulation systems, one for the oscillator and first amplifier which operate well with dyes of the same concentration, and one for the second amplifier. In general, the concentration used in the oscillator and first amplifier was that recommended by Lambda Physik for excimer pumping and that in the second amplifier was a factor of 2-3 lower [Lambda Physik technical data]. The dyes, solvents and concentrations used are summarised in Table 2.3. The dye solutions were replaced every 4 - 6 weeks for the green laser and weekly for the blue.

The amplification of the first amplifiers was in the region of 200-400. In general, there were no optical elements between the amplifiers, the distance between them (approximately 30cm) being sufficient to ensure that the ASE and laser signal were well separated before entering the second amplifier. When operating the blue dye laser, ($\lambda = 401.73\text{nm}$), the wavelength required by the experiment was in the wings of the available

Dye	Solvent	Concentration	
		Oscillator and First Amplifier	Second Amplifier
Coumarin 307 ($\lambda = 499.62\text{nm}$)	Ethanol	10^{-2}M	$4 \times 10^{-3}\text{M}$
Coumarin 30 ($\lambda = 499.62\text{nm}$)	Ethanol	not used	$3 \times 10^{-3}\text{M}$
Diphenylstilben (DPS) ($\lambda = 401.73\text{nm}$)	Dioxan	$6 \times 10^{-4}\text{M}$	$3.5 \times 10^{-4}\text{M}$
PBBO ($\lambda = 401.73\text{nm}$)	Dioxan	10^{-3}M	not used

Table 2.3 Summary of Dyes, Solvents and Concentrations

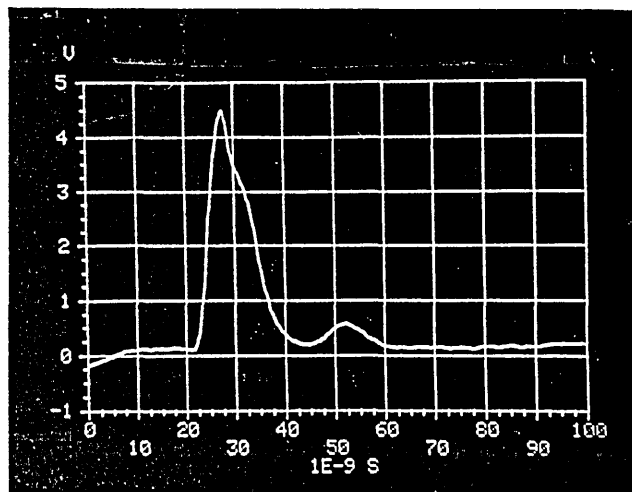


Figure 2.12 Temporal Structure of Green Dye Laser Output

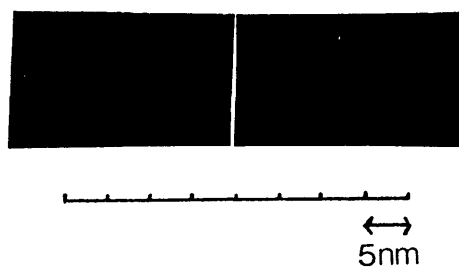


Figure 2.13 Spectral Content of Green Dye Laser Output

dye bandwidth. It was then found that it was difficult to suppress amplification of ASE from the first amplifier in the second amplifier stage. This problem was solved by inserting a dispersing prism and pinhole after the first amplifier. Since the laser and ASE signals were spectrally separated by approximately 4nm for DPS and 6nm for PBB0, this caused sufficient spatial separation of the laser output and ASE, that the ASE from the first amplifier was not coincident with the gain region in the second amplifier. This arrangement is described in more detail in section 6.4.1, together with details of the exact combinations of dyes used.

The amplification of the second amplifiers was approximately 10. The gain here was saturated as shown by the fact that reduction of input signal did not reduce the output of the amplifier. In general, the division of pump power between the amplifiers (Table 2.2) was arranged so that the signal from the first amplifier was slightly more than that required to saturate the second. This arrangement left the maximum pump power possible available for the second amplifier, hence optimising the efficiency of the pumping system, while allowing for some reduction in dye performance without affecting overall laser performance.

Figure 2.12 shows the output pulse from the second amplifier of the green dye laser, pumped by the Lambda Physik laser, measured using a vacuum photodiode (S1 photocathode) and displayed on the Tektronix 7912AD digitiser.

The output of the dye lasers was observed using a 1m spectrograph to ensure that the output was truly in narrow bandwidth and that ASE was suppressed. Figure 2.13 shows the 499nm laser output and indicates that this is indeed the case.

The observed 'width' of the line on the figure is limited by saturation of the film. As described in Section 2.4.1, two different commercial XeCl* discharge pumped excimer lasers were used to pump the dye lasers during the course of this work. The outputs were monitored using a vacuum photodiode with S1 photocathode and a Tektronix 7912AD Transient digitiser of bandwidth 500MHz. A temporal resolution of $\sim 2\text{ns}$ was expected. The performance of the dye lasers is summarised in the Table 2.4 for pumping by both the Lambda Physik EMG-101-E and Lumonics TE-860-4 lasers.

The performance of the dye lasers were comparable, with Lambda Physik and Lumonics pump lasers, in terms of output power. The main differences were:-

(i) Pulse duration.

The longer Lumonics laser pulse durations (see section 2.4.1) resulted in longer dye laser pulses. These are detailed in Table 2.4. In addition, some longitudinal mode beating was evident in the Lumonics pumped dye outputs. However, the depth of modulation was small, indicating the presence of one dominant mode. The mode beating could generally be almost totally eliminated by careful dye oscillator alignment and close-to-threshold pumping.

(ii) Percentage of pump laser output used for pumping.

The beam cross-sectional area of the Lumonics laser was almost double that of the Lambda Physik laser (see Table 2.1). Physical constraints imposed by the design of the optical system meant that the whole Lumonics beam could not be utilised for dye pumping. Hence the higher laser outputs which may have been expected as a result of a 300% increase in pump power were not fully realised.

Dye Laser	Pump Laser			
	Lambda Physik EMG-101-E		Lumonics TE-860-4	
	Energy after 2nd amp	Pulse duration	Energy after 2nd amp	Pulse duration
499.26nm (Coumarin 307)	1.5-2 mJ	8-10 ns	2-2.5 mJ	15-20 ns
401.73nm (DPS)	1 mJ	5-8 ns	1.5 mJ	10-12 ns
401.73nm (PBBO + DPS)	1 mJ	5-8 ns	1.5 mJ	10-12 ns

Table 2.4 Summary of Dye Laser Performance

2.4.3 Second Harmonic Generation in Potassium Pentaborate

The radiation at 249.63nm was generated by frequency doubling the output from one dye laser tuned to 499.26nm. To compensate for the low conversion efficiency of the doubling crystal used, the UV signal was then amplified in a Krypton Fluoride excimer amplifier. This amplification is described in section 2.4.4.

The crystal used for the second harmonic generation, Potassium Pentaborate, ($\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ or more briefly KB5), was first shown to be useful as a frequency doubling crystal for wavelengths as short as 217.3nm in 1975. [Dewey et al, 1975]. Until recently, Ammonium Dihydrogen Phosphate (ADP), Potassium Dihydrogen Phosphate (KDP) and their deuterated derivatives have been popular frequency doubling crystals. ADP, for example has sufficient birefringence for phase matching down to 244.2nm [Dunning et al, 1973]. Lower power second harmonic generation has been observed in Lithium Formate Monohydrate [Dunning et al, 1973] at wavelengths down to 225nm. However, the conversion efficiency was limited by the crystal's absorption in the ultra-violet. More recently, crystalline organic materials have emerged as efficient frequency doublers capable of operation well into the ultra-violet. One such crystal is Urea [Halbout et al, 1979], which typically gives conversion efficiencies of around 10%. However, there are problems with growing crystals of such materials of sufficiently good optical quality. Consequently supply is short and the material available is expensive.

As a KB5 crystal was available for the experiments, it was used despite its low conversion efficiency (approximately 1%), as compensation for this was available via the KrF* excimer amplifier.

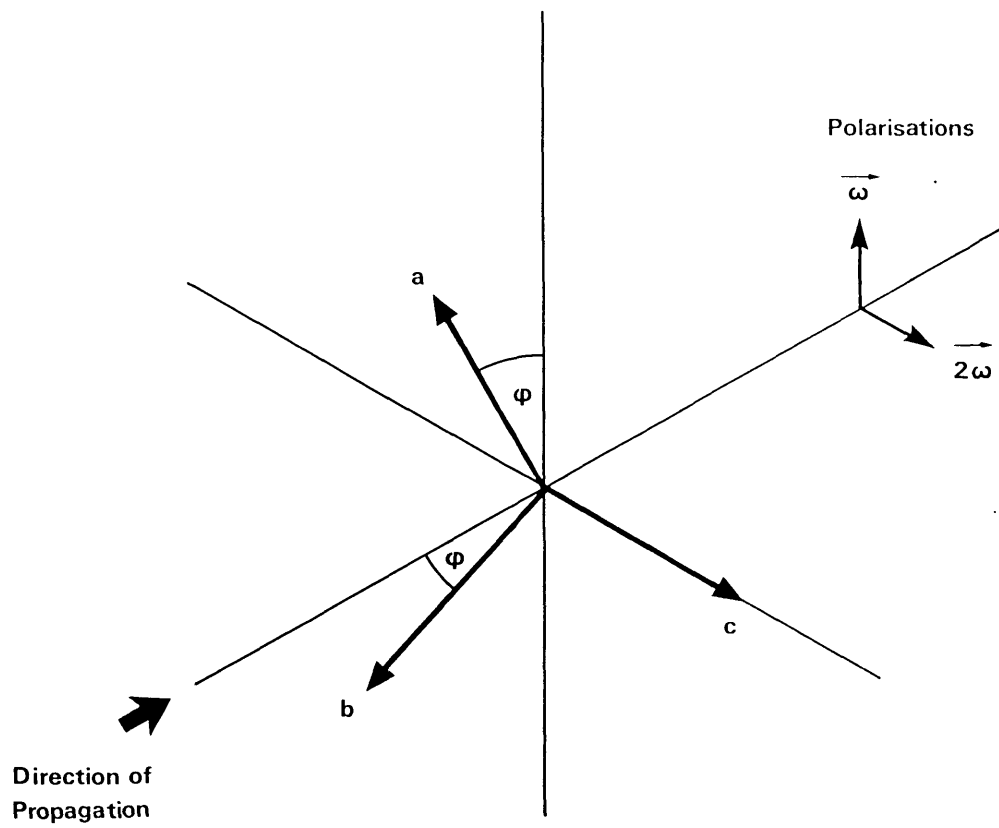


Fig 2.14 Orientation of KB5 Crystal for Second Harmonic Generation

KB5 is a biaxial crystal and Figure 2.14 shows the crystal orientation used for second harmonic generation. The refractive indices n_a , n_b , and n_c for light polarised in the direction of the crystal axes labelled a, b, and c respectively, are shown as a function of wavelength in Figure 2.15. An incident beam polarised in the a-b plane generates its second harmonic polarised in the c- direction. Therefore the velocity of the second harmonic radiation will be $c/n_c(2\omega)$.

For efficient second harmonic generation, the fundamental and second harmonic waves must be phase-matched, i.e. their propagation velocities must be equal. The velocity of the fundamental beam propagating in the a-b plane at an angle φ to the c-axis is $c/n(\omega)$ where the refractive index $n(\omega)$ is given by

$$[n(\omega)]^{-2} = [n_b(\omega)]^{-2} \sin^2\varphi + [n_a(\omega)]^{-2} \cos^2\varphi$$

Therefore the velocities of the fundamental and the second harmonic beams are equalised when $\varphi = \varphi_m$, the phasematching angle, where

$$\sin^2\varphi_m = \frac{[n_c(2\omega)]^{-2} - [n_a(\omega)]^{-2}}{[n_b(\omega)]^{-2} - [n_a(\omega)]^{-2}}$$

Figure 2.16 [after Dewey, 1976] shows the required phase-matching angle for generating wavelengths between 217 and 315nm.

The crystal available for this experiment was a cube of side approximately 10mm, which was mounted in a cell with quartz windows and immersed in phase-matching fluid to protect it from moisture since the crystal is hygroscopic. The crystal orientation was appropriate for generation of radiation at 249.63nm. The crystal was mounted on a kinematic rotation

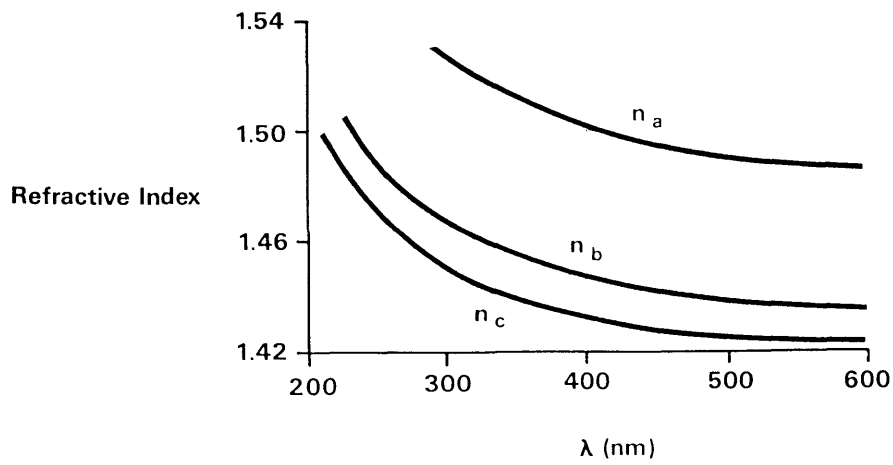


Fig 2.15 Refractive Indices of KB5 (After Dewey et al ,1975)

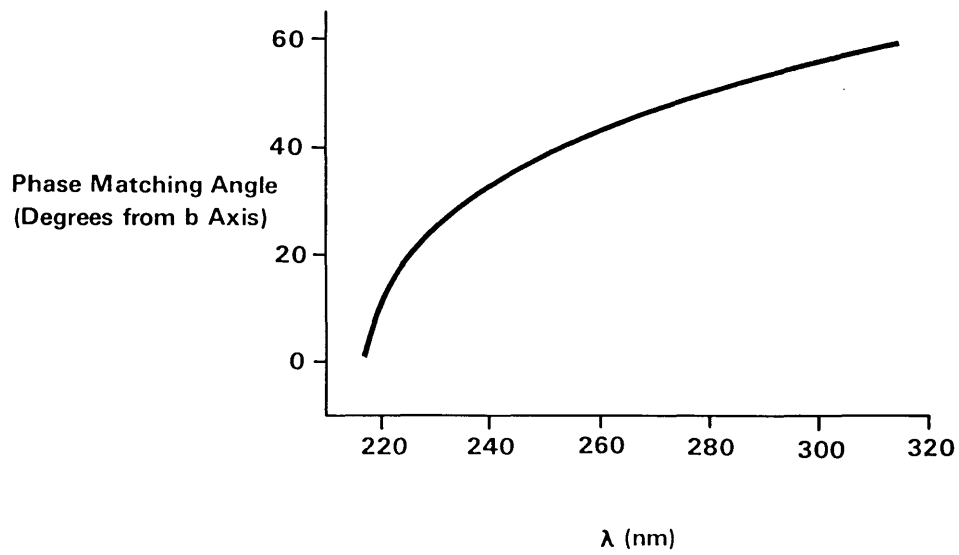


Fig 2.16 Phase Matching Angle against Output Wavelength for KB5 Crystal (After Dewey, 1976)

stage to allow optimisation of its orientation to φ_m .

Initially, the light from the Coumarin 307 dye laser, tuned to 499.26nm, was focused into the crystal using a spherical lens of 15cm focal length, and the ultra-violet radiation generated recollimated by a quartz spherical lens of approximately 20cm focal length. The focal length of the input lens was limited to a minimum of 15cm as it was found that the higher focal power densities produced by shorter focal length lenses caused damage to the crystal. The damage threshold of KB5 is not well documented although Dewey et al, 1975, observed no damage at power densities of up to $1\text{GW}/\text{cm}^2$ for a fundamental input beam at 450nm operating at 15 Hz repetition rate. It is estimated that power densities of at least this magnitude are produced when the dye laser is focused by, for example, a 10cm focal length spherical lens. Assuming a focal spot diameter of approximately 25 μm and an energy of 1mJ in a 10ns pulse, the power density is $20\text{GW}/\text{cm}^2$.

It can be seen from Figure 2.14, that to achieve phase matching the angle that the beam makes with the a-b plane is critical; conversely, the angle which the beam makes with the c-axis is irrelevant. Hence, for a spherically focused beam, second harmonic generation is only phase-matched for a central fan of the beam which is perpendicular to the a-b plane; this is illustrated in Figure 2.17. The fact that only a portion of the input beam contributes to the generation of the second harmonic not only means that maximum conversion efficiency is not being achieved, but also results in the output beam being elliptical in shape. This can cause problems in alignment of the second harmonic beam with beams of more circular cross-sections in, for example, four-wave mixing experiments [Hutchinson and

stage to allow optimisation of its orientation to φ_m .

Initially, the light from the Coumarin 307 dye laser, tuned to 499.26nm, was focused into the crystal using a spherical lens of 15cm focal length, and the ultra-violet radiation generated recollimated by a quartz spherical lens of approximately 20cm focal length. The focal length of the input lens was limited to a minimum of 15cm as it was found that the higher focal power densities produced by shorter focal length lenses caused damage to the crystal. The damage threshold of KB5 is not well documented although Dewey et al, 1975, observed no damage at power densities of up to 1GW/cm² for a fundamental input beam at 450nm operating at 15 Hz repetition rate. It is estimated that power densities of at least this magnitude are produced when the dye laser is focused by, for example, a 10cm focal length spherical lens. Assuming a focal spot diameter of approximately 25um and an energy of 1mJ in a 10ns pulse, the power density is 20GW/cm².

It can be seen from Figure 2.14, that to achieve phase matching

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For a biaxial crystal such as KB5, it is not completely accurate that the angle made with the c-axis is irrelevant, since the refractive index at the fundamental frequency will be altered if the angle between the propagation direction and the a-b plane becomes non-zero. Let this angle be θ . However, it can be shown by calculus that the rate of change of refractive index for the fundamental with respect to θ is substantially smaller (factor of 50) than its rate of change with respect to φ , for the angles used in practice. This theoretically justifies the experimental approach taken and the results observed.

Alternatively, the observed elliptical second harmonic beam profile may be due to walk-off of the fundamental and second harmonic beams as they traverse the crystal.

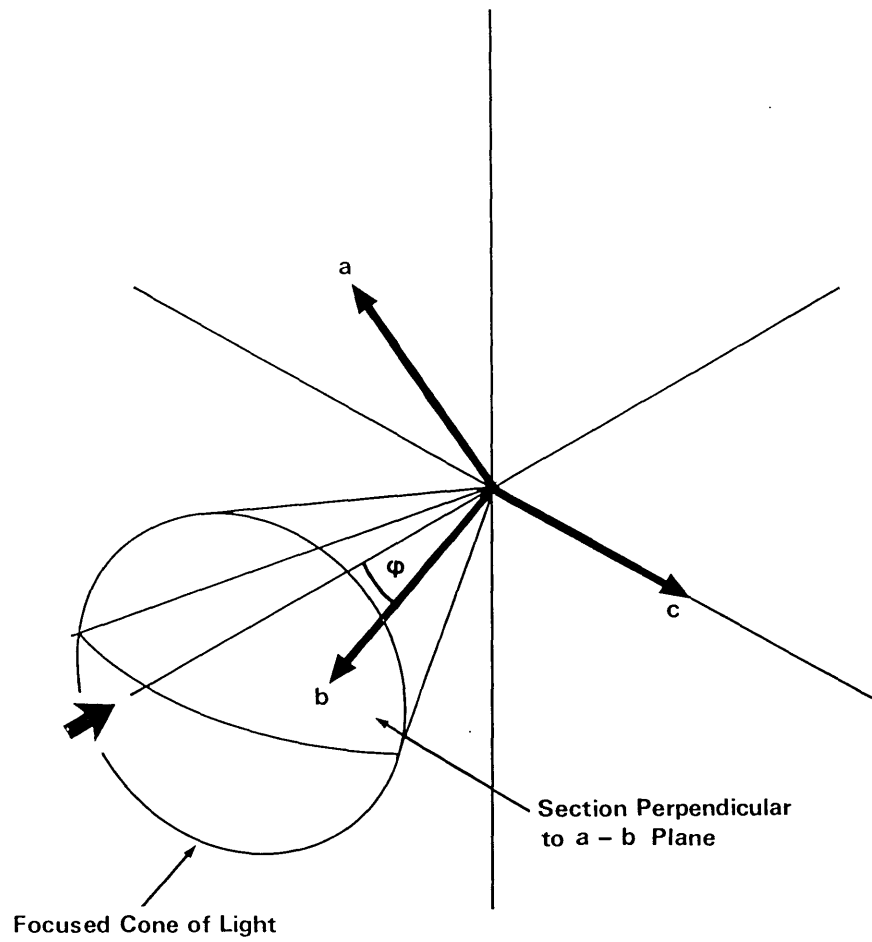


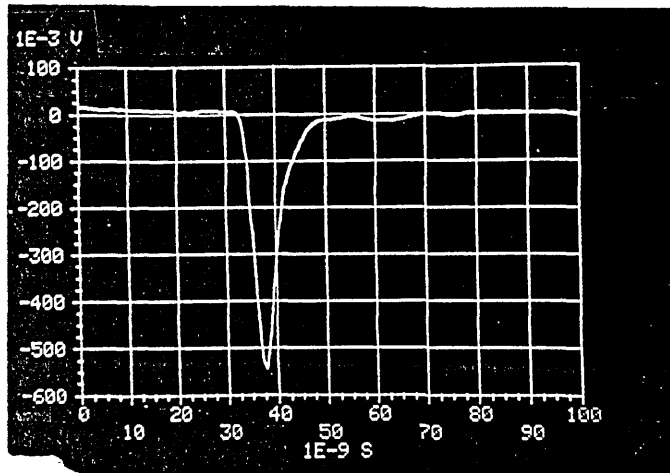
Fig 2.17 Phase - Matching in KB5 for a Focused Beam

Thomas, 1983]. Additionally, analysis of results becomes difficult as most of the theoretical work on non-linear processes considers circularly symmetric Gaussian beams.

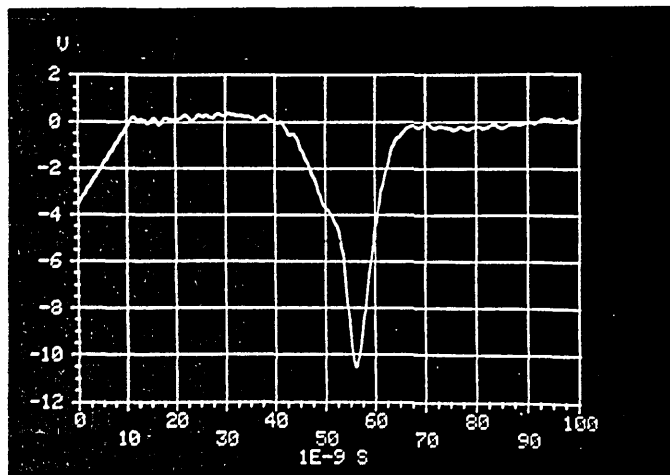
A more satisfactory arrangement uses a cylindrical lens to focus the dye laser radiation into the doubling crystal. By focusing only in the c-axis direction, second harmonic generation occurs for the entire beam as the beam remains collimated with respect to the a-b plane, i.e. the angle which the beam makes with the a-b plane is constant for all parts of the beam. This is the phase matching angle, φ_m . A line focus also produces lower power densities in the crystal than a point focus reducing the likelihood of damage to the crystal. When the ultra-violet radiation generated is recollimated by a second cylindrical lens with its axis parallel to the focusing lens, a beam of circular cross-section can be produced.

Experimentally, a glass cylindrical lens of focal length 10cm was used to focus the dye laser into the crystal and a quartz cylindrical lens of approximate focal length 15cm was used for recollimation. The focal length of the recollimating lens was longer than that of the focusing lens in order to produce a circular output beam, taking account of the natural divergence of the beam in the direction perpendicular to the power of the cylindrical lenses.

After traversing the crystal, the 499.26 nm fundamental beam was removed by UV filter, leaving the 249.63nm second harmonic radiation. Due to the quadratic dependence of the second harmonic intensity on the fundamental intensity, the duration of the second harmonic pulse was shorter than that of the fundamental. This was ~ 7 ns when the dye laser pump source was the Lambda Physik laser and ~ 13 ns for the Lumonics pump laser.



(a) before amplification



(b) after amplification

Figure 2.18 Photodiode Traces of Second Harmonic Pulses

Examples of photodiode traces of the unamplified UV output from the doubling crystal, and after amplification with optimum synchronisation (see following section), are shown in Figures 2.18(a) and (b) respectively. The measurements were made using a quartz windowed UV vacuum photodiode. Absolute measurement of the unamplified second harmonic energy was not possible. The conversion efficiency of the crystal was approximately 1%. Together with reflection losses at the crystal cell windows and a transmission of the UV filter of approximately 50%, this corresponds to a UV output of only approximately 0.45% of the dye laser input, i.e. for an average input from the dye laser of 1.5mJ, the second harmonic energy available for amplification was only 7uJ.

2.4.4 Amplification of UV Radiation in a KrF* Excimer Laser

The low power 249.63nm radiation generated by the Potassium Pentaborate frequency doubling crystal was amplified on a single pass through a Lambda Physik EMG 101 KrF* excimer amplifier, synchronised with the XeCl* excimer pump laser. This was achieved by firing both excimer lasers from an external trigger signal with a fast rising edge (few ns) and relayed to the lasers through lengths of cable appropriate for the delay required. Gain was present in the amplifier for a period of only 12-15ns which was approximately equal to the duration of the pulse to be amplified. Hence, low jitter synchronisation was essential to ensure amplification which was reproducible from shot-to-shot. With the thyatron high voltage switches used in the lasers, a temporal jitter of ~ 2 ns was achieved, which was expected to be adequate to give shot-to-shot reproducibility. The period over which gain was available from the amplifier was not sufficient to allow

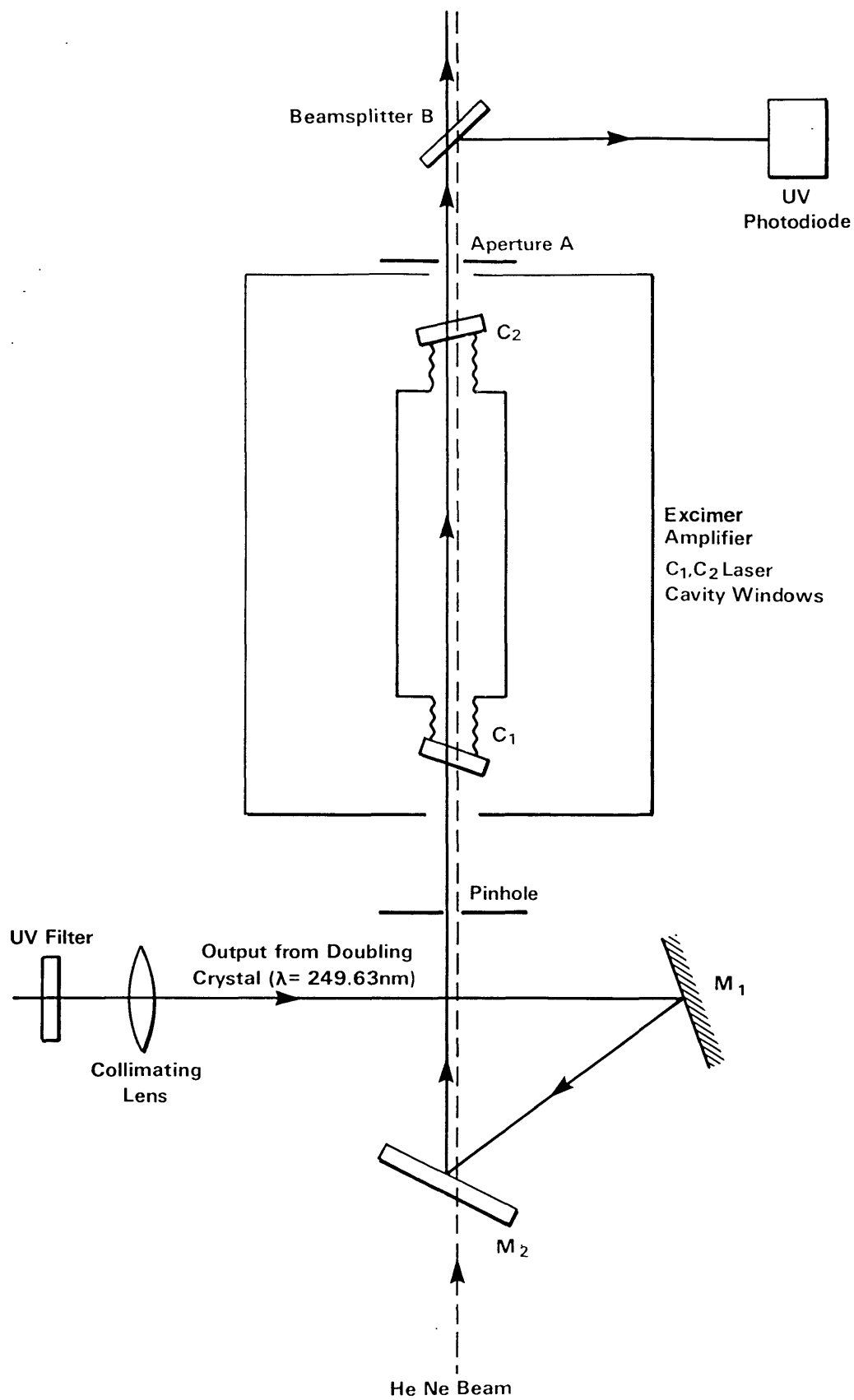


Fig 2.19 KrF Excimer Amplifier

reproducible double-pass amplification.

A He-Ne laser beam ($\lambda = 632.8\text{nm}$) was directed along the centre of the discharge volume of the amplifier to provide a reference for alignment of the second harmonic radiation from the doubling crystal. This is shown in Figure 2.19 together with the two mirrors used for alignment, M_1 and M_2 . M_2 was a dielectric reflector coated for 100% reflectivity at KrF* wavelength of 248nm which allowed the introduction of the unexpanded He-Ne beam into the system by transmission. For clarity the UV and He-Ne beams are shown displaced with respect to each other in Figure 2.19. They were, in fact, aligned to be co-propagating.

The recollimating cylindrical lens after the KB5 crystal was defocused slightly to allow the 249.63nm beam to diverge slightly while traversing the amplifier to increase energy extraction efficiency. The beam passed through a pinhole before entering the amplifier. The purpose of this was to prevent backward travelling fluorescence from the amplifier being focused back into the frequency doubling crystal. The beam diameter at the exit from the amplifier was approximately 8mm, which is comparable with the vertical dimension of the gain region. The amplifier cavity end windows were angled with respect to the incoming beam, at approximately 10° in the horizontal, to prevent feedback between them. An aperture (A in Figure 2.19) removed the amplified spontaneous emission, and an uncoated quartz flat (B in Figure 2.19) acted as a beam splitter to provide a monitor of the amplified output on the UV vacuum photodiode. Attenuators (metal gauze) placed in front of the photodiode ensured that the amplified signal remained within the limits of the linear response of the photodiode. In

this way the gain of the amplifier could be estimated. For collecting data in the experiments described in Chapters 4 and 6, the useful lifetime of a gas-fill in the excimer amplifier was found to be between 2 and 4 hours.

It was found that despite the low temporal jitter in the synchronisation of the injected UV signal and amplifier gain, the output from the amplifier did not show as good shot-to-shot reproducibility as may have been expected.

The ideal mode of operation of such an amplifier is that in which the gain of the amplifier is saturated by the input pulse. This ensures that the final output power from the amplifier is insensitive to slight variations in the input power, arising, for example, from deterioration of the dye laser output due to either pump laser power reduction or dye deterioration, or from tuning of the dye laser without corresponding re-optimisation of the doubling crystal phase-matching angle. In addition, if the amplifier is well saturated, the output is also relatively insensitive to small variations in amplifier pumping power. On the other hand, in the case when the amplifier is unsaturated, if any of the fluctuations mentioned above occur, then these are simply amplified by the exponential gain of the amplifier.

It is postulated that this is the case with the experimental arrangement used. After being collimated and directed into the amplifier, the energy in the unamplified UV beam was estimated to be approximately 4uJ. It was estimated by photodiode measurements with calibrated attenuators, that amplification on a single pass of the amplifier was in the range 50-100. For an output energy of 0.2mJ in a 10ns pulse and output beam area of 0.5cm^2 , the energy density is $0.4\text{mJ}/\text{cm}^2$. From Szatmari and

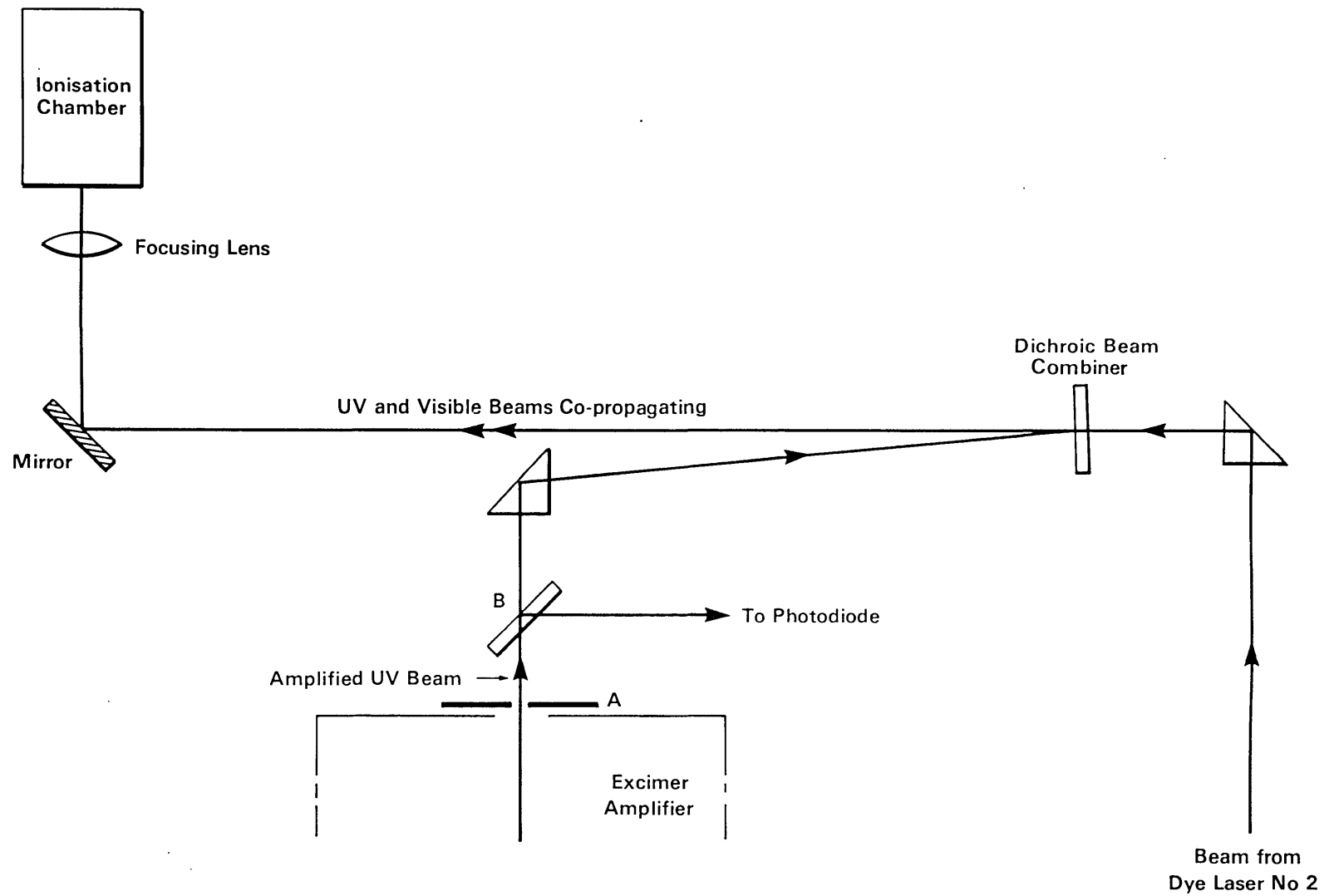


Fig 2.20 Beam Combination

Schafer, 1984, the saturation energy is approximately 2.0 ± 0.2 mJ/cm². Hence it is clear that in this mode of operation the amplifier was running below an output energy at which saturation occurred. Fluctuations in output power could result from this.

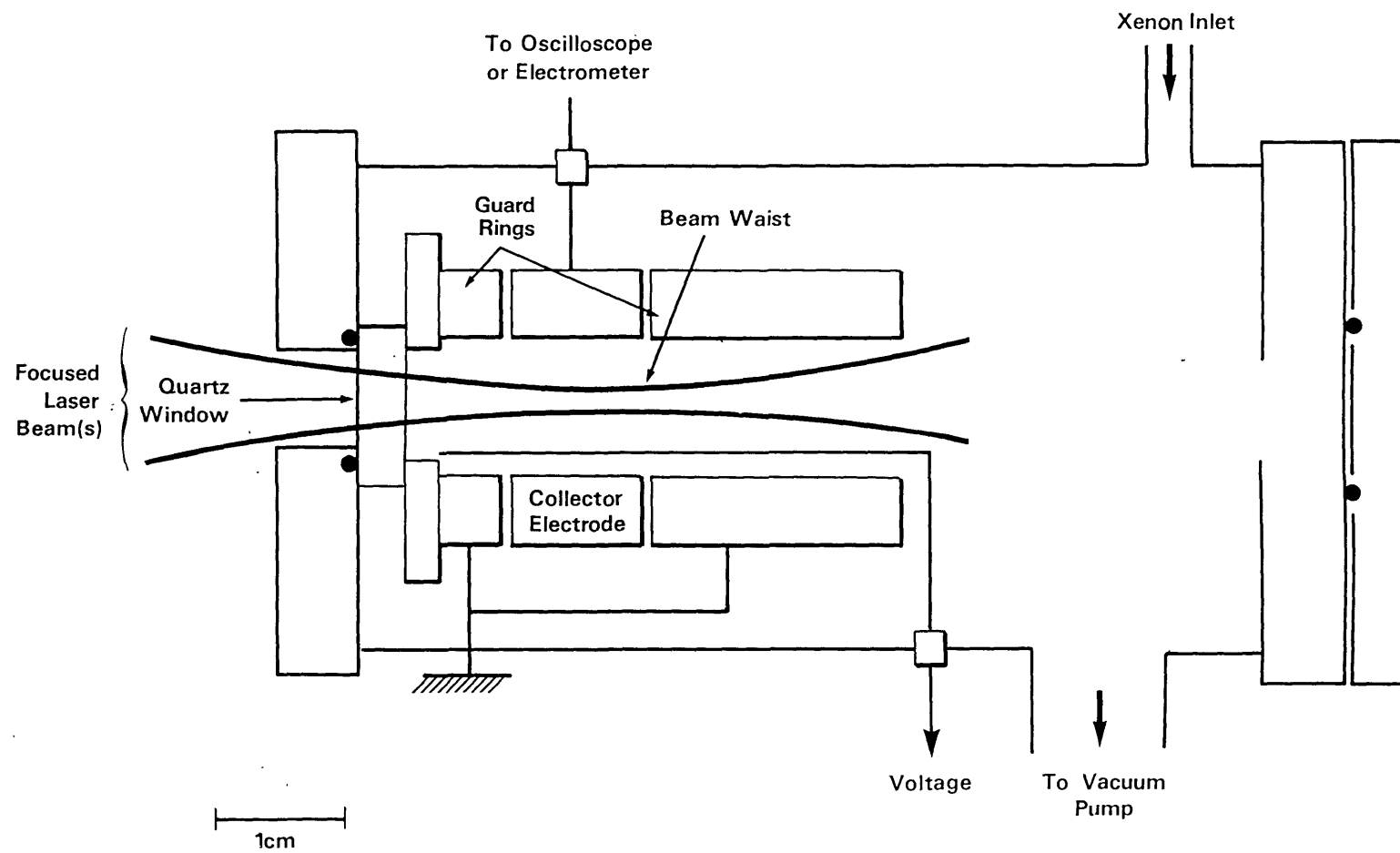
2.4.5 Beam Combination and Ion Detection

For the laser-induced autoionisation experiment described in Chapter 6, it was necessary to overlap the ultraviolet radiation at 249.63nm and the blue dye laser radiation at 401.73nm, and detect the Xenon ions generated by the two beams. The overlap was achieved by alignment of the beams along a common path and focusing arrangements described in detail in section 6.4.2. The Xenon ions were detected by a simple ionisation chamber.

The two beams were combined at a dielectric coated mirror, shown in Figure 2.20, which was nearly 100% reflecting for normal incidence at the ultra-violet wavelength and 95% transmitting at the blue wavelength (neglecting reflection losses). A 45° right angle prism turned the 249.63nm beam emerging from the excimer amplifier and directed it at almost normal incidence onto the dichroic mirror. Another 45° prism mounted on a translation stage and tilting mount was used to turn the beam from the visible dye laser which was travelling parallel to the UV beam traversing the amplifier, and direct it through the dichroic mirror. Once co-propagating, the beams were directed by an aluminium mirror into the ionisation chamber with appropriate focusing optics.

The apparatus used to detect and measure the ionisation of the Xenon atoms consisted of a simple charge detector able to

Fig 2.21 Ionisation Chamber



collect and count the electrons or ions produced by photoionisation. The detector was housed in a photoionisation chamber constructed from Vacuum Generator stainless steel ultra-high vacuum fittings. This chamber was originally used for other experiments in our laboratory where typical experimental pressures of 10^{-1} - 10^{-3} mbar were used, and correspondingly evacuation to pressures in the region of 10^{-6} mbar was required. For the experimental work reported in this thesis working pressures were 2-10 torr of Xenon and evacuation to approximately 10^{-2} torr was typical before filling.

A schematic diagram of the ionisation detector is shown in Figure 2.21. It consisted of three collinear cylindrical electrodes of 12mm internal diameter. Dimensions were small to reduce path lengths and the possibility of electron-ion recombination. The central electrode collected charge over a well-defined length. The outer electrodes were separated from the collector electrode by 0.25mm thick mylar spacers. The purpose of the two outer electrodes was to provide a uniform electric field inside the central electrode and to serve as earthed guard rings so that the length of the central electrode was clearly defined. A 0.7mm thick stainless steel wire, slightly displaced from the collector axis carried a small voltage (up to +/- 400V).

Although the experimental procedure is described in Chapter 4, the detector operation is illustrated in Figure 2.22 which shows two-photon-resonant three-photon ionisation signal versus ionisation chamber voltage. The UV laser intensity was $1\text{GW}/\text{cm}^2$ and the Xenon pressure 10 torr. For positive voltages there is no evidence of saturation of the charge collected with voltage, which would indicate collection of the total charge generated.

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A positive voltage indicates that the wire is at a positive potential with respect to the collector electrode, which in these circumstances will collect generated ions. Conversely, a negative voltage on the wire corresponds to the collector electrode being the a collector of generated photo-electrons. Hence, in the usual mode of operation of the chamber, (wire at negative potential with respect to collector), electrons are collected and generate the detected signal.

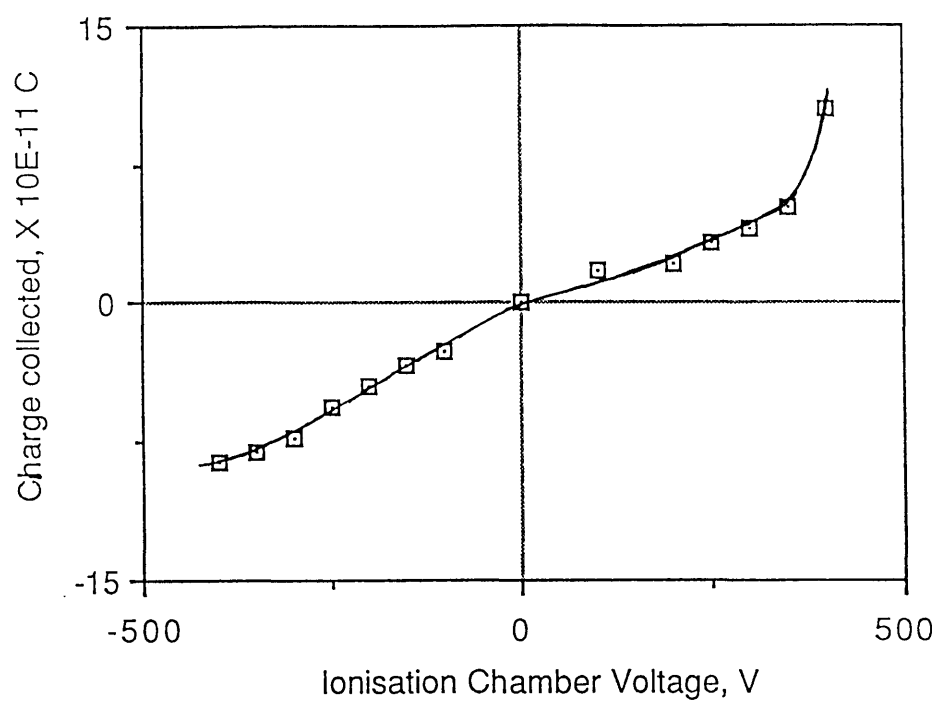


Figure 2.22 Ionisation Chamber Voltage Characteristic

Indeed the rapid increase in charge at $V = 400V$ is attributed to avalanching in the chamber; this is substantiated by the increased fluctuations in the charge collected from shot-to-shot at this voltage. Conversely, for negative voltages, there is no evidence of avalanching and a flattening out of the charge collected versus voltage is observed. A working voltage of $-350V$ was used as reliable operation at $-400V$ could not be guaranteed due to occasional arcing in the chamber.

A simple gas handling system, constructed from quarter inch plastic and stainless steel tubing and Swagelock vacuum fittings allowed the cell to be evacuated by an Edwards rotary pump to a pressure of approximately 10^{-2} torr (measured using an Edwards Pirani gauge) and filled with known pressures of Research Grade Xenon up to 1 atmosphere. The gas handling system and ionisation chamber were tested to be leak-free.

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CHAPTER 3

SATURATION OF TWO-PHOTON RESONANTLY-ENHANCED NON-LINEAR PROCESSES.

3.1 Introduction

This chapter contains an overview of saturation mechanisms which may occur in two-photon-resonant processes in Xenon, such as resonant multiphoton ionisation and non-linear mixing. The results of the analysis presented in this chapter are used in Chapter 4 to interpret experimental results of two-photon-resonant three-photon ionisation and associated processes in Xenon.

Saturation is an inherent feature of resonantly-enhanced non-linear processes, being caused by any mechanism which limits the efficiency of the process of interest. In general terms, saturation occurs because there has been some significant change in the non-linear medium itself during the irradiation required to produce the non-linear process under examination. This description may also encompass the effects of competing processes both linear and non-linear. Effectively this results in a modification to the initial conditions, important both for parametric and non-parametric processes. It is also found that such changes usually only occur for high laser powers and hence are normally neglected when calculating process efficiencies.

Experimentally, saturation effects in resonant processes manifest themselves in two ways. Firstly, the dependence of the generated signal on the input signals will depart from that expected from simple non-linear theory. For example, in two-photon-resonant third harmonic generation, it is found that

close to the resonance, the generated signal no longer shows a cubic dependence on the fundamental power when saturation is present. Secondly, the resonance linewidth will be broadened for the following reason. Tuning through a resonance, the effect of saturation will be greatest exactly on resonance. This causes the maximum enhancement, expected from the simplistic approach, to be suppressed relative to the wings leading to a broadened lineshape.

Attaining an exact two-photon resonance has an advantage over single or three-photon resonances in enhancement of non-linear processes, namely the lack of linear absorption and associated dispersion [Wynne and Sorokin, 1975]. For this reason, such resonances have been used extensively by researchers aiming to improve the efficiency of third order non-linear processes, such as third harmonic generation [see for example Leung, Ward and Orr, 1974 or Egger et al, 1980] and four-wave mixing [see for example Hodgson, Sorokin and Wynne, 1974 or Yui, Bonin and McIlrath, 1982].

Saturation of such two-photon resonantly-enhanced non-linear processes has been observed by several researchers. In particular, saturation of two-photon resonantly-enhanced third harmonic generation in Cesium vapour has been reported by Ward and Smith, 1975 and by Georges et al, 1976. Saturation of the same process in Thallium vapour has been reported by Wang and Davis, 1975. More recently, Hager and Wallace, 1982, and Hutchinson and Thomas, 1983, have observed the saturation of four-wave mixing, difference frequency generation, in Xenon.

One major factor leading to saturation of parametric processes is depopulation of the ground state and processes associated with non-zero populations of excited states. The depopulation

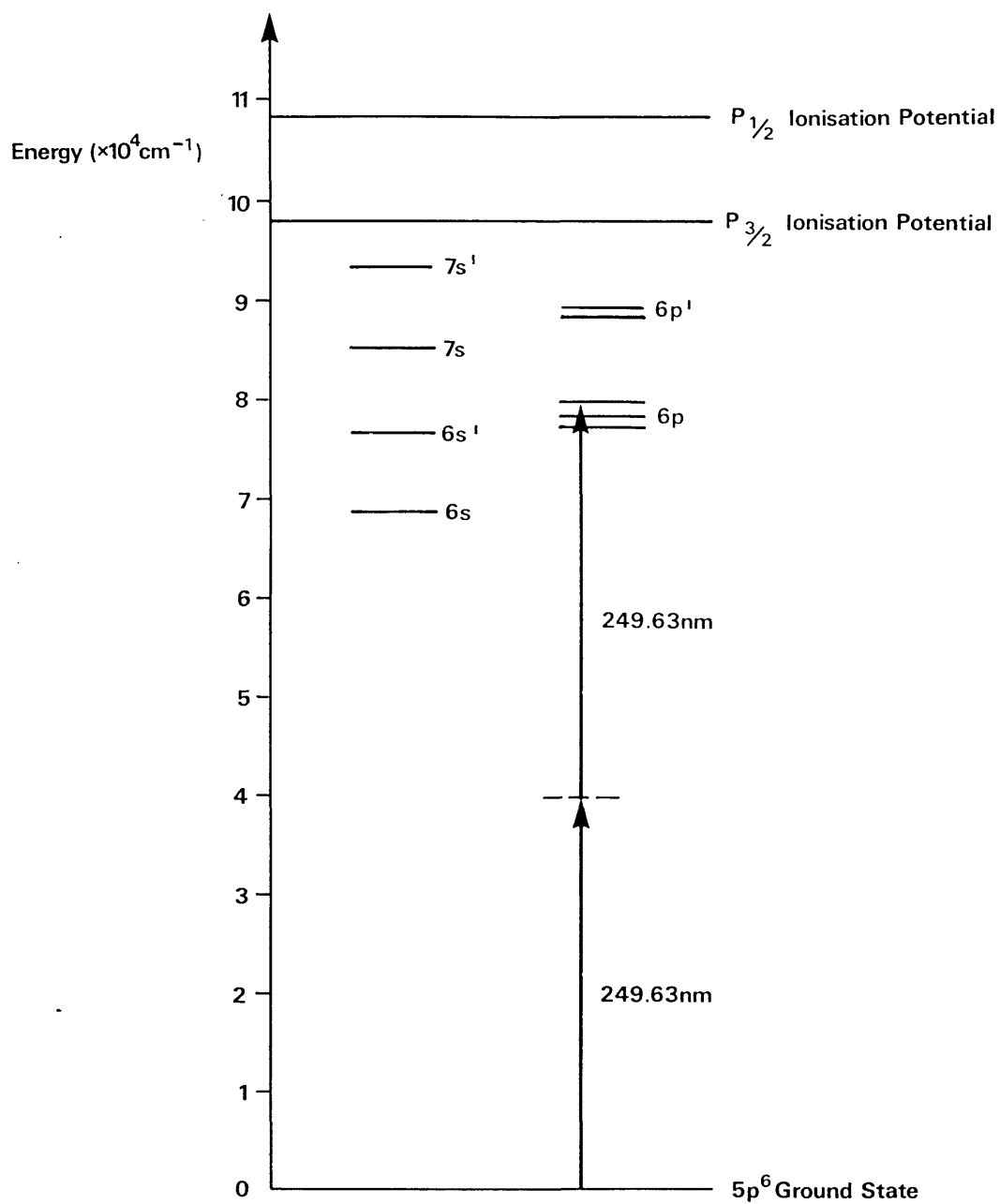


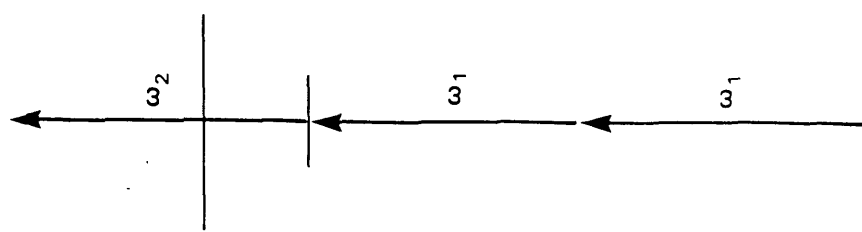
Fig 3.1 Xenon Partial Energy Level Diagram showing Two-Photon Resonance at 249.63nm with 6p, J = 0 State

of the ground state may lead to direct saturation resulting from the reduced number of ground state atoms available to participate in the process of interest. Alternatively, the redistribution of population can cause a change in the refractive index leading to the breaking of phase matching conditions. In addition, the population of excited states can lead to a variety of competing processes which can limit the efficiency of the desired process. The perturbation of atomic energy levels by strong electric fields, known as Stark effects, can also lead to saturation.

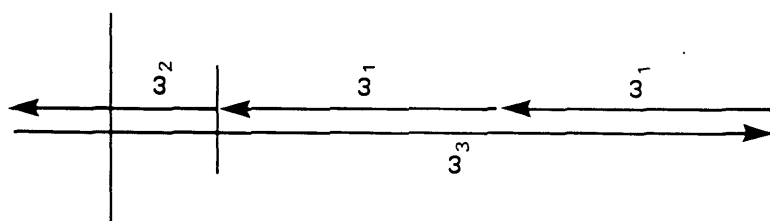
In general, the mechanisms which lead to saturation are intensity dependent. Hence the width of the saturated resonance will show an intensity dependence. In systems where one saturation mechanism dominates over a wide intensity range, then such dependence can be of use in identifying the saturation mechanism. However, it is often the case that a range of saturation mechanisms have effect in different intensity regions. The resonance linewidth will then show a more complicated and less easily interpretable intensity dependence.

3.2 Saturation Mechanisms in Two-Photon-Resonant Non-Linear Processes in Xenon

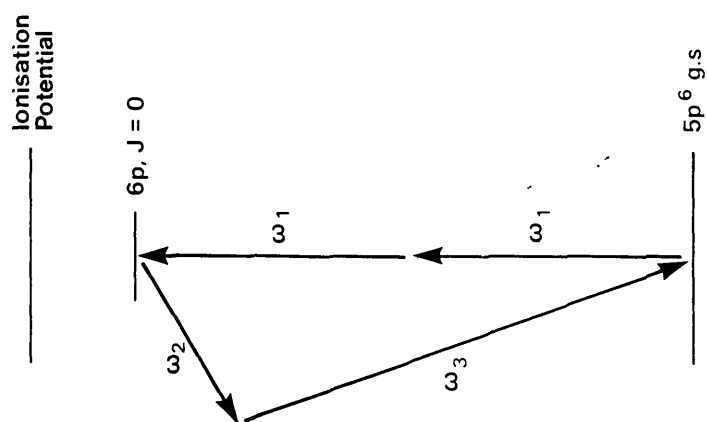
The discussion which follows is applied specifically to a two-photon resonance in Xenon. The two-photon-resonant state is the $5p^5 (2P^0_{3/2})$, $6p (J=0)$ state. Experimentally, this state is of interest because the photon energy required to achieve the two-photon resonance corresponds to a wavelength of 249.63nm which falls within the spectral gain bandwidth of the KrF* excimer, as discussed in Chapter 2. However, the principles of the discussion could be applied to any two-photon



Multiphoton Ionisation
 $\omega_2 \text{ can } = \omega_1$



Four Wave Mixing Sum
 Frequency Generation
 $\omega_3 = 2\omega_1 + \omega_2$
 THG if $\omega_2 = \omega_1$



Four Wave Mixing Difference
 Frequency Generation
 $\omega_3 = 2\omega_1 - \omega_2$
 Degenerate 4WM if $\omega_2 = \omega_1$
 then $\omega_3 = \omega_1$

Fig 3.2 Two-Photon Resonantly Enhanced Non-Linear Processes in Xenon

resonance.

The position of the two-photon resonance is shown on the Xenon partial energy level diagram in Figure 3.1 and some two-photon resonantly-enhanced non-linear processes are shown in Figure 3.2.

3.2.1 Power Broadening

This is the term used to describe saturation which occurs as a result of redistribution of population between the ground and two-photon excited states. Power broadening is dependent on the rate of change of populations, rather than on the simple presence of non-zero excited state populations.

The removal of population from the ground state and the reduction in population difference between the states decreases the number of atoms available to contribute to a desired non-linear process. This can also lead to saturation. Additionally, redistribution of population can affect the efficiency of parametric non-linear processes by altering the refractive index of the medium, leading to breaking of phase-matching conditions.

The degree of saturation resulting from power broadening itself depends both on the magnitude of the population excited by the laser pulse and the subsequent behaviour of this population; that is, on the laser pulse duration, on the effective lifetime of the excited state and on the final state of the atoms. For example, ionisation may occur or the atom may return to the ground state via some cascade process. The natural lifetime of the excited state can be reduced by processes such as photoionisation or stimulated emission. These processes will be discussed in Section 3.2.3.

Consider the rate equation for two-photon pumping,

$$\frac{dN_2}{dt} = \frac{\alpha I^2}{\hbar\omega} N_0 - \frac{N_2}{\tau}$$

where N_0 and N_2 are the ground and excited state populations respectively,

α is the two-photon absorption cross-section

I is the laser intensity

$\hbar\omega$ is the photon energy

and τ is the effective lifetime of the two-photon state.

If the lifetime of the two-photon-resonant state, τ , is long compared with the pulse duration, T_p , then we can ignore loss of population from the excited state during irradiation, and use the following approximation to estimate a saturation intensity, I_{sat} . I_{sat} is defined as being the intensity required to produce an excited state population equal to half the initial ground state population during the laser pulse. If we assume that the laser pulse has a square wave intensity profile,

$$I(t) = I_0 [H(0) - H(T_p)],$$

one can write

$$I_{sat} = \sqrt{\frac{\hbar\omega}{2\alpha T_p}}$$

Alternatively, if the pulse duration, T_p , is longer than the lifetime of the state, τ , then we can estimate the saturation intensity as that which excites half of the ground state population in a time equal to the excited state lifetime. In this case,

$$I_{sat} = \sqrt{\frac{\hbar\omega}{2\alpha \tau}}$$

In general, therefore, we can say that

$$I_{\text{sat}} = \sqrt{\frac{\hbar \omega}{2\alpha T}} \quad (3.1)$$

where T is the shorter of τ , the excited state lifetime and T_p , the pulse duration.

I_{sat} is, of course, only a crude estimate of the intensity region where power broadening becomes significant, since it takes no account of, for example, laser pulse shape. It is, nevertheless, a useful parameter in semi-quantitative analysis. In addition, it is consistent with formulae which can be used in calculations of the width of the broadened state.

For a homogeneously broadened two-photon transition, the power broadened linewidth, $\Delta\nu_s$, is given, [Wang and Davis, 1975], by

$$\Delta\nu_s = \Delta\nu_0(1 + S)^{1/2} \quad (3.2)$$

where $\Delta\nu_0$ is the line width at zero intensity and $S = 2TR$ is the saturation parameter.

R is the two-photon transition rate at line centre and T is the effective lifetime of the excited state or the laser pulse duration, whichever is shorter. The zero intensity linewidth of the two-photon state is given, [Marx et al, 1978], by

$$\Delta\nu_0 = (2 \Delta\nu_L^2 + \Delta\nu_D^2)^{1/2}$$

where $\Delta\nu_L$ is the laser linewidth assuming an approximately Gaussian laser spectral intensity distribution and $\Delta\nu_D$ is the Doppler width of the two-photon transition.

This is given [see, for instance, Yariv, 1976] by

In general, therefore, we can say that

$$I_{\text{sat}} = \sqrt{\frac{\hbar \omega}{2 \alpha T}} \quad (3.1)$$

where T is the shorter of τ , the excited state lifetime and T_p , the pulse duration.

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Page 127 - Addendum

In terms of saturation intensity defined above,

$$S = \left(I / I_{\text{sat}} \right)^2$$

$$\Delta \nu_0 = (2 \Delta \nu_L^2 + \Delta \nu_D^2)^{1/2}$$

Page 127 - Corrigendum

Power broadening does not lead to a broadening of the inhomogeneous Doppler linewidth, but rather to a broadening of the natural homogeneous linewidth. For the 6p state, the natural linewidth, $\Delta \nu_n$, is 5.3 MHz. Power broadening will increase this by a factor of $(1 + S)^{1/2}$. Even for severe saturation, this is a negligible effect and can be ignored in the calculation of the inhomogeneous zero intensity linewidth

$$\Delta \nu_0 = (2 \Delta \nu_L^2 + \Delta \nu_D^2)^{1/2}$$

$$\Delta\nu_D = \nu_0 \left(\frac{8kT \ln 2}{Mc^2} \right)^{1/2}$$

where ν_0 is the frequency of the two photon transition

k is Boltzmann's constant

T is the absolute temperature

M is the atomic or molecular mass:

for Xenon, $M = 2.2 \times 10^{-25}$ Kg

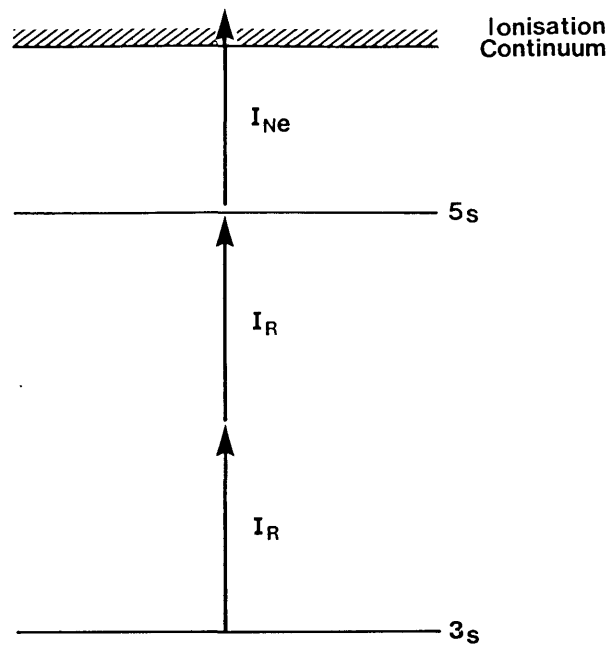
For $T = 300K$, we find that $\Delta\nu_D = 2.6GHz$

For a laser linewidth of 1GHz then $\Delta\nu_0 = 3.0$ GHz.

For $I = I_{sat}$, we find that $2RT = 1$, i.e. $S = 1$, according to Wang and Davis' description of the situation.

It can be seen that the degree of saturation resulting from power broadening is dependent on the upper state lifetime, since this affects the relative population difference. Estimation of the power-broadened linewidth is difficult without accurate knowledge of this lifetime. Let us consider the case where the upper state lifetime is long compared with the laser pulse duration. As we have seen, the pulse duration then becomes the important parameter for power broadening estimation. The natural lifetime of the $6p$ ($J = 0$) state in Xenon is 30ns [Verolainen and Osherovich, 1969]. Taking parameter values representative of experimental conditions, e.g. for a pulse duration of 10ns, and a two-photon absorption cross-section on line centre of $\sigma = 2.4 \times 10^{-28} \text{ cm}^4\text{W}^{-1}$ for a laser linewidth of 1 GHz [Bischel et al, 1979], we find that $I_{sat} \sim 400 \text{ MW/cm}^2$.

For $I = 1 \text{ GW/cm}^2$, the saturation parameter $S = 6$. Hence the expected broadened linewidth would be 8 GHz.



$I_R : \lambda = 6022\text{\AA}$
 $I = 1 - 10 \text{ MW/cm}^2$

$I_{Ne} : \lambda \approx 7000\text{\AA}$
 $I = 0.01 - 10 \text{ GW/cm}^2$

Fig 3.3 Three - Photon Ionisation of Sodium (after Allen et al 1985)

Clearly, if the upper state lifetime is reduced via, for example, photoionisation or stimulated emission, then the magnitude of power broadening is dependent on this reduced lifetime. Generally, in such circumstances, power broadening will be a secondary saturation mechanism and some other mechanism will dominate.

The dependence of the linewidth on intensity can be deduced from Equation 3.2. Assuming an excited state lifetime which is independent of intensity, this dependence will be approximately linear, since

$$\begin{aligned}\Delta\nu_s &= \Delta\nu_0 (1 + 2RT)^{1/2} \\ &= \Delta\nu_0 \left(1 + \frac{2\alpha I^2}{\hbar\omega} T\right)^{1/2} \\ &\approx \Delta\nu_0 \left(\frac{2\alpha T}{\hbar\omega}\right)^{1/2} I \quad \text{for } 2RT \gg 1,\end{aligned}$$

i.e. a strongly saturated system.

3.2.2 The a.c. Stark Effect

When atoms are subjected to an optical frequency electric field, there is a repartitioning of the energy in the atom-field system which causes shifts in the energy levels in the atom. This is known as the a.c. Stark effect. The induced shifts are intensity dependent, so that for a pulsed laser in a focused geometry the magnitude of the induced shift has both a temporal and spatial dependence. The a.c. Stark effect can lead to saturation of resonant processes by altering the frequency condition for resonance.

Allen et al, 1985, investigated two-photon resonant three-photon ionisation in Sodium. The relevant energy levels are shown in Figure 3.3. Extremely large a.c. Stark shifts, ($\sim 300\text{GHz}$), were observed. For high incident intensities,

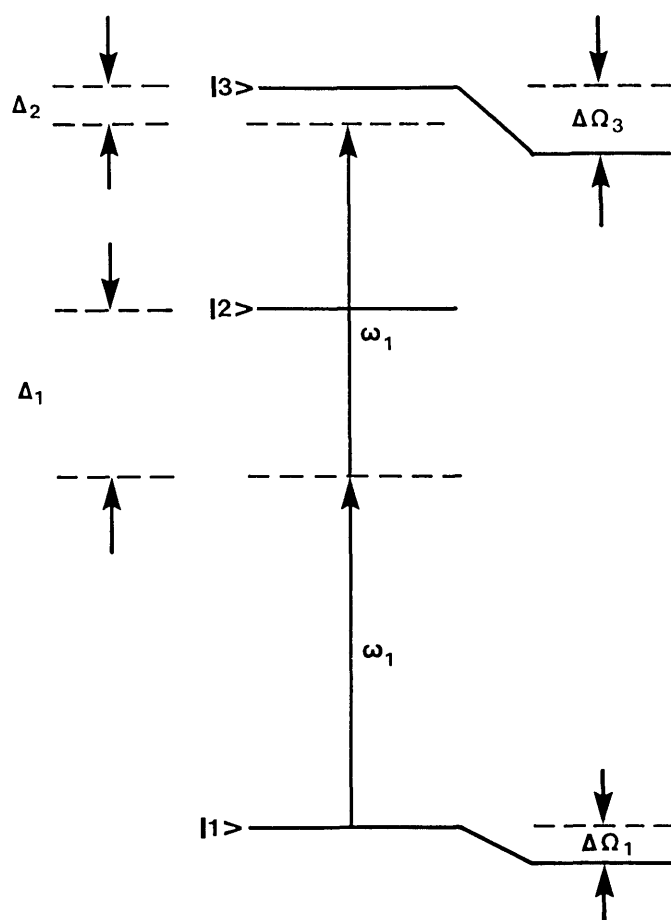


Fig 3.4 Energy Level Diagram for Estimation of a.c. Stark Shift

($I \sim 1\text{GW}/\text{cm}^2$), this resulted in a decrease in ion yield with increased intensity. Allen and co-workers point out that, in some situations, namely atomic beam experiments, the ion signal can be maximised by retuning the resonant laser to the shifted resonant frequency. This is not appropriate, however, for experiments employing focused beam geometries due to the spatial intensity variations.

As will be seen from the theory to be presented, such large optical Stark shifts may have been expected in Allen's experiment due to the proximity of an intermediate single-photon resonance with the 3p state. The detuning from single-photon resonance with the 3p, $J=1/2$, state was 350 cm^{-1} .

Consider the energy level diagram shown in Figure 3.4 of a two-photon resonance and intermediate single-photon resonance, for the case of detuning below both single- and two-photon states by Δ_1 and Δ_2 respectively. The induced a.c. Stark shifts are $\Delta\Omega_3$ and $\Delta\Omega_1$ for states $|3\rangle$ and $|1\rangle$ respectively. It can be shown [Hanna, Yuratich and Cotter, 1979] that when the levels are a.c. Stark shifted, the detuning from the two-photon resonance, $\Delta_2 + (\Delta\Omega_1 - \Delta\Omega_3)$ is

$$\Delta_2 + \frac{1}{2\Delta_1} \left\{ |\mu_{12}|^2 \bar{E}_1^2 - |\mu_{23}|^2 \bar{E}_2^2 \right\} \quad (3.3)$$

where E_1 and E_2 are the electric field strengths,

Δ_1 and Δ_2 are the detunings from single- and two-photon resonance

μ_{12} and μ_{23} are the relevant dipole matrix elements and the assumption that $\Delta_2 \ll \Delta_1$ has been made.

Equation 3.3 arises from a more complicated equation [Butcher, 1965] which involves sums over intermediate energy levels, for

the case when one term dominates the sum. This approximation can be made in Xenon for our experimental conditions.

For the case of exact resonance, that is, no detuning from the unshifted two-photon-resonant level, and $E_1 = E_2$, Equation 3.3 reduces to

$$\frac{E^2}{2\hbar^2\Delta_1} \left\{ |\mu_{12}|^2 - |\mu_{23}|^2 \right\} = \frac{I}{c\epsilon_0\hbar^2\Delta_1} \left\{ |\mu_{12}|^2 - |\mu_{23}|^2 \right\} \quad (3.4)$$

Hence the shift is linearly dependent on intensity.

The dipole matrix elements can be calculated from tabulated values of oscillator strengths [Hanna, Yuratich and Cotter, 1979] using the following relationship

$$|\mu_{xy}|^2 = \frac{e^2\hbar}{2m_e\omega_{xy}} f_{xy} \frac{3(l+1)}{2l+3}$$

where f_{xy} is the oscillator strength for the transition from state x to state y

l is the angular momentum of state x

$\omega_{xy} = 1/\hbar (E_y - E_x)$ is the angular frequency associated with the transition

m_e is the electronic mass

and e is the electronic charge.

It should be noted that only the magnitude of the dipole matrix element and not its sign can be calculated in this way.

For our experimental conditions in Xenon, the intermediate state closest to single photon resonance for two-photon excitation of the $5p^56p$ ($J = 0$) state is the $5p^56s$ ($J = 1$) state at 68,045 cm^{-1} . The oscillator strength for the $5p^6 - 5p^56s$ transition is 0.26 [Geiger, 1977] and that for the $5p^56s - 5p^56p$ transition is estimated to be 0.1 since no published

value is available. This is consistent with the 30ns spontaneous lifetime of the $5p^56p$ ($J = 0$) state [Verolainen and Osherovich, 1969].

Substitution of these values in Equation 3.4 gives an a.c. Stark shift of the two-photon-resonant frequency of $2.2 \text{ GHz}/(\text{GW}/\text{cm}^2)$.

For intensities in the region of $1\text{GW}/\text{cm}^2$ this is comparable with the Doppler broadened linewidth. Hence the a.c. Stark effect may be expected to lead to some saturation of two photon resonant processes at high intensities, with associated broadening of the resonance linewidth.

3.2.3 Lifetime Broadening

According to Heisenberg's Uncertainty Principle, any process which leads to a reduction in the lifetime of a state will cause a corresponding increase in the energy distribution of the state. Hence the linewidth of the state will be broadened.

In the Xenon system considered, there are two processes which could potentially reduce the lifetime of the two-photon-resonant state. These are ionisation broadening resulting from the rapid photoionisation of the two-photon-resonant state population, and broadening resulting from stimulated emission of radiation due to a population inversion between the resonantly excited $6p$ ($J = 0$) and initially unpopulated $6s$ ($J = 1$) state. These two processes are considered in the following sections.

3.2.3.1 Ionisation Broadening

The two-photon-resonant state population can be ionised by a single photon with sufficient energy to excite the atom above the ionisation limit. The ionisation rate can be calculated from rate equations as follows

$$\frac{dN_i}{dt} = \frac{\sigma_p I}{h\nu} N_2$$

where σ_p is the photoionisation cross-section

N_2 is the population of the two-photon-resonant 6p state

N_i is the ion population

and I is the laser intensity.

The cross-section for single-photon ionisation from the 6p, (J=0), state at $\lambda = 249.63\text{nm}$ is $\sigma_p = 1.3 \times 10^{-18}\text{cm}^2$ [Pindzola, 1981].

One can estimate the saturation intensity, I_{sat} , for ionisation broadening in a similar way to power broadening (Section 3.2.1), by assuming a rectangular laser pulse and defining I_{sat} as the intensity for which half the excited state population is ionised.

Hence,

$$I_{\text{sat}} = \frac{h\nu}{2\sigma_p T_p}$$

where T_p is the laser pulse duration.

For a laser pulse duration of 10ns, $I_{\text{sat}} = 25 \text{ MW/cm}^2$.

Such single-photon ionisation would be expected to produce a broadening which is directly proportional to the intensity. For an intensity of 1GW/cm^2 , the ionisation rate is $1.6 \times 10^9 \text{ s}^{-1}$, corresponding to a lifetime of 0.6ns. This is

substantially shorter than the spontaneous lifetime of 30ns, and would lead to line broadening of a magnitude comparable with Doppler broadening.

It is interesting to consider the effect of the reduced lifetime due to ionisation from the 6p state on other broadening mechanisms. For example, for power broadening,

$$I_{\text{sat}} = \sqrt{\frac{\hbar \omega}{2\alpha T}} \quad (3.1)$$

For an effective lifetime of $T = 0.6\text{ns}$, $I_{\text{sat}} = 1.7\text{GW/cm}^2$. In such conditions, the power broadened linewidth, for $I = 1\text{GW/cm}^2$, is $1.4\Delta\nu_0$ where $\Delta\nu_0$ is the zero intensity linewidth. Hence it is clear that, in the presence of ionisation broadening, the effect of power broadening is reduced.

3.2.3.2 Broadening due to Stimulated Emission of Radiation

Since the transition from the two-photon-resonant state to the ground state is not an allowed dipole transition, radiative decay from this state must occur by a cascade process via intermediate states. As shown in Figure 3.1, the number of intermediate states in Xenon is limited. The most likely route is via the 6s ($J = 1$) state at $68,045\text{cm}^{-1}$. The wavelength associated with this transition is 828.2nm . There is also a 6s' ($J = 1$) state at $77,185\text{cm}^{-1}$; decay to this state results in emission at 3410nm . However, this energy level corresponds to the $2P_{1/2}$ configuration of the atomic core in contrast to the 6p ($J = 0$) and 6s ($J = 1$) states which correspond to $2P_{3/2}$ core configurations. Consequently, the dominant decay route is expected to be via the 6p ($J = 0$) to 6s ($J = 1$) transition.

It is clear that even under modest two-photon pumping rates, a

substantial population inversion can exist between the 6p ($J = 0$) and 6s ($J = 1$) levels. For example, at an intensity of 250 MW/cm^2 and a Xenon pressure of 5 torr, simple two-photon pumping calculations indicate that an inversion of $2 \times 10^{17} \text{ cm}^{-3}$ could be possible.

The stimulated emission cross-section on line centre for the transition can be estimated from the following relationship [Yariv, 1976]

$$\sigma_{\text{stim}} = \frac{\lambda^2}{4\pi^2 \tau_{\text{sp}} \Delta\nu_0} \quad (3.5)$$

where $\lambda = 828.2 \text{ nm}$

τ_{sp} = spontaneous lifetime = 30ns [Verolainen and Osherovich, 1969].

and $\Delta\nu_0$ = transition linewidth = 2.6 GHz, the Doppler linewidth (Section 3.2.1)

Substitution of these values into Equation 3.5 gives

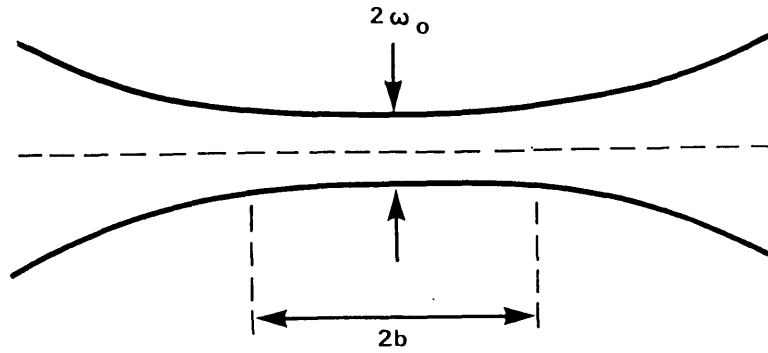
$$\sigma_{\text{stim}} = 2.2 \times 10^{-12} \text{ cm}^2$$

From this large value of σ_{stim} , it is realistic to expect that stimulated emission of radiation will occur. In the absence of a suitable cavity this will appear as amplified spontaneous emission.

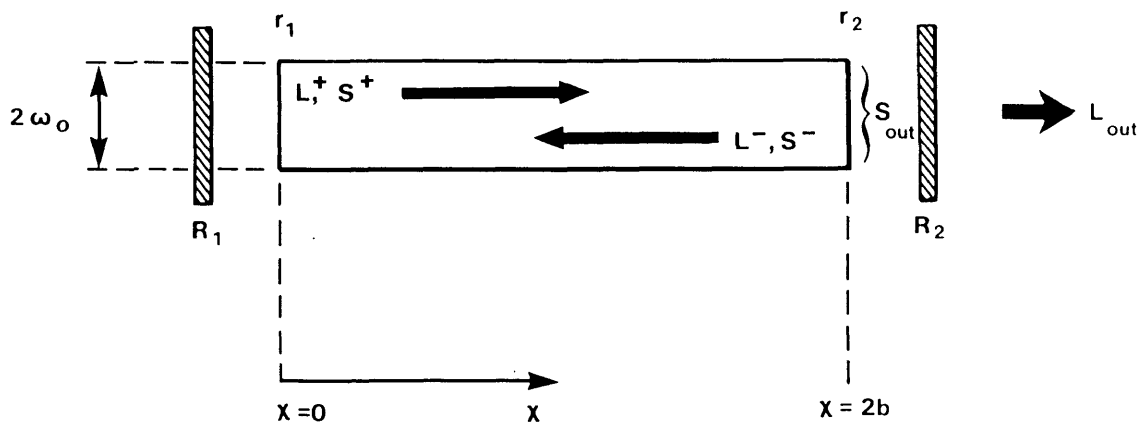
This simple calculation of the stimulated emission cross-section for the 6p ($J = 0$) to 6s ($J = 1$) transition clearly indicates that stimulated emission may be a process of considerable importance. The small signal gain coefficient, g , calculated as

$$g = \Delta N \sigma_{\text{stim}}$$

where σ_{stim} is the stimulated emission cross-section



(a) Gaussian Focus



(b) Cylindrical Approximation of Focal Gain Region

Laser Flux — $L^{\pm}$

ASE Flux — $S^{\pm}$

Laser Feedback — R_1, R_2

ASE Feedback — r_1, r_2

ASE Laser Output Flux — L_{out}

ASE Laser Output Flux — S_{out}

Fig 3.5 Schematic of Beam Waist used in ASE Calculations

and ΔN is the population inversion,

is hence large due to the large magnitude of both σ_{stim} and ΔN . For example, using a value of ΔN of $5 \times 10^{16} \text{ cm}^{-3}$, calculated as realistic from two-photon pumping estimations, we find

$$g = 1.1 \times 10^5 \text{ cm}^{-1}$$

The relationship between this high gain for stimulated emission and the broadening of the two-photon-resonant state resulting from saturation effects due to the emission, is not obvious. The analysis requires detailed consideration of the theory of amplified spontaneous emission (ASE), and leads to a greater understanding of the physical processes leading to saturation under extreme conditions such as the high stimulated emission cross-section encountered here.

The analysis presented here follows the work of Haag et al [Haag, Munz and Marowsky, 1983].

The geometric configuration in the focal region formed in the Xenon cell is shown in Figure 3.5. The focal spot diameter is $2\omega_0$ and the confocal parameter is b . The x-axis is as shown, parallel to the beam propagation direction. The focal region can be approximated by a cylinder of diameter $2\omega_0$ and length $2b$. Within this region, plane-wave propagation is assumed.

Furthermore, it is assumed that stimulated emission occurs in this volume only. Both forward and backward propagating ASE must be considered, having equal intensities. By considering coupled rate equations, Haag et al develop a theory which includes both laser emission and amplified spontaneous emission, allowing feedback of both within the system. Application of their theory to our case of ASE only with no

feedback is achieved by setting some of the coefficients in the general analysis to zero.

The starting point for their analysis is the following set of radiative one-dimensional transport equations.

$$\frac{dL^\pm}{dx} = \pm L^\pm (g - \alpha) \quad (3.6)$$

$$\frac{dS^\pm}{dx} = \pm [S^\pm (g - \alpha) + Ag] \quad (3.7)$$

where $L^\pm$ are the forward and backward propagating laser intensities

$S^\pm$ are the corresponding ASE intensities

g is the (saturable) gain

α is the (non-saturable) losses

and A describes the properties of the ASE flux

$$A = \frac{d\Omega}{4\pi} \cdot \frac{\tau_u}{\tau_s} \cdot \frac{\Delta\nu_n}{\Delta\nu_s}$$

where τ_u is the excited state lifetime

τ_s is the spontaneous lifetime

$\Delta\nu_s$ is the bandwidth of the spontaneous fluorescence

$\Delta\nu_n$ is the width of the narrowed ASE line

and $\frac{d\Omega}{4\pi}$ is the solid angle contributing to the ASE output, as introduced by Allen and Peters, 1973.

$$\frac{d\Omega}{4\pi} = \frac{(1 + q - \sqrt{1 + q^2})}{2q}$$

where q is the aspect ratio L/D (L length and D transverse dimension). For pencil-like geometries, i.e. $L \gg D$, the coefficient A may be considered to be spatially independent. In our terminology (Figure 3.5), $q = b/\omega_0$.

Haag et al apply generalised boundary conditions in their solution of Equations 3.6 and 3.7 to allow for laser and ASE emission both with and without externally coupled inputs into the system. Additionally, feedback of laser and ASE signals are included by considering reflectivities of R_1 and R_2 for the laser coherent flux and r_1 and r_2 for the ASE flux at each end of the active region. This is illustrated in Figure 3.5 together with the co-ordinates using an x-axis parallel to the propagation direction and the origin at the one end of the active region.

Application of the theory to the analysis of a single pass laser amplifier lends itself most easily to our situation of stimulated emission of radiation as ASE. Consider first a single pass amplifier with the parameters $\alpha = 0$, i.e., no linear losses, and $R_1 = R_2 = 0$, i.e., no feedback of laser emission. For the moment let us allow $r_1 = r_2 = r = 0$, i.e. there may be feedback of the ASE signal.

Additionally, let $L^+(x = 0) = \Phi$, which is some injected signal.

The solution of Equations 3.6 and 3.7 with the relevant boundary conditions leads to an expression most easily described in terms of the integrated gain

$$G = \exp \left[\int_0^L g(\sum(x)) dx \right]$$

where $\sum(x) = L^+(x) + S^+(x) + S^-(x)$

i.e. the sum of both laser and ASE outputs, assuming laser emission is in the positive x-direction only.

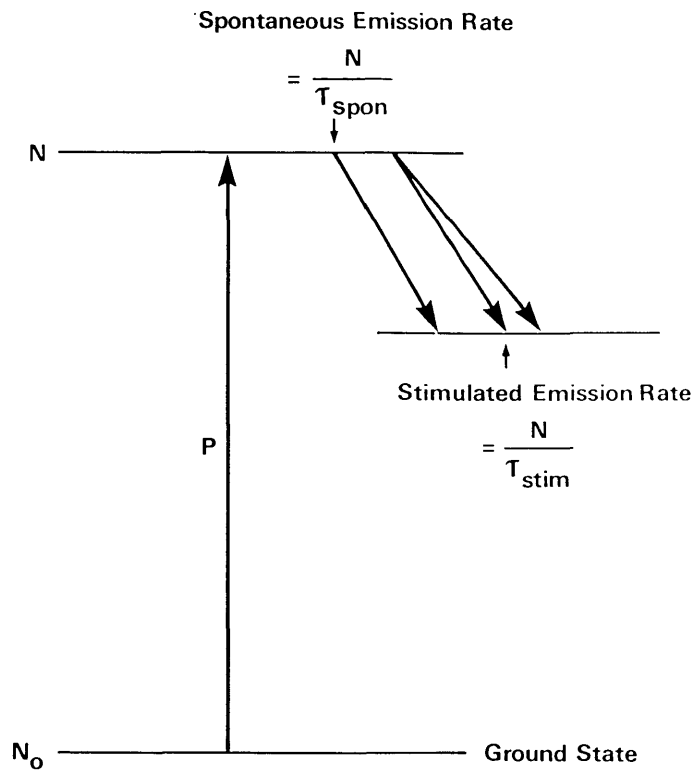


Fig 3.6 Spontaneous and Stimulated Emission from Excited State of Population N

This integrated gain is equivalent to the signal out divided by the input signal, i.e.

$$G = \frac{L_{out}}{\Phi}$$

Haag et al show that a transcendental equation for G can be found, namely

$$(1 - 2A) \ln G + (G-1) \left[\Phi + \frac{2A(1 - r)}{(1 - rG)} \right] = g_0 L \quad (3.8)$$

where g_0 is the small signal gain. If we set $\Phi = r = 0$, i.e. no ASE feedback and no laser input, Equation 3.8 becomes

$$(1-2A) \ln G + (G-1)2A = g_0 L$$

If $\ln G \gg 1$, as is the case for high gain systems, and $A \ll 1$, as is the case for high aspect ratio configurations, this becomes

$$\ln G + 2AG = g_0 L$$

$$\text{i.e. } \ln G + 2AG = \ln G^0$$

where G^0 is the small signal integrated gain; $G^0 = \exp (g_0 L)$.

Let $\ln G = \ln G^0 - \int$ to take account of the reduction in gain due to saturation of the transition by the ASE.

$$\text{Then } 2AG = \int$$

Hence we have a relationship between the saturated and unsaturated integrated gains in terms of the factor A which describes the properties of the ASE flux. However, we must now calculate the relationship between these gains and the resultant broadening of the resonance line.

Consider pumping of the upper "laser" level at rate P and spontaneous and stimulated lifetimes of τ_{spont} and τ_{stim} as shown in Figure 3.6. Then the upper state population, N, is

described by the rate equation

$$\begin{aligned}\frac{dN}{dt} &= P - \frac{N}{\tau_{\text{spon}}} - \frac{N}{\tau_{\text{stim}}} \\ &= P - N (A_{\text{spon}} + A_{\text{stim}})\end{aligned}$$

where $A = 1/\tau$

For a steady state, $\frac{dN}{dt} = 0$

Therefore the steady state population N^A , is given by

$$P = N^A (A_{\text{spon}} + A_{\text{stim}}) = N^0 A_{\text{spon}}, \quad (3.9)$$

in the absence of ASE.

Now consider the integrated gains G^0 and G^A , G^0 being the unsaturated gain in absence of ASE and G^A being the saturated gain in the presence of ASE. These can be expressed as follows

$$G^0 = \exp [\sigma N^0 L]$$

assuming $N^0 = \text{constant}$ throughout the volume of excitation.

$$G^A = \exp \left[\int_0^L \sigma N^A dl \right]$$

If saturation occurs rapidly, however, then we can make the assumption that $N^A = \text{constant}$ throughout the volume of excitation.

Then

$$G^A = \exp [\sigma N^A L]$$

and

$$\begin{aligned}\frac{G^A}{G^0} &= \exp [\sigma L (N^A - N^0)] \\ &= \exp \left[\sigma L N^0 \left[\frac{A_{\text{spon}}}{A_{\text{spon}} + A_{\text{stim}}} - 1 \right] \right]\end{aligned}$$

from Equation 3.9.

$$\begin{aligned} \text{Hence } \ln \frac{G^A}{G^0} &= \sigma_L N^0 \left[\frac{A_{\text{stim}}}{A_{\text{spon}} + A_{\text{stim}}} \right] \\ \text{i.e.} \quad &= \sigma_L N^0 \left[1 + \frac{A_{\text{spon}}}{A_{\text{stim}}} \right]^{-1} \end{aligned}$$

For $A_{\text{stim}} \gg A_{\text{spon}}$, as in the case of extreme broadening,

$$\ln G^0 - \ln G^A \approx \sigma_L N^0 \left[1 - \frac{A_{\text{spon}}}{A_{\text{stim}}} \right]$$

using the binomial expansion.

Hence,

$$g_0 L - \ln G^A \approx g_0 L \left[1 - \frac{A_{\text{spon}}}{A_{\text{stim}}} \right]$$

Finally,

$$\frac{\ln G^A}{\ln G^0} = \frac{A_{\text{spon}}}{A_{\text{stim}}} = \frac{\tau_{\text{stim}}}{\tau_{\text{spon}}} = \frac{\Delta \omega_{\text{spon}}}{\Delta \omega_{\text{stim}}} \quad (3.10)$$

Hence we have a simple relationship between the saturated and unsaturated integrated gains and the broadened and unbroadened transition linewidths. Although Equation 3.10 is an approximation for a high gain situation, the simple estimation of stimulated emission cross-section together with the experimental observations presented in Chapter 4, indicate the validity of using this assumption for the experimental conditions encountered. Numerical evaluation of the theory is presented in Chapter 4 for the experimental parameters encountered.

3.2.4 Stark Broadening by Photoelectrons

The presence of large populations of ions and photoelectrons, which could easily be produced by the two-photon-resonant three-photon ionisation process, can result in broadening and

shifting of the levels of the remaining neutral atoms via the d.c. Stark effect. If the perturbing electric field, due to a charged particle, which acts on an atom is due to a single charge, Ze , at a distance R , then the energy shift ΔE of an unperturbed state $|b\rangle$ is given, [Butcher 1965], by

$$\Delta E = \left(\frac{Ze}{4\pi\epsilon_0 R^2} \right)^2 \sum_a \frac{|\langle b | \mu_{ab} | a \rangle|^2}{E_b - E_a}$$

The sum is over all other states $|a\rangle$ and μ_{ab} are the relevant dipole matrix elements. In general this expression can be simplified by making the valid assumption that one term will dominate the summation. Hindmarsh, 1974, showed that, within the impact approximation, the Stark broadened linewidth, (FWHM, rad s^{-1}), is given by

$$\gamma = 22.8 \left(\frac{C_4}{\hbar} \right)^{2/3} (\bar{v})^{1/2} N \quad (3.11)$$

where

$$C_4 = \left(\frac{Ze}{4\pi} \right)^2 \sum_a \frac{|\langle b | \mu_{ab} | a \rangle|^2}{E_b - E_a}$$

and N is the number density of perturbing charged particles whose mean speed is $\bar{v}$.

The dominant broadening is therefore due to photoelectrons rather than ions because of their higher velocities. There are two assumptions made in arriving at this equation. One is that

$$\Delta E \ll (\hbar \bar{v})^{4/3} (C_4)^{-1/3}$$

This is valid for shifts, due to electron broadening, of less than several hundreds of wavenumbers (few THz). The other assumption is that spin-orbit coupling is ignored. This is

valid for alkali metals such as Sodium and Cesium, but it is known that in the rare gases spin-orbit coupling is an important effect. It leads to the two ionisation potentials of rare gases arising from two configurations of core electrons [Sobel'man, 1972]. This is indeed a significant effect, the energy difference in Xenon, for example, being $10,537\text{cm}^{-1}$.

Consequently, it seems unlikely that evaluation of Equation 3.11 will produce broadenings for Xenon which are quantitatively correct. However, qualitatively, we see, for example, that the linewidth has a linear dependence on the density of ions and such information is useful in the assessment of experimental results.

While not being directly comparable, it is interesting to consider Stark broadening due to photoelectrons in other atoms. It has been calculated, for example, [Butcher, 1965] that in Cesium, for an electron density of $N = 10^{16}\text{cm}^{-3}$, linewidths of tens of GHz are likely. Such electron densities are comparable with those likely under modest pumping of the two-photon resonance in Xenon.

Under extreme conditions, the initial photoelectrons can gain energy by inverse Bremsstrahlung absorption and then by an avalanche ionisation process finally form an opaque plasma [Miles and Harris, 1973]. However, such a process would be detectable when measuring ion yield and was not encountered in the experiments described in Chapter 4.

3.3 Rate Equation Calculations

3.3.1. Introduction

An alternative approach to analysing two-photon pumping of Xenon is the numerical solution of the relevant rate equations. While such an analysis does not give direct information about saturation and line broadening, it can provide a useful insight into the magnitudes and timescales of population redistribution under a variety of intensities of laser excitation.

Some saturation mechanisms such as power broadening and ionisation broadening are inherently included in the rate equation approach. The interdependence of such mechanisms is automatically included. Other mechanisms such as lifetime broadening due to stimulated emission can be included although a rigorous analysis is difficult: rather this term is more easily included by a reduced two-photon-resonant state lifetime. Other broadening mechanisms, such as Stark broadening due to photoelectrons, are not included in the rate equation approach.

As previously mentioned, information about the expected magnitude of line broadening is not obtained. However, expected dependency of, for example, ion population on pumping intensity, can be easily extracted from the rate equation calculations. Behaviour on- and off-resonance can be calculated by controlling the magnitude of the two-photon absorption cross-section.

The results obtained from solving the rate equations has proved useful both in the analysis of the three-photon ionisation experiments described in Chapter 4 and the laser-induced autoionisation experiments described in Chapter 6.

3.3.2 Numerical Solution of Rate Equations

The rate equations for the relevant Xenon ground and excited state time-dependent populations were solved for two-photon-resonant pumping of the 6p ($J = 0$) state by a laser pulse of Gaussian temporal profile. The model allowed for ground state population depletion and repopulation via the 6p ($J = 0$) $\rightarrow$ 6s ($J = 1$) $\rightarrow$ ground state channel. Only the two-step process of resonant two-photon excitation followed by single-photon ionisation was included in the model. By comparison, the probability of direct three-photon ionisation was assumed to be negligible.

The effect of recombination of ions and electrons was not considered as the timescale for this process was much longer than the pulse duration, which was typically 10ns. Collisional quenching of excited state atoms was also ignored as it has little effect at the low pressures considered (5-10 torr). The effect of collisional quenching can be estimated by considering the average time between collisions. This is calculated to be 25ns for a pressure of 5 torr at 20°C. Hence collisional quenching is not expected to be significant on the timescale of the laser excitation.

Initially, stimulated emission between the 6p ($J = 0$) and 6s ($J = 1$) levels was not included in the model, but was later introduced indirectly by reducing the 6p level lifetime.

The equations solved are as follows:

ground state population, N_0

$$\frac{dN_0}{dt} = - \frac{\alpha I^2}{\hbar \omega} N_0 + \frac{N_3}{\tau_3}$$

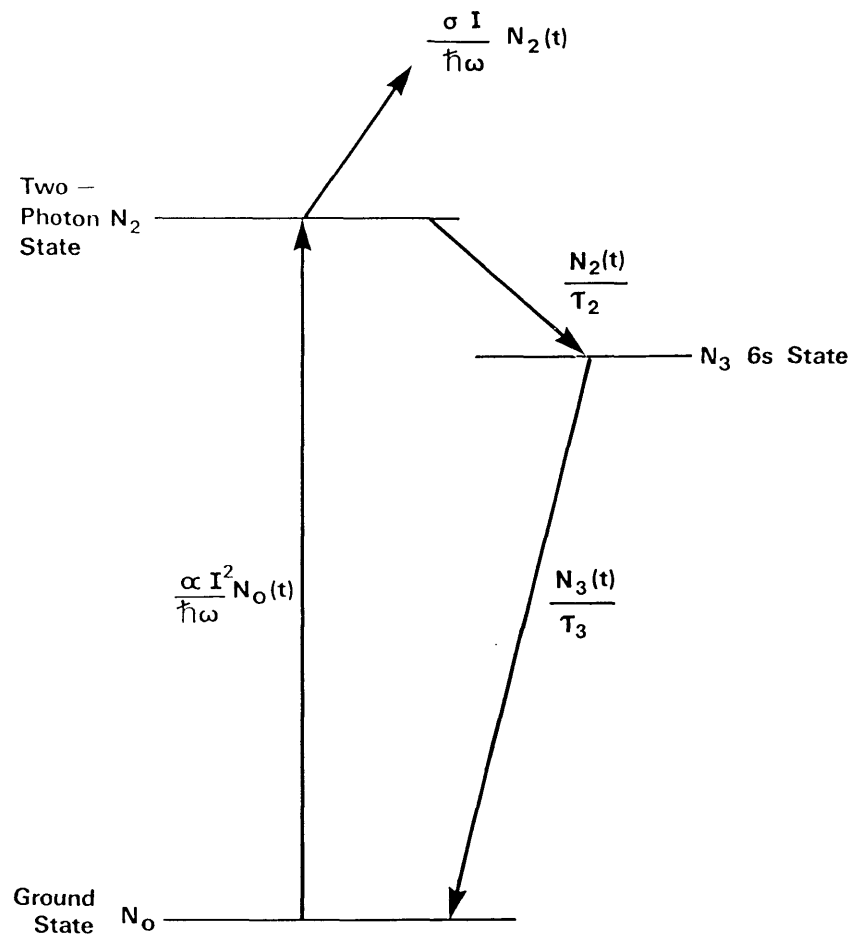


Fig 3.7 Diagrammatic Representation of Model to Solve Rate Equations

two-photon-resonant state population, N_2 ,

$$\frac{dN_2}{dt} = \frac{\alpha I^2}{\hbar \omega} N_0 - \frac{\sigma_p I}{\hbar \omega} N_2 - \frac{N_2}{\tau_2}$$

ion population, N_i ,

$$\frac{dN_i}{dt} = \frac{\sigma_p I}{\hbar \omega} N_2$$

6s state population, N_3

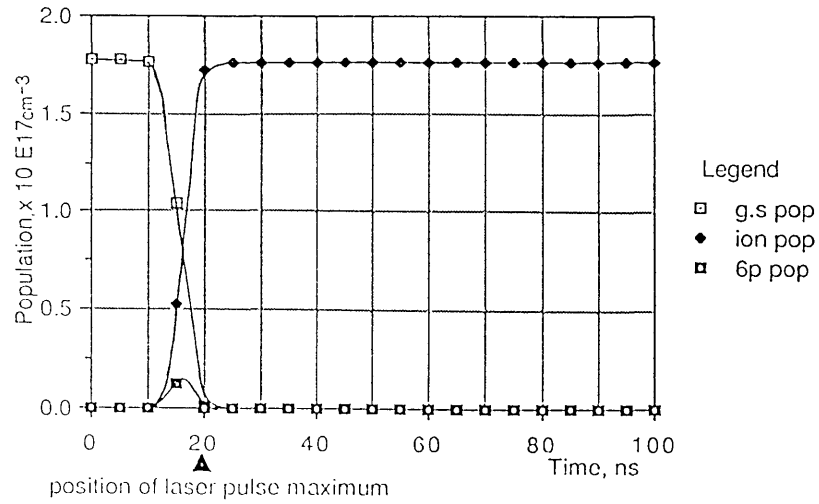
$$\frac{dN_3}{dt} = \frac{N_2}{\tau_2} - \frac{N_3}{\tau_3}$$

where α is the two-photon absorption cross-section
 σ_p is the ionisation cross-section
 τ_2 is the effective lifetime of 6p level due to
radiative decay to the 6s level
 τ_3 is the spontaneous lifetime of 6s level
and ω is the angular frequency of laser excitation

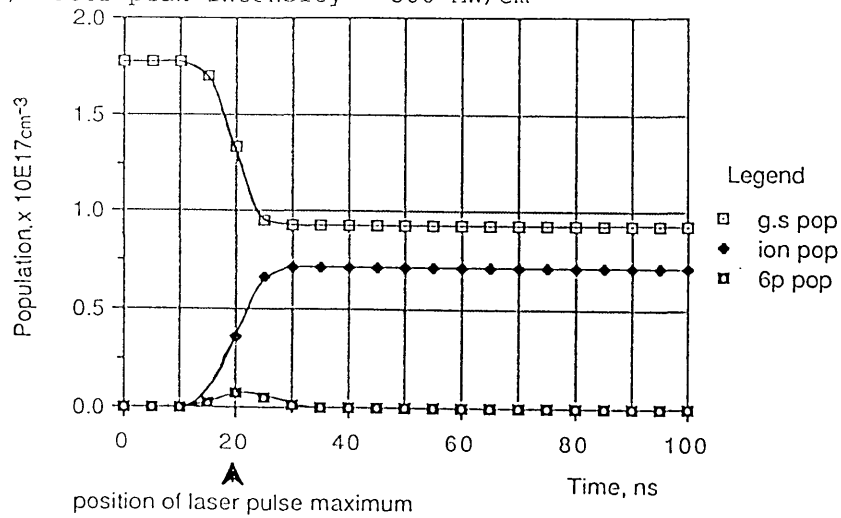
The system of equations is shown schematically in Figure 3.7.

The spontaneous lifetime of the 6s level, τ_3 was calculated, from the oscillator strength for the transition, to be 4ns. The value used for the on-resonance two-photon absorption cross-section was $2.4 \times 10^{-28} \text{cm}^4 \text{W}^{-1}$ [Bischel et al, 1979], assuming a laser linewidth of 1GHz. This value is consistent with the experimental results of Bobb and Rankin, 1984. A reduced value of two-photon absorption cross-section (typically one third the on-resonance value) was used to simulate behaviour in the wings of the two-photon transition. The value used for σ_p , the ionisation cross-section, was $1.3 \times 10^{-18} \text{cm}^2$ [Pindzola, 1981].

(a) Laser peak intensity = 2 GW/cm^2



(b) Laser peak intensity = 500 MW/cm^2



(c) Laser peak power = 50 MW/cm^2

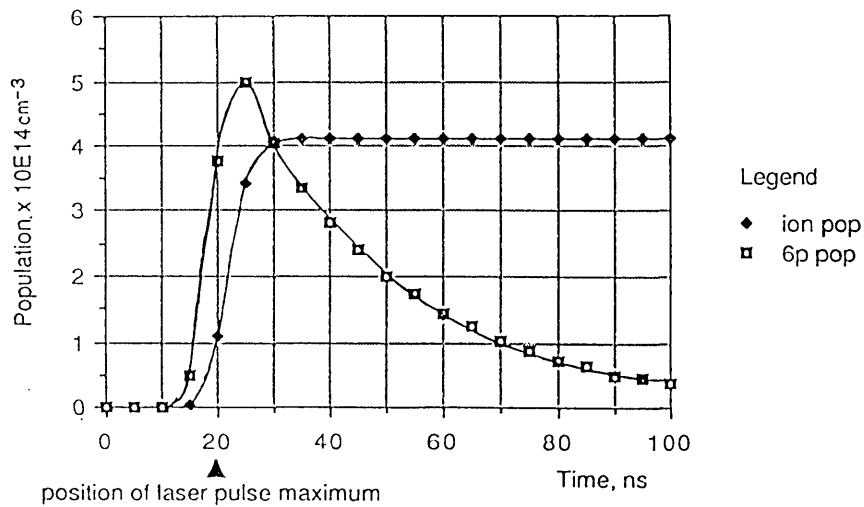


Figure 3.8 Xenon Population Evolution during the Passage of a 10ns Pulse, $\lambda = 249.63\text{nm}$
(parameter details in text)

The laser excitation was modelled by a Gaussian pulse of variable duration and peak intensity.

Initial calculations involved the solution of the equations for a variety of laser intensities up to $2.5\text{GW}/\text{cm}^2$. The typical pulse duration used was 10ns. The ground state, two-photon-resonant state and ion populations were plotted out for the period 20ns before and 80ns after the peak of the excitation pulse. The equations were solved iteratively with a computation step of 0.1ns.

3.3.3 Results

Figure 3.8 relates to the rate equation calculations for the following parameters:

Two photon-absorption cross-section, $\alpha = 2.4 \times 10^{-28} \text{cm}^4 \text{W}^{-1}$
(on resonance)

Two-photon-resonant state lifetime, $\tau_2 = 30\text{ns}$

Ionisation cross-section, $\sigma_p = 1.3 \times 10^{-18} \text{cm}^2$

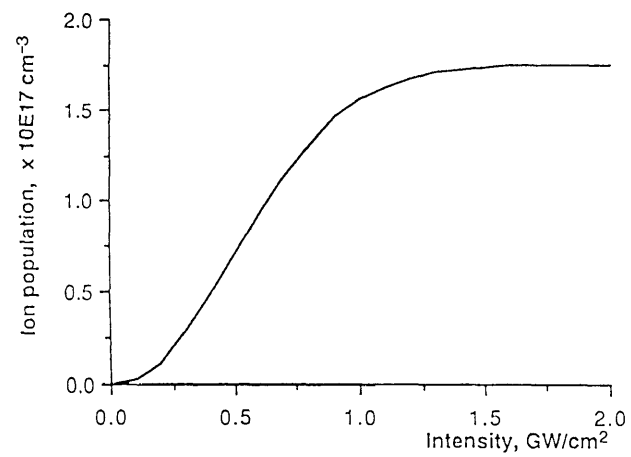
Pulse duration = 10ns

Xenon pressure = 5torr.

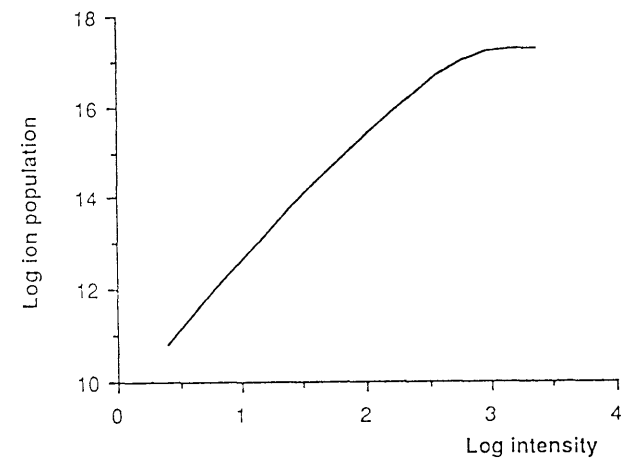
Figure 3.8(a) shows the evolution of the ground state, two-photon-resonant state and ion populations for a laser peak power of $2 \text{GW}/\text{cm}^2$. The most striking feature of this calculation is the complete ionisation predicted and the role of the two-photon-resonant state in this ionisation. It appears that at these high intensities, ionisation is complete in a time which is substantially less than the pulse duration; the ground state is entirely depleted before the peak of the pulse arrives. Since ionisation is a loss to the system, there is no repopulation of the ground state. In this process the two-photon-resonant state acts merely to channel the population

Figure 3.9 Dependence of Xenon Ion and Two-Photon-Excited State (6p) Populations on Intensity for Parameters Quoted in Text

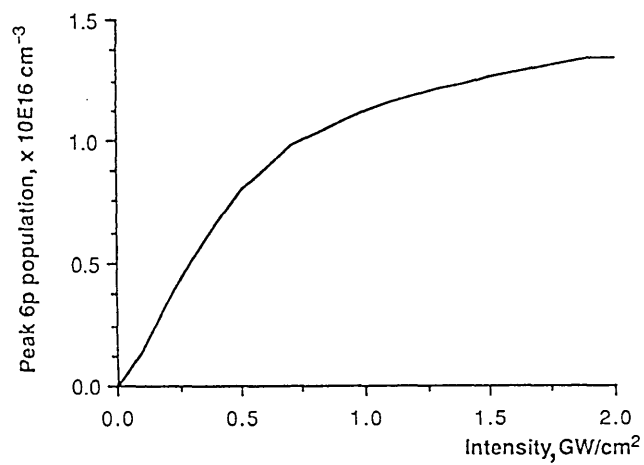
(a) Ion population vs Intensity



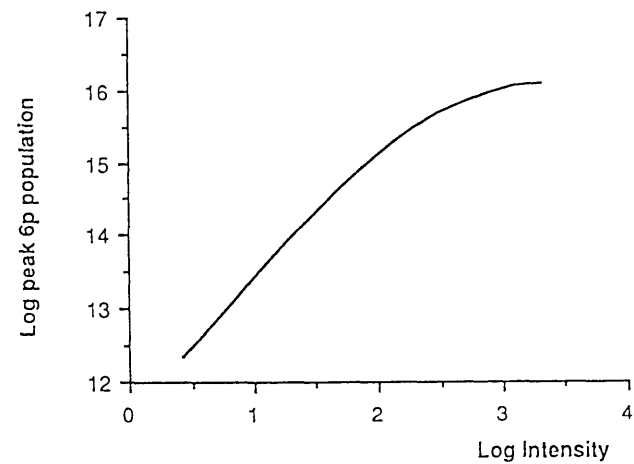
(b) Log-log plot of ion population vs intensity



(c) Peak 6p population vs Intensity



(d) Log-log plot of peak 6p population vs intensity

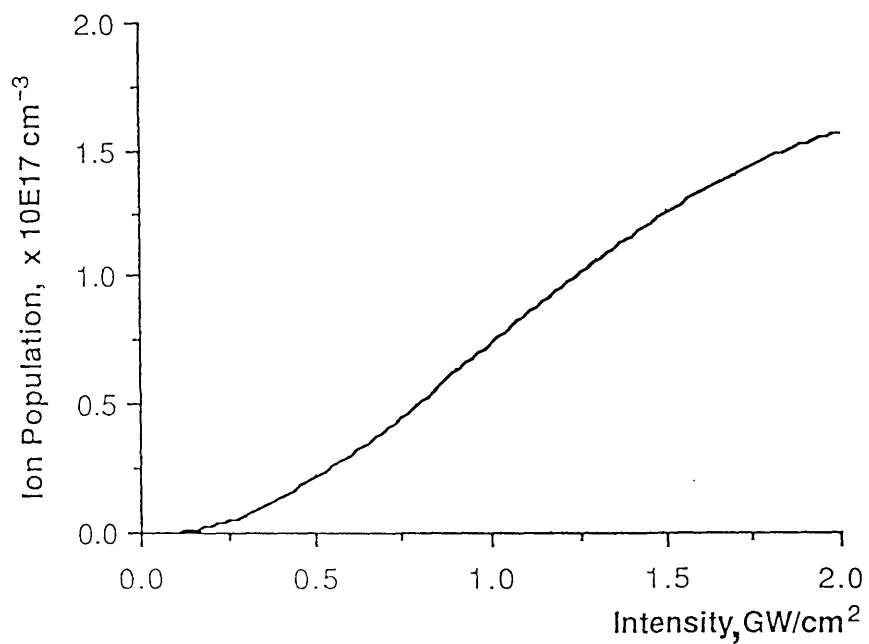


through to the continuum. The peak population in the 6p state is $1.4 \times 10^{16} \text{cm}^{-3}$ which is only 8% of the initial ground state population. This would confirm the hypothesis that power broadening probably has a negligible effect in this system, due to the rapid removal of population from the 6p state by ionisation, or possibly by other routes such as stimulated emission.

Calculations at lower intensities show behaviour which may be expected from a comparison of the two-photon-absorption rate and the ionisation rate. At an intensity of 500 MW/cm^2 , ionisation is no longer complete. For intensities below 50 MW/cm^2 , the results show that the peak excited state population exceeds the ion population. This corresponds to the ionisation channel being unsaturated at these low intensities. In this regime, the 6p level could be used as a "storage" level such as required, for example, for proposed laser-induced collision experiments [White, 1980]. These results are illustrated in Figures 3.8(b) and 3.8(c).

For the same parameters, Figure 3.9(a) shows a plot of ion population against intensity for intensities up to 2 GW/cm^2 . Saturation is indicated by the departure of the ion density from the expected cubic dependence on intensity. For intensities greater than 1.5 GW/cm^2 , total saturation is evident. A log-log plot of the data is shown in Figure 3.9(b). The intensity-dependence of the ion density is cubic up to intensities of only 25 MW/cm^2 . Thereafter, a quadratic dependence is seen for the intermediate intensity region $25 \text{ MW/cm}^2 - 1 \text{ GW/cm}^2$. Together with the corresponding calculations for the peak 6p population (Figures 3.9(c) and 3.9(d)), this confirms that in this intensity region, the final

(a) Ion density vs intensity



(b) Log-log plot of ion population vs intensity

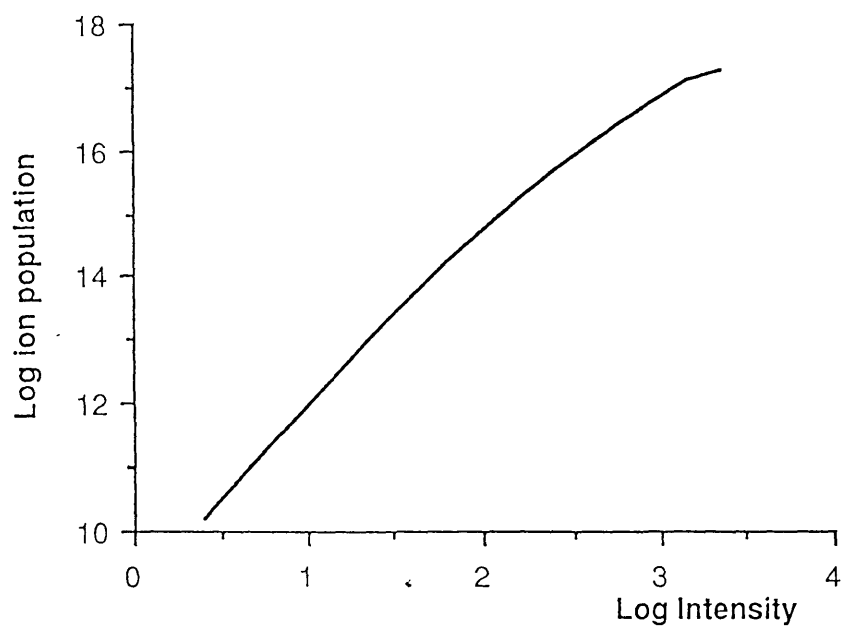


Figure 3.10 Dependence of Xenon Ion Population on Intensity
for a Reduced Two-Photon Absorption Cross-section

ionisation step from the 6p state to the continuum is saturated, i.e. the ionisation rate exceeds the two-photon excitation rate. The complete saturation at intensities $> 1.5 \text{ GW/cm}^2$ is a result of depletion of ground state atoms, which leads to saturation of the two-photon absorption step.

The rate equation calculations were also solved using a reduced value of the two-photon absorption cross-section to simulate behaviour in the wings of the resonance transition, or alternatively in the presence of the a.c. Stark effect. Results, for ion density versus intensity, for $\alpha = 0.6 \times 10^{-28} \text{ cm}^4 \text{ W}^{-1}$, one third the on-resonance value are shown in Figures 3.10(a) and 3.10(b). Saturation is evident even at these reduced absorption cross-sections.

Lifetime broadening due to stimulated emission between the two-photon-resonant 6p and 6s states is not easily included in the rate equation model without detailed knowledge of the stimulated emission cross-section, gain (saturated and unsaturated) and stimulated emission intensity. However, some indication of its effect can be gained by artificially reducing the radiative lifetime of the 6p state.

The rate equations were solved for a 6p lifetime of 0.5ns. (The radiative lifetime in the absence of stimulated emission is 30 ns [Verolainen and Osherovich, 1969]). A typical result plotting the evolution of the relevant populations is shown Figure 3.11 for a laser peak power of 1 GW/cm^2 . In contrast with the loss mechanism of ionisation, repopulation of the ground state is evident, although not within the duration of the laser excitation. This repopulation of the ground state is a graphic indication of the fact that at the reduced lifetimes considered, the stimulated emission channel dominates over

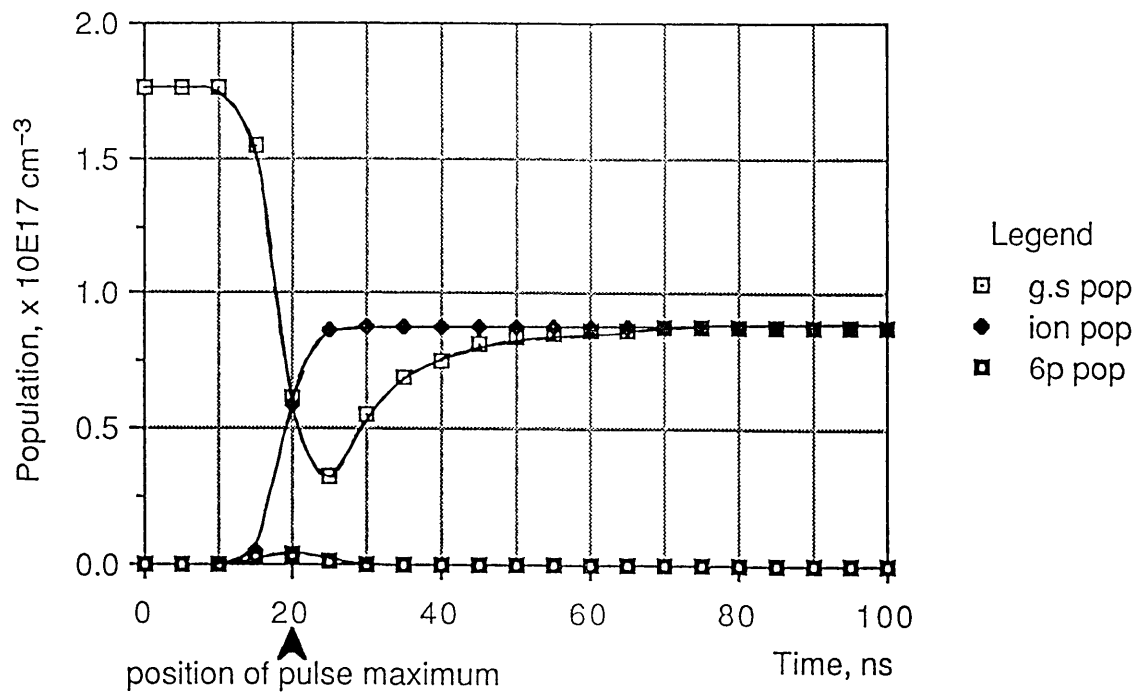


Figure 3.11 Xenon Population Evolution during the Passage of a 10 ns pulse, $\lambda = 249.63 \text{ nm}$, for Reduced Two-Photon-Resonant State (6p) Lifetime, $\tau_2 = 0.5 \text{ ns}$

ionisation, i.e. the stimulated emission transition rate is greater than the ionisation rate out of the 6p state. The exact nature of the saturation of the two-photon-resonant process which may result from this is not easily extracted from the calculation. The discussion of Section 3.2.3 gives a clearer physical interpretation of the situation.

These theoretical predictions are compared with experimental results in Chapter 4.

3.3.4 Discussion

We have seen in this section that although it is not appropriate to include all physical effects in the rate equation approach, the results obtained can be used to predict general trends.

Firstly, it is clear that at high intensities power broadening is not a significant mechanism due to the rapid removal of population from the two-photon-resonant state by ionisation or stimulated emission. It is indeed less significant than initial calculations of Section 3.2.1. indicate, since excited state population depletion must be considered.

Lifetime broadening due to ionisation is, as previously discussed, likely to be insignificant, particularly in view of the effect of simulated stimulated emission. Stark broadening due to photoelectrons must certainly be considered to be of importance in view of the large ion densities predicted. A.c. Stark shifting cannot be effectively included in this model except by some reduction in the two-photon absorption cross-section to simulate level shifting.

The solution of the rate equations has given us a useful

insight into the complete Xenon system and the interaction of some physical processes leading to population redistribution. Some conclusions about the relative significance of saturation mechanisms have been made.

3.4 Conclusions.

This chapter has aimed to present an overview and theoretical analysis of the mechanisms which may contribute to the saturation of two-photon resonant processes in Xenon.

Consideration of mechanisms individually, together with the results of solving the relevant rate equations has lead to an assessment of the magnitude and associated importance of each mechanism. Naturally most effects are intensity dependent; others are additionally dependent on other factors. For example, Stark broadening due to photoelectrons is pressure dependent and stimulated emission effects are dependent on the beam geometry.

The theory and calculations presented in this chapter are used in Chapter 4 in the analysis of the experimental results on two-photon resonant three-photon ionisation in Xenon. The experiments and analysis described in Chapter 4 lead to an understanding of the saturation mechanisms in such two-photon resonant processes.

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CHAPTER 4

EXPERIMENTAL INVESTIGATION OF SATURATION MECHANISMS IN TWO-PHOTON RESONANTLY ENHANCED PROCESSES IN XENON

4.1 Introduction

This chapter describes experiments carried out to investigate some of the processes described in Chapter 3 as potentially causing saturation of two-photon resonantly enhanced processes in Xenon. The results are discussed with the aim of assessing the dominant mechanism(s) contributing to the broadening of the two-photon-resonant state. The experimental work fell into two sections, monitoring two processes which result from two-photon-resonant pumping.

These processes were:

- (i) Two-photon-resonant three-photon ionisation.
- (ii) Stimulated emission at $\lambda = 828 \text{ nm}$, due to the population inversion between the $6p, J = 0$ and $6s, J = 1$ levels.

The experimental system described in Chapter 2 was used in these studies: the ultra-violet source at $\lambda = 249.63 \text{ nm}$ only was required for the experiments reported in this chapter.

The three-photon ionisation experiment is described in Section 4.2 and the stimulated emission study in Section 4.3. In Section 4.4 the theoretical predictions of Chapter 3 are compared with the experimental findings and conclusions are presented in Section 4.5.

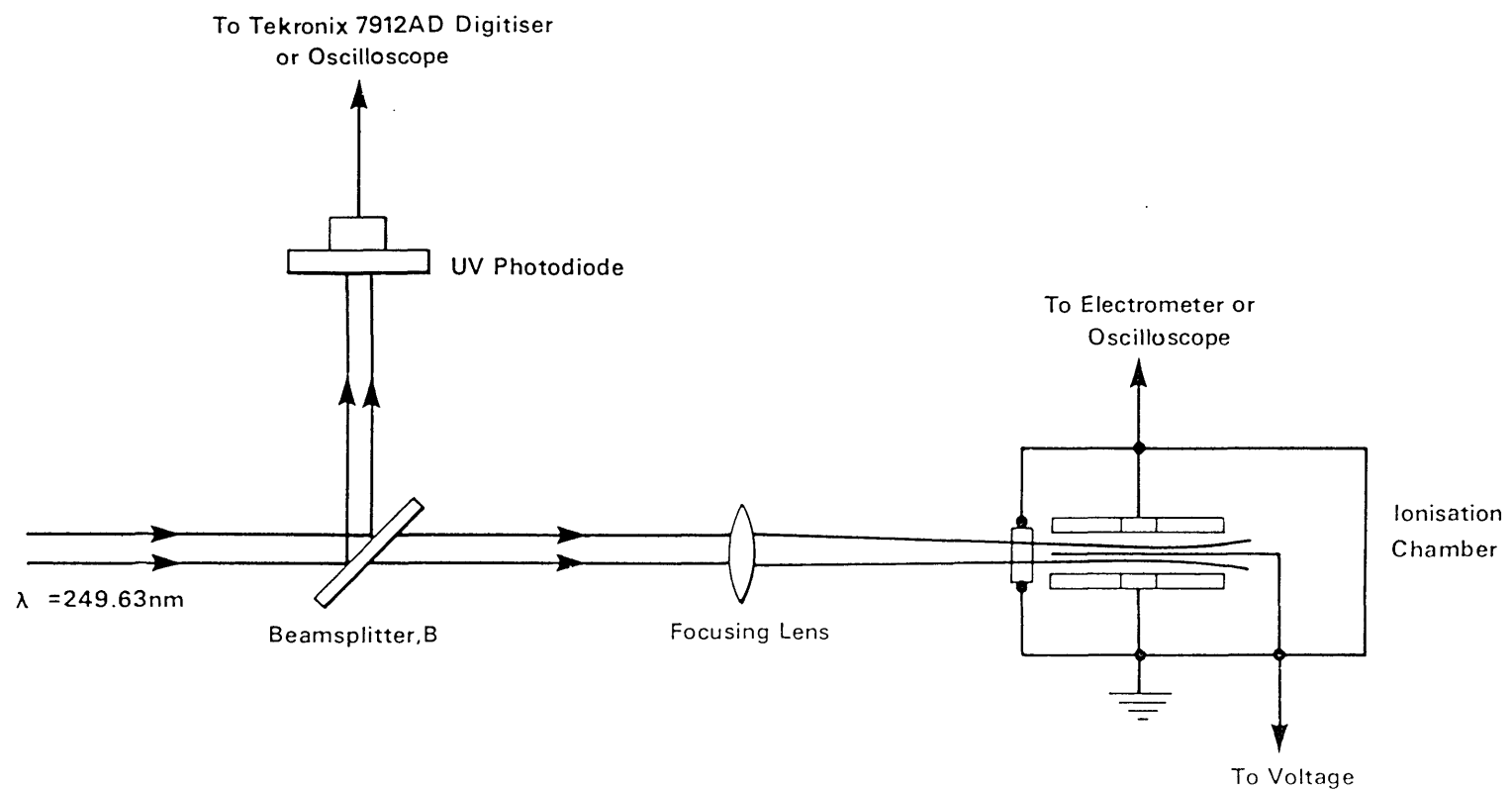


Fig 4.1 Detection of Three-Photon Ionisation Signal: Experimental Arrangement

4.2 Two-Photon-Resonant Three-Photon Ionisation

4.2.1 Experimental Method

Recapping from Chapter 2 (Sections 2.4.4 and 2.4.5), the coherent radiation at 249.63 nm, emerging from the KrF* excimer amplifier, was focused into the ionisation chamber. The ions produced were monitored using either an oscilloscope or electrometer. The experimental system arrangement was as shown schematically in Figure 4.1. The design of the ionisation chamber is shown in detail in Figure 2.20.

The light was focused between the ionisation chamber electrodes using a quartz biconvex singlet lens. The power density in the chamber was varied by two methods as follows:

- (i) For a focusing lens of fixed focal length, the power fluctuations in the output at $\lambda = 249.63$ nm, discussed in Section 2.4.5, allowed the ionisation signal to be measured for a range of intensities. Typically, the range of intensities, which could be studied by this effect over a full resonance scan, was a factor of around 3 or 4. Attenuation of the beam was not used as a method of further increasing the range of intensities investigated since the small ionisation signals produced in such circumstances were difficult to measure with reasonable accuracy. Instead, lower power densities were produced by
- (ii) The use of a range of lenses of focal lengths between 20 and 130 cm. In this way, the full energy available from the laser system was always used, and the larger focal volumes ($V \approx \text{area of focal spot} \times \text{confocal parameter}$, 2b) produced by the longer focal length lenses resulted in a more easily measured ionisation signal.

It should be noted that, due to the different focal volumes produced by each lens, it was not possible to accurately correlate absolute ionisation measurements made with lenses of different focal lengths. In addition, at high intensities, the effective focal volume becomes intensity-dependent, since there can be a significant contribution to the ionisation signal from regions outwith that strictly specified as the focal volume.

The objective of the multiphoton ionisation experiment was to investigate saturation mechanisms via two routes.

- (i) Measurement of the linewidth of the two-photon-resonant state and its dependence on intensity.
- (ii) Study of the dependence of the two-photon-resonant three-photon ionisation signal on input power, in the spectral region of the resonance.

Data was acquired as follows. Shot-to-shot fluctuations of up to 100% in the output from the KrF* excimer amplifier, as previously described in Section 2.4.5, necessitated data collection on a single shot basis. The frequency of the UV radiation was stepped through the two-photon resonance by tuning the green dye laser. Re-optimisation of the second harmonic crystal phase-matching angle during a scan of the resonance was not found to be necessary.

Due to backlash on the fine tuning control of the green laser, it was necessary to acquire data while tuning in one direction only and consequently data from more than one experimental run could not be combined. Each of the sets of results presented in this chapter and in Chapter 6 was collected on a single experimental run.

For each tuning position data was collected to produce a graph

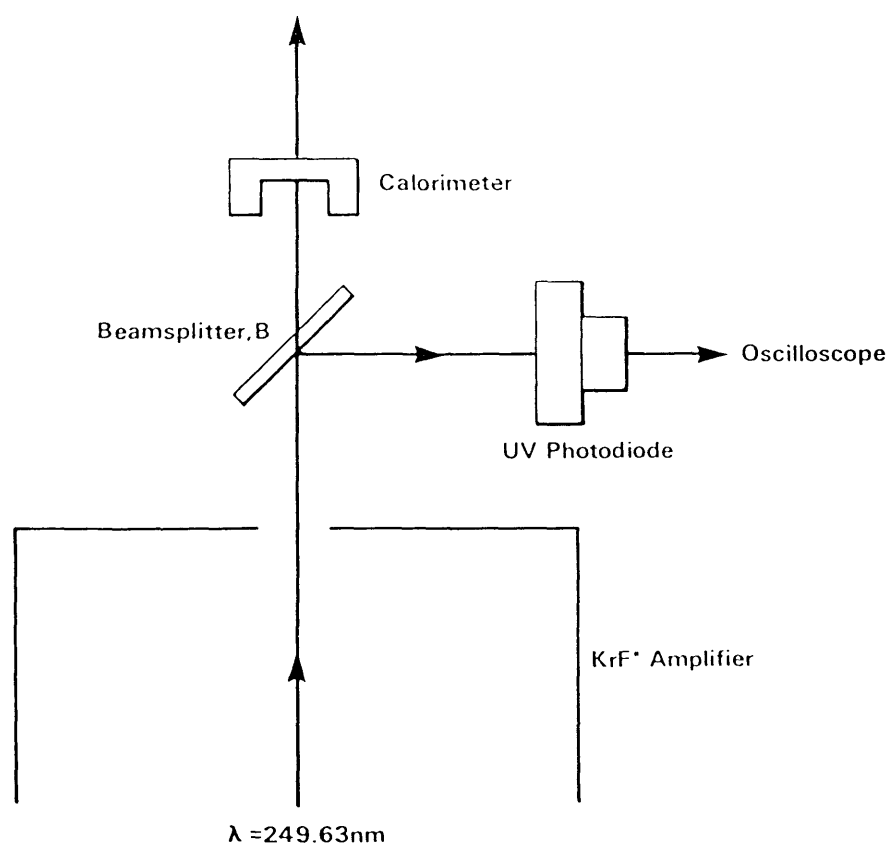


Fig 4.2 Calibration of Ultra-Violet Photodiode: Experimental Arrangement

of ion yield versus power density. The laser system was operated either single-shot via an external trigger, or at a low repetition rate of approximately 0.5 Hz. A Tektronix 7912AD digitiser and PDP-11 computer were used for data acquisition and storage in conjunction with either a Keithley electrometer or a Tektronix 7834 storage oscilloscope. Two modes of data acquisition were employed depending on equipment availability, and are summarised in Table 4.1.

Sets of pairs of peak UV signal and ion yield were stored for each tuning position. Generally around 15 data pairs were collected for each tuning position, this number being restricted by the total volume of data which could be collected in a single run of the experiment. The duration of a run was determined by the KrF* excimer amplifier gas fill lifetime and was approximately 2-3 hours.

The peak UV signal was converted to intensity, and hence to power density in the focal region, by a two step process, as follows. Firstly, the UV photodiode used was calibrated to provide a pulse energy measurement using the arrangement shown in Figure 4.2. The plot of pulse energy against peak UV signal shown in Figure 4.3 is the result of this calibration. The linear relationship is expected since, for a fixed pulse duration, the energy in a Gaussian pulse, to which the UV pulse-shape approximates, is proportional to the maximum pulse height. Further losses at optical elements between the calibration point and the ionisation chamber, none of which were anti-reflection coated, were included in calculations of the final energy delivered to the Xenon in the ionisation chamber.

Secondly, the peak power was estimated by dividing the pulse energy by the FWHM pulse duration. For Gaussian and 'top-hat'

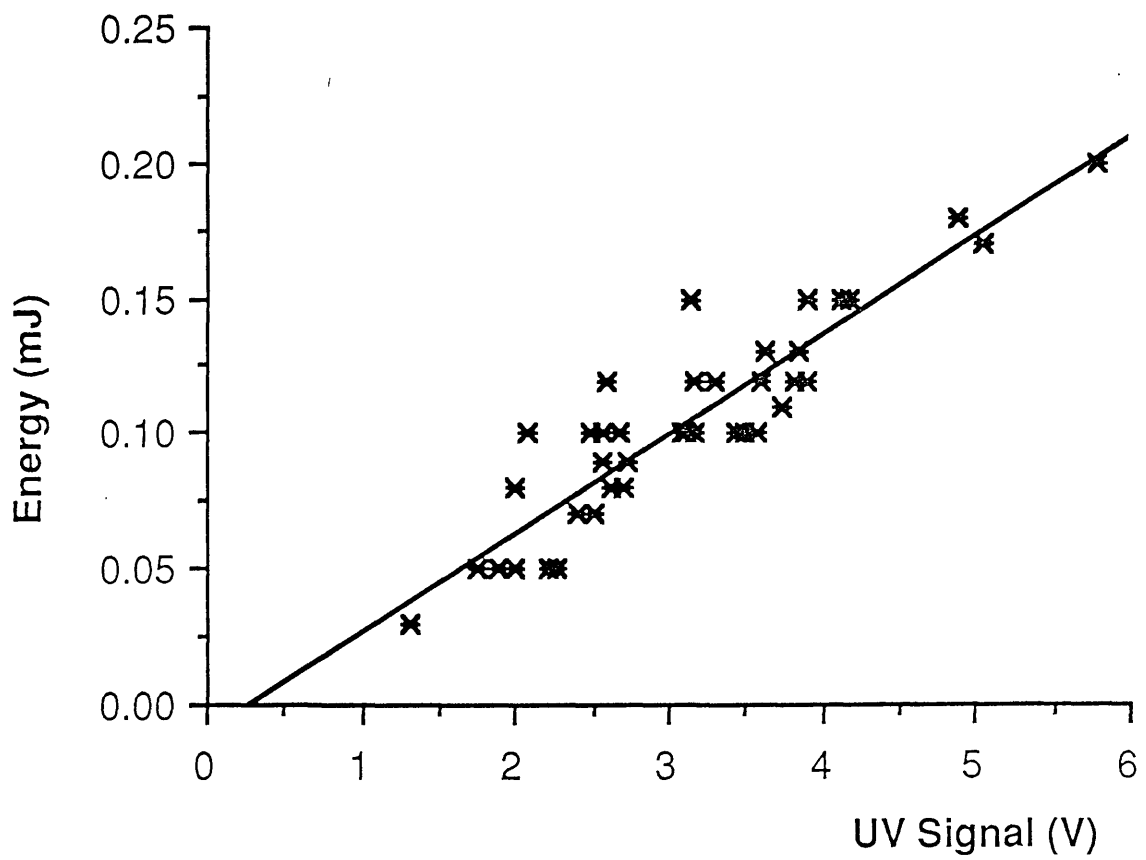


Figure 4.3 Calibration of Ultra-Violet Photodiode:
Calibration Graph

	UV Signal	Ionisation Signal
(i)	Tektronix 7912AD digitiser	Keithley electrometer
(ii)	Tektronix 7834 storage oscilloscope	Tektronix 7912AD digitiser

Table 4.1 Data Collection Instrumentation

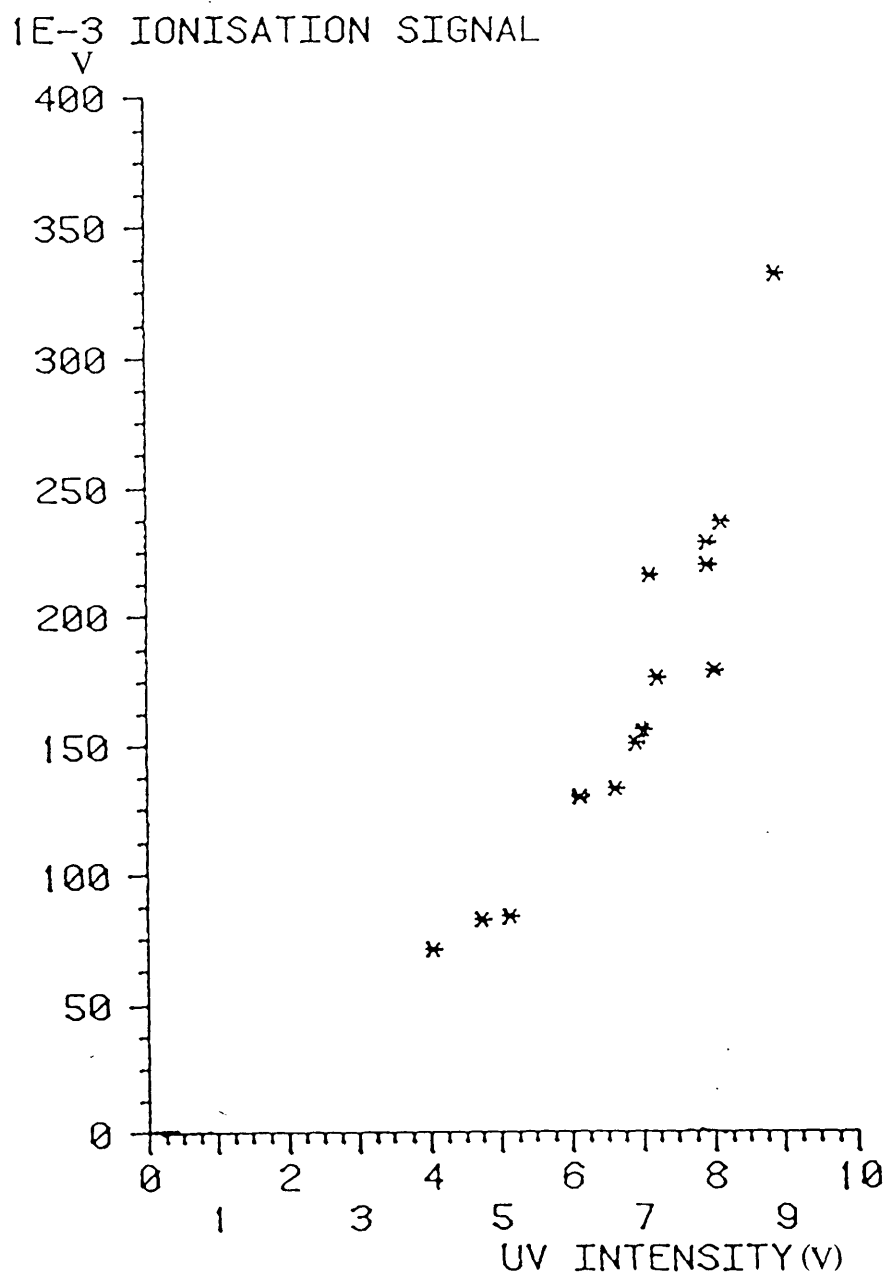


Figure 4.4 Three-Photon Ionisation Yield versus Intensity

pulses of the same total energy and FWHM, the peak powers differ by only 6%. Hence, the 'top-hat' approximation introduces only a small error. For a constant pulse duration then, pulse peak power is proportional to the pulse height.

It can be shown that, once calibrated for a given pulse duration, this calculation is valid for any pulse duration. Focal spot sizes were estimated using precision calibrated pinholes. Confocal parameters were calculated using Gaussian beam propagation formulae, with corrections to account for the foci being approximately 3 x diffraction limited.

Absolute ionisation densities could be estimated from measurements using the oscilloscope or Keithley electrometer and the estimated focal volume, assuming that all the ionisation signal is generated within that volume and is collected by the ionisation chamber electrodes. This is believed to be the case for a chamber voltage of -350V, as shown by Figure 2.22, the voltage/ionisation signal characteristic of the chamber. The electrometer gave a direct measure of ionisation signal. When the ionisation signal was displayed directly on the oscilloscope, a triangular pulse shape was observed, with the signal decaying on a timescale of a few milliseconds. The peak signal was hence proportional to the total charge collected which could be estimated as the area under the voltage graph divided by the input impedance of the oscilloscope (50Ω). These calculations were useful for estimating the proportion of atoms being ionised, for comparison with rate equation calculations, particularly for high intensity ($\sim 1 \text{ GW/cm}^2$) studies.

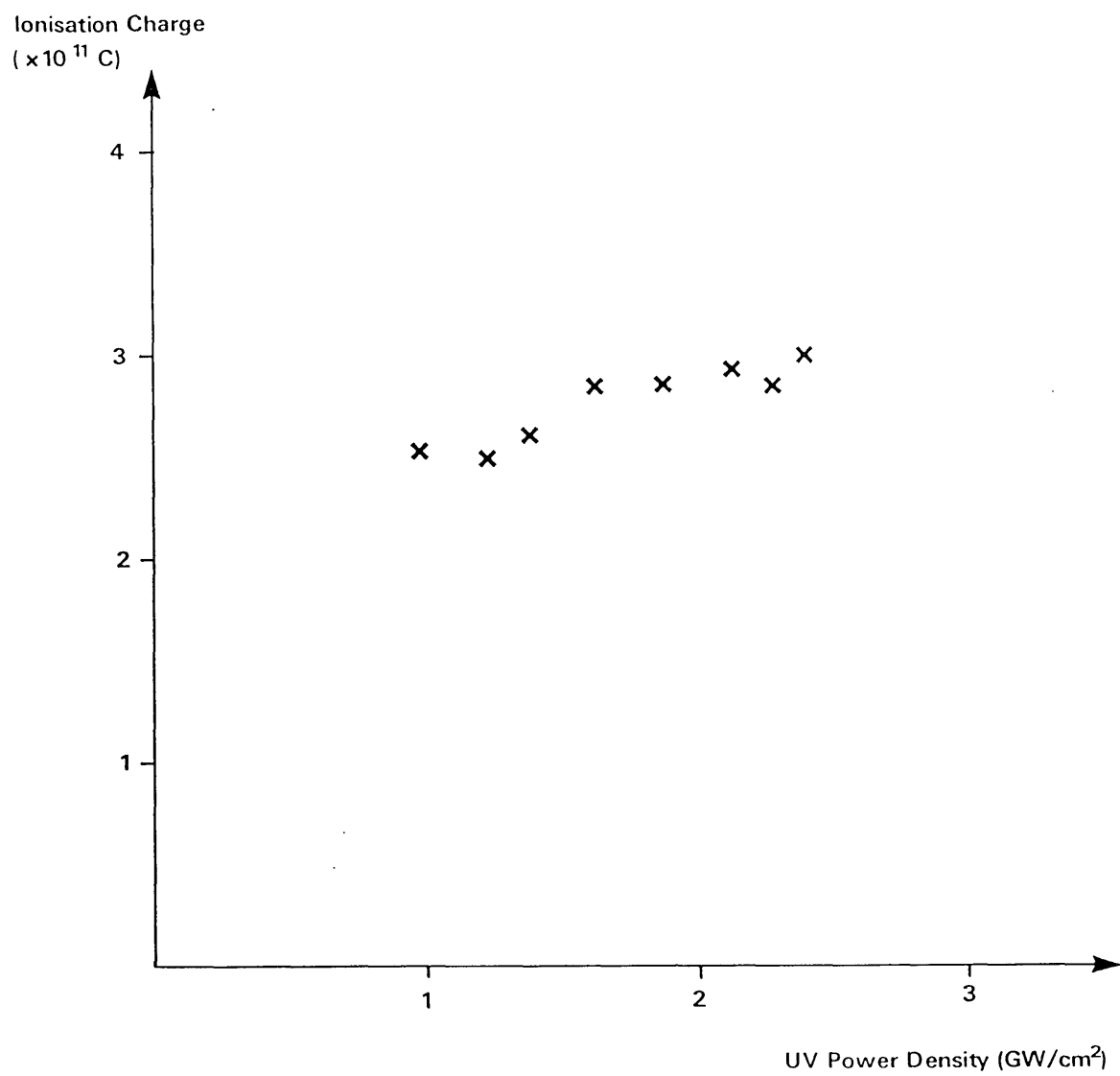


Fig 4.5 Ionisation Charge Collected Versus Intensity (Off-Resonance)

4.2.2 Data Analysis

Data was initially extracted from the plots of ion yield versus intensity for each tuning position by fitting the best curve by eye to the data, and reading off ion yields for several intensities, typically 3 or 4, within the range available. A typical data plot is shown in Figure 4.4. For this example it is clear that there is a power law dependence between ionisation signal and UV peak power. In this case, a log-log plot of the data would be useful in determining the order of the dependence, and this could then be used in assessing the degree to which saturation were present. It must be noted, however, that in a number of experimental runs the range of UV powers which could be investigated was inadequate to give meaningful results to this kind of analysis. In those cases, a straight line was usually plotted through the data.

Errors in the ion signal were estimated from the scatter of experimental data points and were typically of the order of 10-20%. There are a variety of sources of this error, including jitter in the laser frequency and small fluctuations in the duration and pulse shape of the amplified UV pulse.

Such pulse duration fluctuations also contributed to the experimental error the power density measurement. Together with other approximations, discussed in the previous section, and estimation of reflection losses and focal spot sizes, the error in the power densities calculated are estimated to be approximately $\pm 20\%$.

From data analysed in the way described, scans of the two-photon resonance were built up.

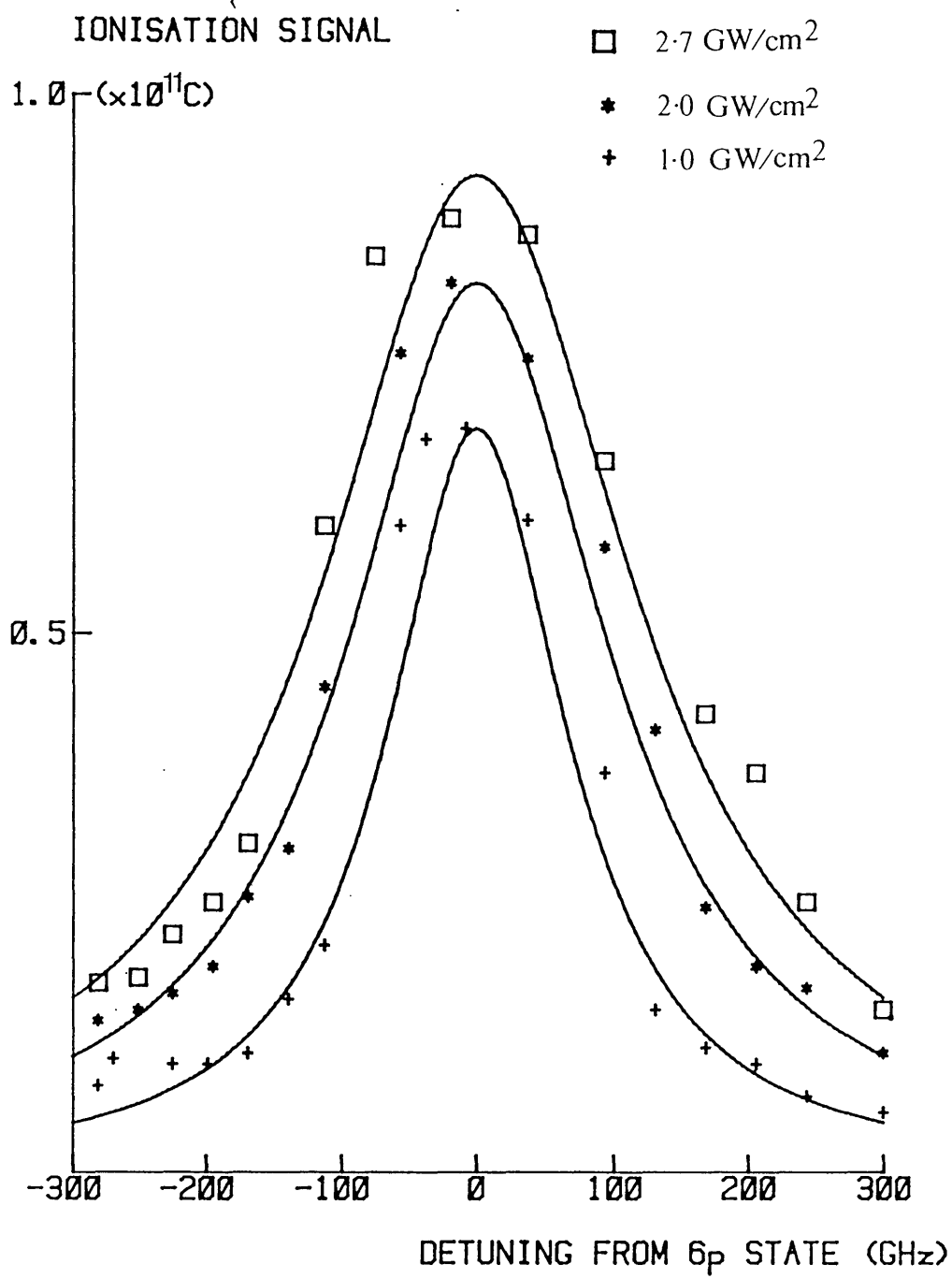


Figure 4.6

Measured Three-Photon Ionisation Signals in the Region of
Two-Photon Resonance with the 6p, ($J=0$), state for
Intensities in the Range 1 - 2.7 GW/cm²

4.2.3 Experimental Results

Initially the two-photon-resonant three-photon ionisation was investigated at high laser intensities, typically $1\text{--}3\text{ GW/cm}^2$. These intensities were produced by focusing the incident UV radiation with a 20cm focal length lens. The focal spot diameter, $2\omega_0$, was estimated to be 25 μm and the corresponding confocal parameter, $2b$, to be 0.15cm. For data collected over a range of UV intensities, the gradients of straight lines fitted to log-log plots of ionisation signal versus intensity were used to assess the degree of saturation as the UV frequency was tuned through the two-photon resonance. For these high intensities, substantial saturation was observed, even in the wings of the resonance.

Under such circumstances, it was found that the ionisation signal was almost independent of the UV power density. Figure 4.5 is a plot of ion yield versus intensity for the intensity region where this is the case. This behaviour indicates strong saturation of both the two-photon excitation and the single-photon ionisation steps of the three-photon ionisation process. The small increase in ionisation signal with intensity could be due to the dependence of the focal volume on intensity at these high intensities. In the wings of the resonance, it was found that the ionisation signal was $\propto I^n$, where $1 < n < 2$.

Figure 4.6 shows the two-photon resonance lineshapes measured when the resonance was scanned for intensities of $1\text{--}2.7\text{ GW/cm}^2$, produced by focusing the incident radiation into the ionisation chamber, containing Xenon at a pressure of 10 torr, using a 20cm focal length lens. The frequency scale shows real detuning from the $6p, J = 0$, two-photon-resonant state. The solid lines are fitted Lorentzian lineshapes with widths (FWHM)

Δ FOUR WAVE MIXING SIGNAL $I = 1\text{GW}/\text{cm}^2$
 $\square$ IONISATION SIGNAL

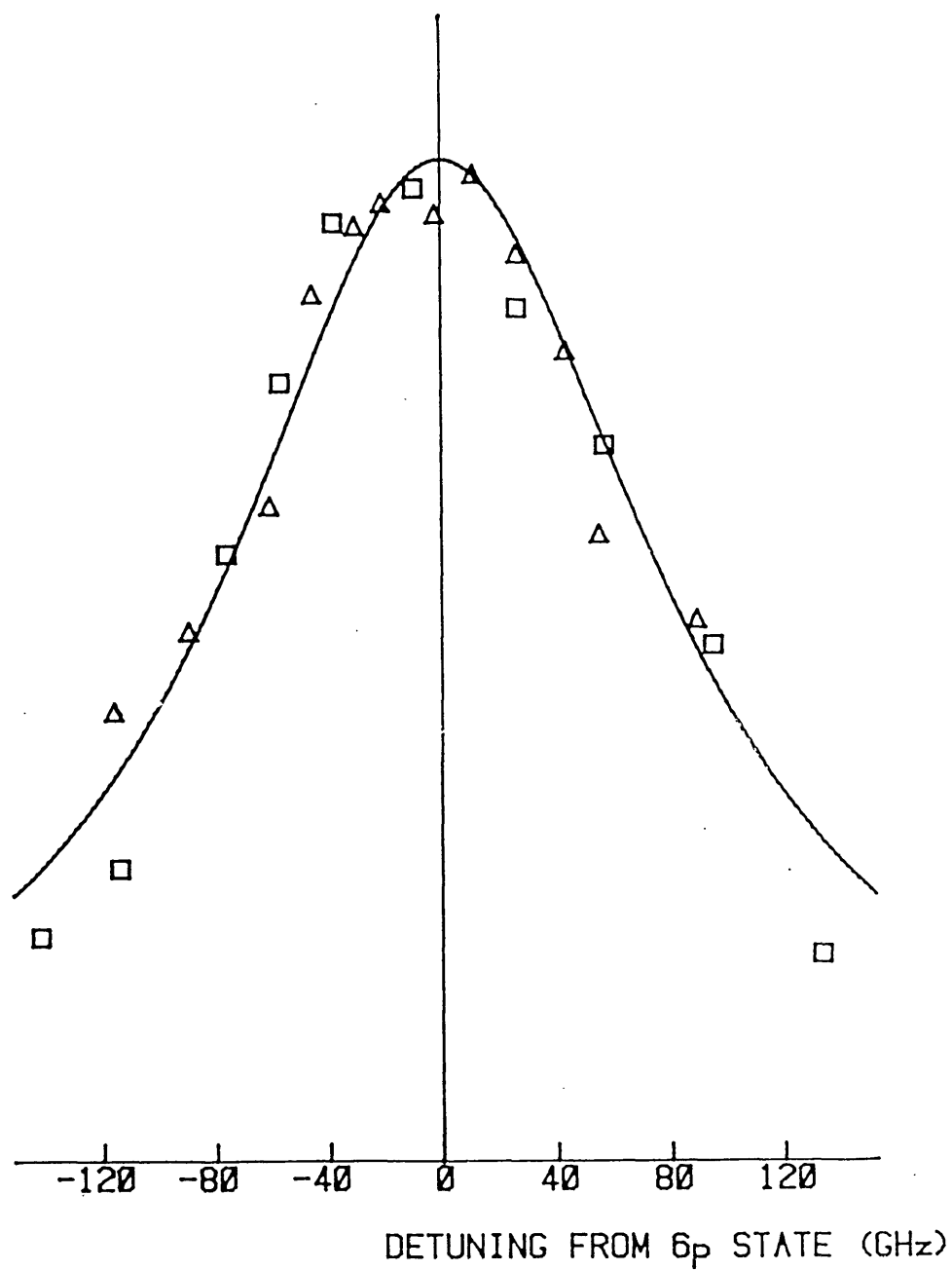


Figure 4.7

Comparison of Linewidth of Two-Photon Resonance Measured
 via Three-Photon Ionisation and Four-Wave Mixing

in the range 160-280 GHz.

In Figure 4.7, we compare the two-photon resonance linewidth measured via the two-photon-resonant three-photon ionisation signal and that measured by Hutchinson and Thomas, 1983, via a two-photon-resonant four-wave mixing, difference frequency generation, signal at 155nm ($\omega_4 = 2\omega_1 - \omega_2$), where $\omega_1 = 249.63\text{nm}$ and $\omega_2 \sim 630\text{nm}$). We see that for a UV intensity of 1 GW/cm^2 , the results can be fitted to the same Lorentzian lineshape, showing excellent correlation between the two experiments.

By focusing the UV radiation weakly using a 130 cm focal length lens, intensities of around 10 MW/cm^2 were produced in the region between the electrodes of the ionisation chamber. This was two orders of magnitude smaller than those intensities previously investigated. Here the focal spot diameter was found to be approximately $125\text{ }\mu\text{m}$, and the confocal parameter estimated to be 3.3cm . This is longer than the collecting region of the ionisation chamber leading us to assume a collimated beam throughout the ionisation chamber measurement region.

Figure 4.8 shows the measured linewidths in this low intensity region, for a Xenon pressure of 10 torr. We see that the state is still substantially broadened, Lorentzians of widths (FWHM) of around 80 GHz being fitted to the data.

Again, the power law dependence of ionisation signal on intensity was monitored through the resonance from the gradient of straight lines fitted to log-log plots of the data. In the wings of the resonance, around 120 GHz from line centre, it was found that the dependence was cubic. However, this reduced towards the line centre, where the dependence was found to be

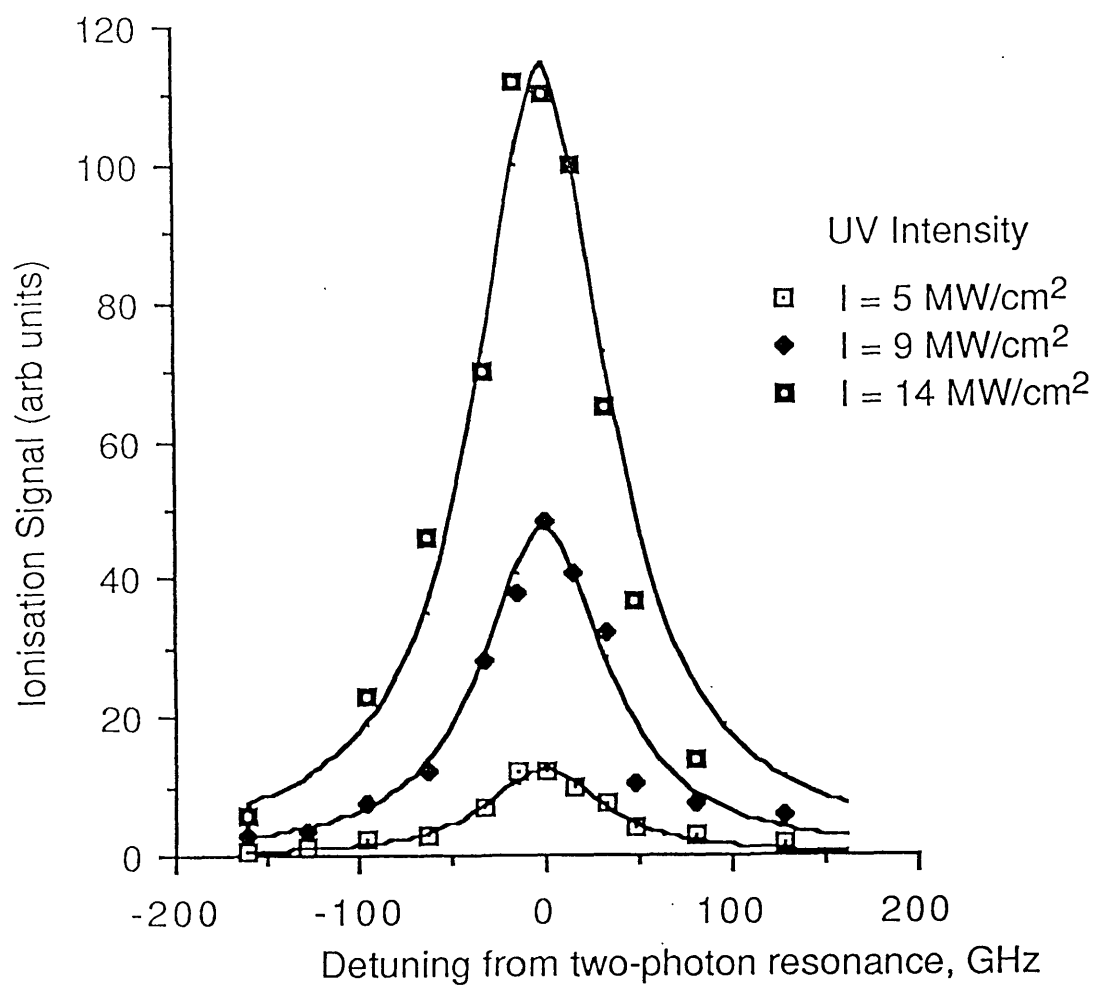


Figure 4.8

Measured Three-Photon Ionisation Signals in the Region of Two-Photon Resonance with the $6p$, ($J=0$), state for Intensities in the Range $4 - 14 \text{ MW/cm}^2$

almost exactly quadratic.

The combined results of low and high intensity regime two-photon resonance linewidth measurements are plotted in Figure 4.9 which shows linewidth against intensity. Errors in the linewidth measurement are not shown, but are estimated, from the errors on Figures 4.6 and 4.8, to be approximately $\pm 10\%$. A linear relationship between linewidth and intensity is observed, with a straight line being fitted to the data.

The possible presence of shifting of the energy levels due to the d.c. Stark effect resulting from the electric field present in the ionisation chamber was investigated and found to be an unmeasurably small effect for our experimental conditions.

The most striking feature of the results is the fact that the linewidth is substantially broadened over the expected Doppler linewidth (2.6GHz), even at low intensities. In Section 4.4, we consider quantitatively the mechanisms discussed in Chapter 3 as being potentially responsible for the observed linewidths. We attempt to identify the mechanism leading to the experimental results over the range of intensities investigated.

4.3 Stimulated Emission from the Two-Photon-Resonant State

4.3.1 Experimental Method and Data Analysis

As discussed in Section 3.2.3.2 it is clear that under the two-photon pumping rates used in the three-photon ionisation experiments, a substantial population inversion can be produced between the $6p$, $J = 0$, and $6s$, $J = 1$, levels. Coupled with a large calculated value for the stimulated emission cross-section ($2.2 \times 10^{-12} \text{ cm}^2$), this indicated a high probability of stimulated emission between the states. The expected

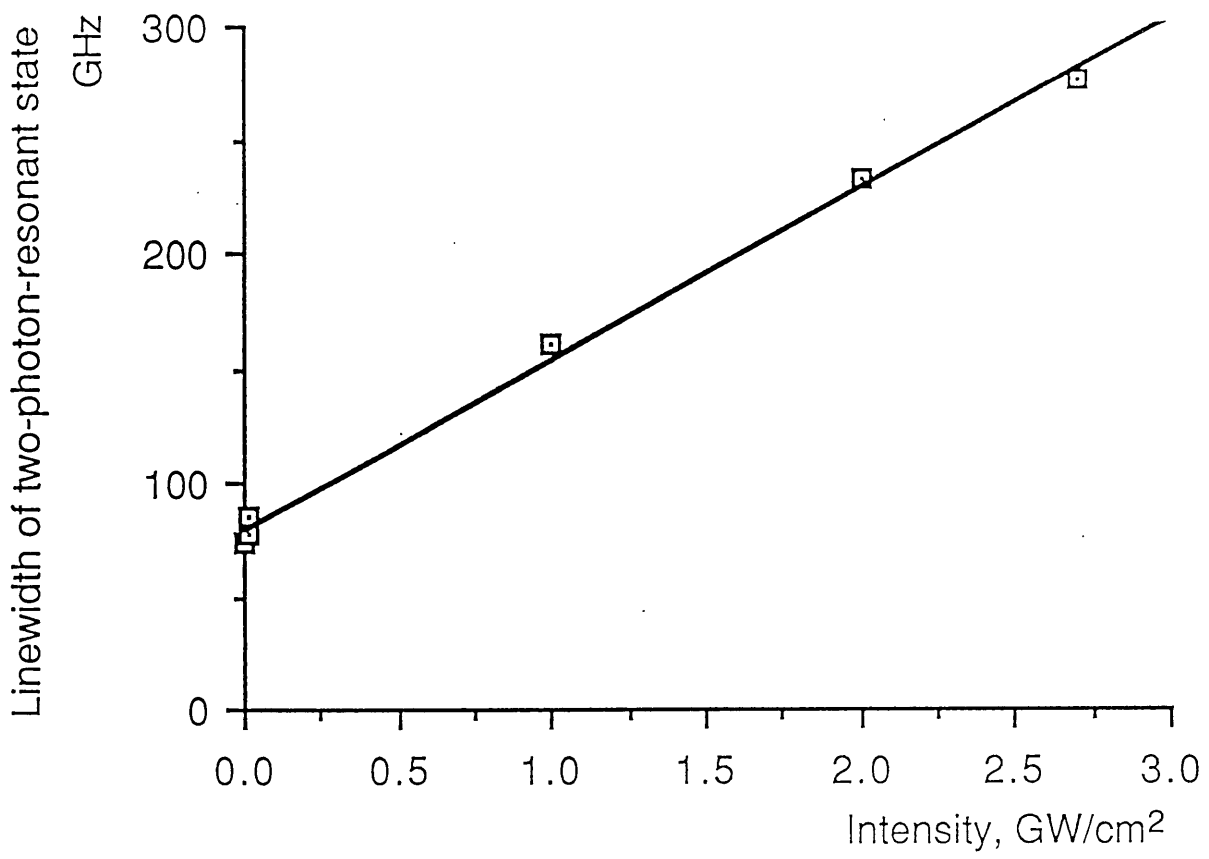


Figure 4.9 Linewidth of Two-Photon-Resonant State
versus Intensity

wavelength of emission is 828.24 nm.

A simple experimental arrangement was used to investigate this process and is shown in Figure 4.10. The radiation at 249.63nm was focused into a simple Xenon cell connected to the gas handling system described in Section 2.4.5. The transmitted and forward-emitted radiation was collected and focused onto the entrance slit of a 1m spectrograph. Glass filters were used to remove the UV radiation and a photomultiplier on the exit slit of the spectrograph detected the infra-red radiation at $\lambda = 828\text{nm}$. Both entrance and exit slits of the spectrograph were used fully open to ensure collection and detection of as much infra-red radiation as possible.

As in the case of the three-photon ionisation experiments, the shot-to-shot fluctuations of the UV laser power required data collection on a single shot basis. The UV input signal and the IR emission were monitored simultaneously on a Tektronix 7834 storage oscilloscope and Tektronix 7912AD digitiser. Sets of about 10 pairs of points were recorded for each tuning point as the UV radiation frequency was scanned through the two-photon resonance by tuning the green dye laser. Data analysis was as described in Section 4.2.2.

4.3.2 Experimental Results

The infra-red emission was observed for low intensity pumping of the two-photon-resonant state, using the geometry described for low intensity measurement of the two-photon-resonant three-photon ionisation signal. A 130 cm focal length lens produced a focal region of waist diameter of 125 μm and estimated confocal parameter 3.3cm in the 10 cm long cell containing Xenon at a pressure of 10 torr.

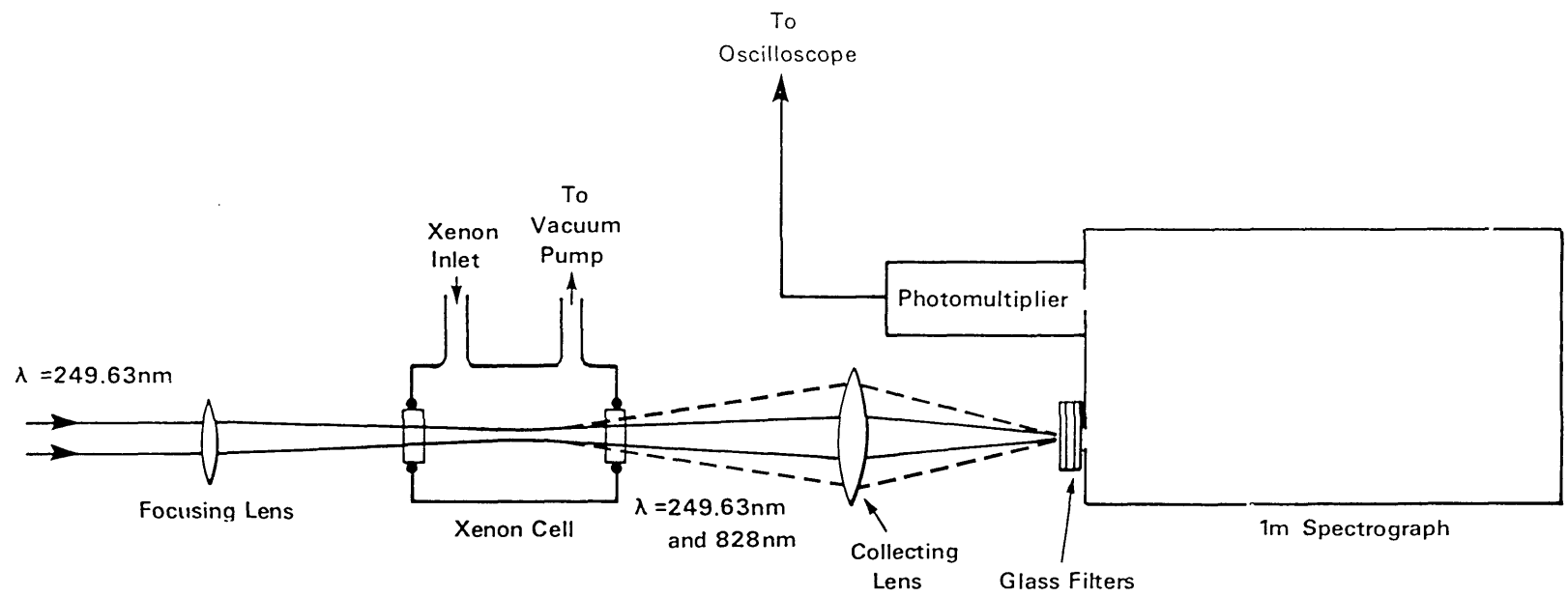


Fig 4.10 Detection of Stimulated Emission Signal: Experimental Arrangement

Initial observation of the infra-red signal with on-resonance excitation showed that the emission was probably stimulated. The spontaneous lifetime of the upper level is 30 ns [Verolainen and Osherovich, 1969] and as can be seen from the output of the photomultiplier shown in Figure 4.11, the observed IR pulse has a duration which is substantially shorter than this. The FWHM pulse duration measured from the oscilloscope trace is approximately 4 ns. However, this represents an upper limit for the pulse duration resulting from the integration time of the photomultiplier. Equipment was not available to permit higher resolution measurement of the pulse duration. The long duration background present on the trace was a result of scattered light and was present even when there was no Xenon in the cell. The short duration stimulated emission signal disappeared when the Xenon was removed from the cell.

Meaningful estimation of the intensity of the generated infra-red radiation was difficult for a number of reasons. Firstly, the efficiency of the collection optics, including the efficiency of the spectrometer grating at this wavelength, was not known. Secondly, the radiation detected was sufficiently intense to produce signals thought to be capable of saturating the photomultiplier when operating at its recommended voltage of 2.5kV. For this reason, a reduced operating voltage of 1.8kV was used which made accurate estimation of operating efficiency difficult with available operating data. Under these circumstances, peak signals of over 20 V (into a 50 Ω oscilloscope plug-in) were still recorded. Attempts to measure the signal with a fast-rise-time PIN photodiode were, however, unsuccessful, due to the energy available being insufficient to generate a measurable signal. Thirdly, as will be described,

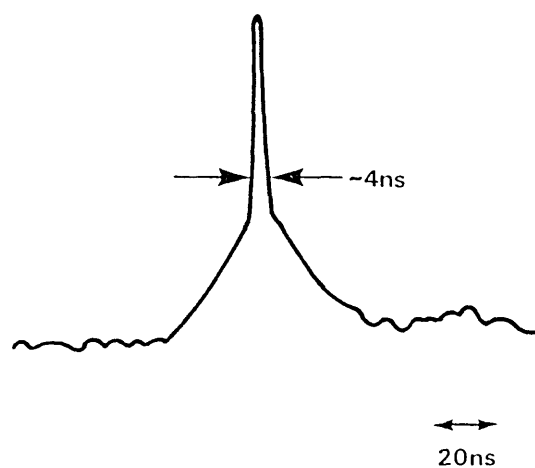


Fig 4.11 Oscilloscope Trace of Stimulated Emission at $\lambda = 828.2\text{nm}$ Measured Using Photomultiplier

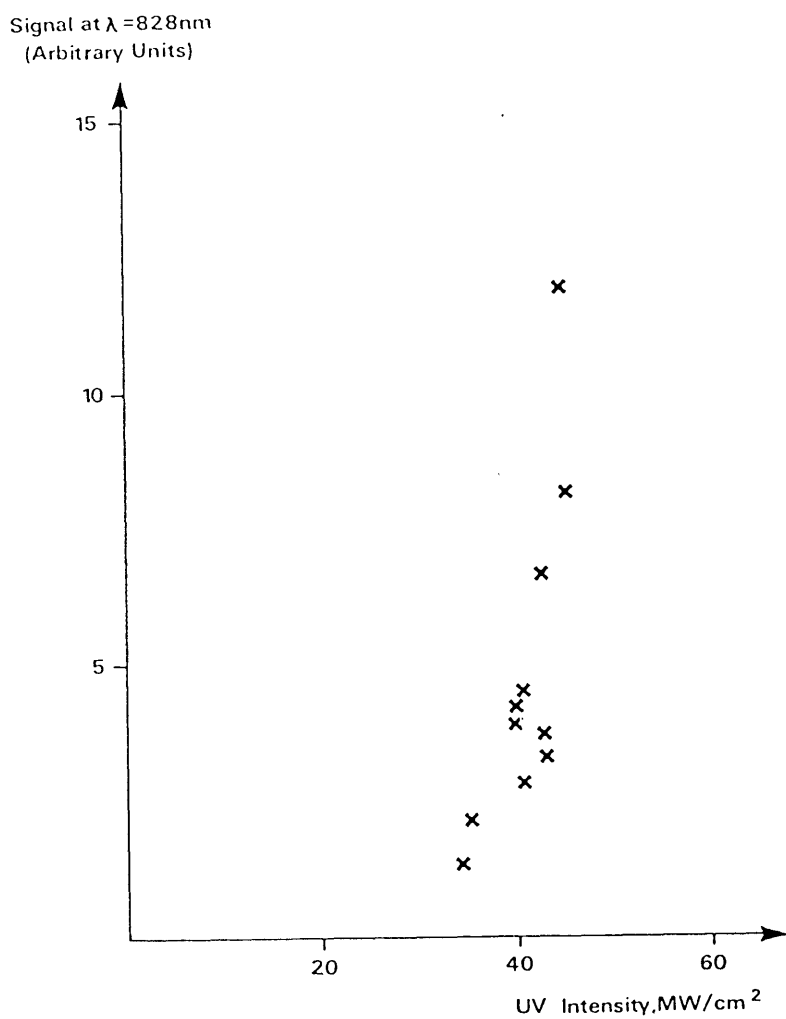


Fig 4.12 Generated Infra-Red Signal Versus Ultra-Violet Intensity

the infra-red output fluctuated greatly in intensity. Despite these difficulties, we draw the tentative conclusion, on the basis of a number of estimations that the peak power of the stimulated emission output was in the region of a few hundred Watts.

Qualitatively it was found that the infra-red intensity was very strongly dependent on the input ultra-violet intensity, indicating the possibility of exponential gain. Figure 4.12 shows a plot of the peak IR signal versus UV intensity. Data would be required over a much wider range of UV intensities in order to determine the exact dependence of I_{IR} on I_{UV} . From such results, scans constructed of the dependence of the generated IR signal on UV intensity while tuning through the two-photon resonance were subject to large experimental errors. An example of the resonance measured in this way is shown in Figure 4.13. The UV intensity was 40 MW/cm^2 and the Xenon pressure 10 torr. The FWHM is approximately 50 GHz which is comparable with the width measured at these UV intensities via the two-photon-resonant three-photon ionisation signal.

The dependence of the infra-red signal on pressure was investigated and an approximately linear relationship was found at pressures up to approximately 300 torr, as shown in Figure 4.14. Non-linearity at higher pressures could be due to the presence of Xenon dimers.

The linear dependence of the stimulated emission signal on pressure is evidence of the severe saturation of the stimulated emission process. In unsaturated circumstances, we would expect to see an exponential dependence of the signal on the small signal gain, $g_0 l = \sigma_{stim} \Delta N l$, and hence on pressure. The linear dependence observed indicates that the gain is

the infra-red output fluctuated greatly in intensity. Despite these difficulties, we draw the tentative conclusion, on the basis of a number of estimations that the peak power of the stimulated emission output was in the region of a few hundred Watts.

Qualitatively it was found that the infra-red intensity was very strongly dependent on the input ultra-violet intensity, indicating the possibility of exponential gain. Figure 4.12 shows a plot of the peak IR signal versus UV intensity. Data would be required over a much wider range of UV intensities in order to determine the exact dependence of I_{IR} on I_{UV} . From such results, scans constructed of the dependence of the generated IR signal on UV intensity while tuning through the two-photon resonance were subject to large experimental errors.

Further discussion of Figure 4.12

From Figure 4.12, we estimate a process 'threshold' of approximately 25 MW/cm^2 . In the absence of a laser cavity, it has been shown [Hanna, Yuratich and Cotter, 1979] that it is appropriate to equate 'threshold' with a small signal gain exponent value of 30. Hence, at threshold,

$$\sigma_{\text{stim}} \Delta N l = 30$$

and for our experimental conditions

$$\Delta N = 4 \times 10^{12} \text{ cm}^{-3}.$$

From consideration of two-photon pumping rates, this 6p population corresponds to a pump intensity (UV) of 3 MW/cm^2 for a pressure of 10 torr as used. This differs somewhat from the observed threshold. However, in view of the possible errors in the large number of parameters involved, such as stimulated emission cross-section, two-photon excitation cross-section, confocal parameter, pulse duration and UV power density, the result shows reasonable agreement.

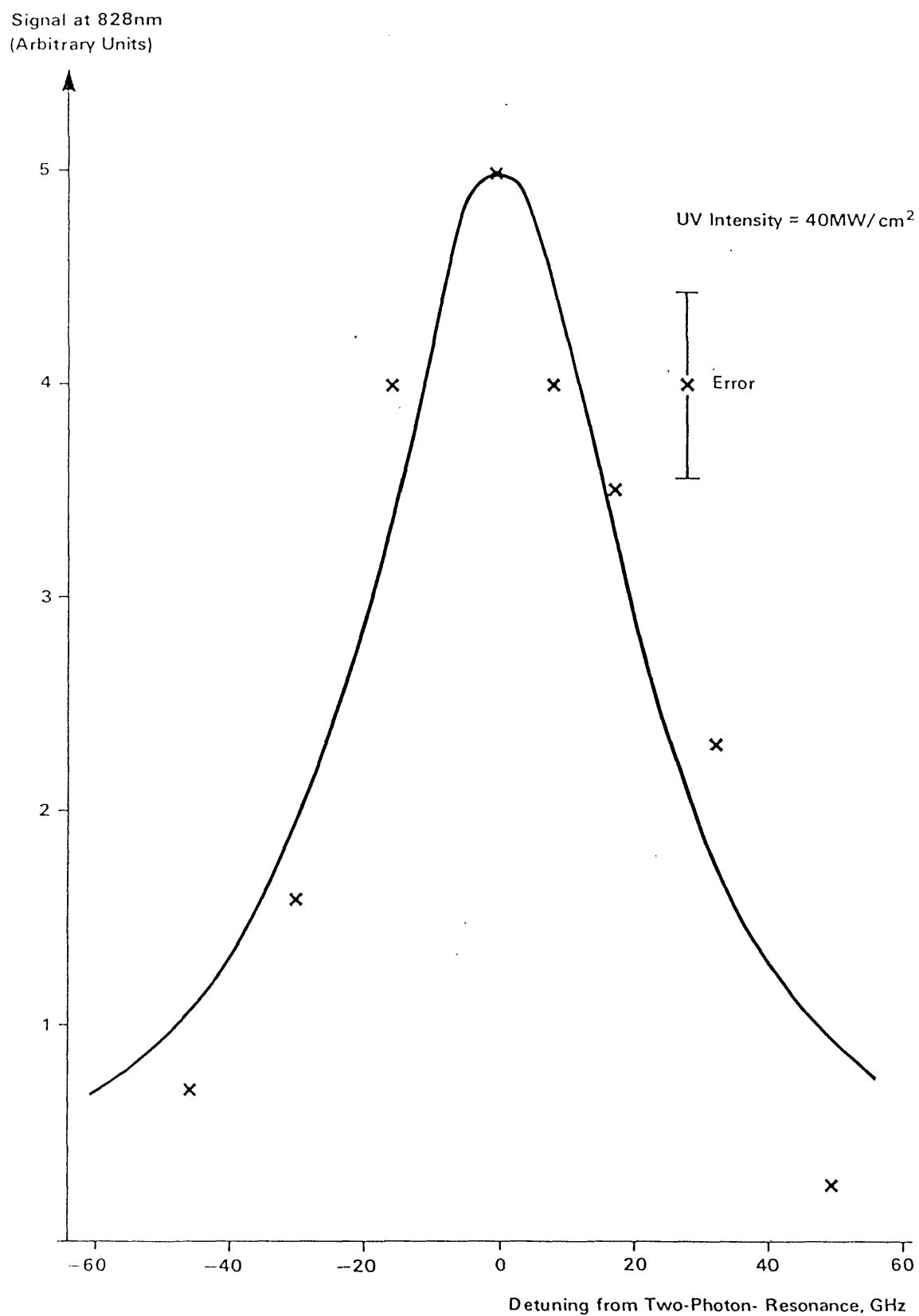


Fig 4.13 Stimulated Emission Signal at 828nm as a Function of Detuning of UV Radiation from Two-Photon Resonance

Superfluorescence vs ASE

We consider the possibility that the emission observed at 828nm is not ASE but superfluorescence (SF), a co-operative phenomenon which has been observed by a number of researchers and attracted interest, particularly in the late 1970s [see the review article by Vreken and Gibbs, 1982 for details and further references].

Superfluorescence is the co-operative emission of radiation by a system of many two-level atoms which are all initially in the upper (excited) state. Superfluorescence is characterised by the emission of a delayed pulse with peak intensity proportional to N^2 (N = total number of atoms) within a narrow cone in both directions along the sample axis. This normally occurs in thin pencil geometries as used in our experimental work.

A distinction can be drawn between superfluorescence and superradiance as described by Dicke, 1954, in that superfluorescence builds up from noise while superradiance, generated by giant dipole effects, is always a co-operative phenomenon.

For emission to be superfluorescent, the characteristic time of the process must be shorter than the relaxation times which can destroy the co-operative interactions between radiating atoms. If this condition is not satisfied, then there is a gradual transition between superfluorescence and ASE.

One can assess whether a process is superfluorescent by considering the following set of inequalities [Vreken and Gibbs, 1982]. For superfluorescence,

$$\tau_E < \tau_C < \tau_R < \tau_D < T_1, T_2', T_2^*$$

where τ_E is the sample escape time $= L/c$, where L is the length of the medium

$$\tau_C \text{ is the co-operation time } = \sqrt{\tau_E \tau_R}$$

τ_R is the superfluorescence time defined by

$$\tau_R = \frac{8\pi\tau_0}{3 N \lambda^2 L} \quad \text{where}$$

τ_0 is the partial lifetime of the SF transition and is $\geq$ the radiative lifetime of the upper state

N is the inversion density

λ is the SF wavelength

and L is the length of the medium

τ_D is the delay time

and T_1, T_2' and T_2^* are the dephasing times determined by radiative spontaneous emission, gas collisions, escape from the light beam, Doppler broadening or inhomogeneous external static fields.

Typically, τ_D is 10 to 100 times longer than τ_R .

Additionally, the inversion preparation time i.e. the excitation pulse duration, τ_p , should be less than the delay time, τ_D , and a long thin beam geometry is required as characterised by a Fresnel number of approximately 1, i.e.

$$F = \frac{A}{\lambda L} \approx 1$$

where A is the beam cross-sectional area.

We now calculate the relevant parameters for our experimental conditions

$$F \approx 0.5,$$

$$\tau_E = 0.11\text{ns},$$

$$\tau_R = 220\text{ns (for } I_{UV} = 10 \text{ MW/cm}^2),$$

$$\tau_C = 4.9\text{ns}.$$

Hence the geometry is appropriate and the first part of the inequality $\tau_E < \tau_C < \tau_R$ is satisfied.

However, no measurable delay in the output of the IR signal was observed, as indicated by Figure 4.11 which shows the IR pulse super-imposed on background scattered excitation light. Delays of $> 10\text{ns}$ would have been required to satisfy $\tau_p < \tau_D$. Nor is the emitted IR intensity $\propto N^2$ (Figure 4.14). More significantly, dephasing due to Doppler broadening of the upper state occurs on a nanosecond timescale as indicated by the 2.6 GHz Doppler width. Hence the second part of the inequality, $\tau_R < \tau_D < \text{dephasing times}$, is not satisfied. We conclude that superfluorescent emission cannot occur due to rapid dephasing which prevents co-operative phenomenon from becoming established. Hence we conclude that the IR emission observed is ASE.

References

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Topics in Current Physics, Volume 27: "Dissipative Systems
in Quantum Optics", Chapter 6 "Superfluorescence
Experiments" ed. R Bonafacio, pub. Springer Verlag, 1982
- DICKE R H:
Phys Rev 93, 99, (1954)

saturated to the extent that all available atoms are contributing to the stimulated emission process.

4.4 Comparison of Theoretical Predictions and Experimental Results

In this section, we attempt to provide an understanding of the experimental results presented in the previous sections, by relating these results to the theoretical analysis presented in Chapter 3.

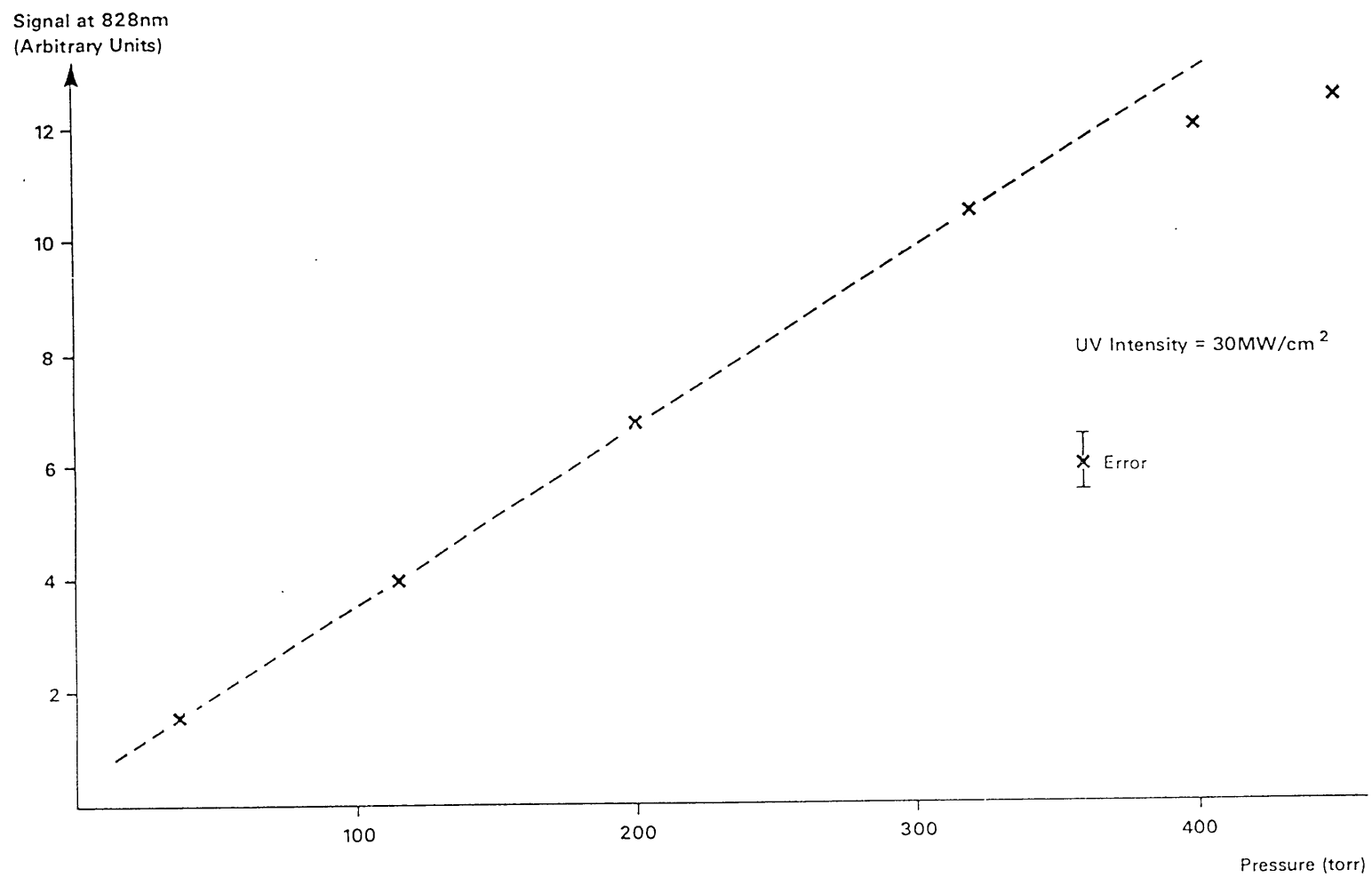
Firstly, in Section 4.4.1, we compare the observed dependence of ionisation signal on intensity, in the region of the two-photon resonance, with that predicted by rate equation calculations.

Secondly, using the preliminary calculations presented in Chapter 3, we draw a number of conclusions about the role of specific saturation mechanisms in producing the observed broadening of the two-photon-resonant state. We also consider the stimulated emission results in relation to broadening of the two-photon-resonant state. Each mechanism is considered in turn in Section 4.4.2 to 4.4.5.

4.4.1 Dependence of Ion Signal on Intensity

At high intensities, ($\sim 1 \text{ GW/cm}^2$), we observed heavy saturation, both exactly on resonance and in the resonance wings, from measurements of ion signal versus intensity. From estimates of the proportion of Xenon atoms being ionised, we have confirmed the expectation that, on resonance, the majority of the atoms in the irradiated region are ionised. Exactly on resonance, therefore, saturation must occur, at least to a certain extent, from the removal of the ground state

Fig 4.14 Dependence of On-Resonance Stimulated Emission Signal on Xenon Pressure



population. As expected for complete ionisation, the rate equations predict a sub-linear dependence of ionisation signal on intensity, as borne out by experiment. In the resonance wings, the rate equation analysis predicts a quadratic relationship between ion signal and intensity. Experimentally, the gradients of log-log plots were found to be between 1 and 2 in the resonance wings. This indicates the possible presence of a saturation mechanism not included in the rate equation analysis.

At low intensities, (~ 10 MW/cm²), we have measured a cubic dependence of the ion signal on intensity in the wings of the resonance, in agreement with the rate equation predictions. However, on the resonance maximum, we have found that the expected cubic dependence of the ion signal on intensity was reduced to quadratic. From this we can postulate that the two-photon excitation stage of the process is unsaturated. However, we must also postulate that there is a saturation mechanism occurring which is not fully accounted for in the rate equation formulation.

4.4.2 Power Broadening

In Section 3.2.1, we calculated that for an intensity of 1GW/cm², the expected linewidth due to power broadening would be 8 GHz, the linewidth showing a linear dependence on intensity. This estimate neglects the reduction in two-photon-resonant state lifetime as a result of other processes, predicted by rate equation calculations, which would reduce the effect of power broadening. We hence reject power broadening as a significant saturation mechanism in the broadening of the two-photon-resonant state.

4.4.3 The a.c. Stark Effect

Our calculations of the a.c. Stark effect, (Section 3.2.2) predict an associated line broadening of $2.2 \text{ GHz}/(\text{GW}/\text{cm}^2)$ for our experimental conditions. This mechanism does not appear to be responsible for the significant broadening observed, particularly at low intensities since linewidth is again predicted to show a linear dependence on intensity.

4.4.4 Lifetime Broadening

4.4.4.1 Ionisation Broadening

Of the two lifetime broadening mechanisms considered, ionisation broadening (Section 3.2.3.1) is expected to produce a linewidth comparable with the Doppler linewidth at high intensities ($1 \text{ GW}/\text{cm}^2$), with a much reduced effect at lower intensities ($\Delta\nu \propto I$). This is not large enough to explain the large linewidths observed experimentally.

4.4.4.2 Broadening due to Stimulated Emission of Radiation

On the basis of preliminary calculations of the stimulated emission cross-section, (Section 3.2.3.2), and the expected population inversion, broadening due to the stimulated emission of radiation from the two-photon-resonant state appears to be potentially capable of producing the broadened linewidths observed. Clearly, our measurements of stimulated emission radiation indicate that it could be a significant process.

In Section 3.2.3.2 we derived the following relationship, for our experimental conditions, between the saturated and unsaturated (small signal) gains for stimulated emission of radiation between the $6p$, ($J=0$) and $6s$, ($J=1$) states as a result of the population inversion produced by two-photon

excitation to the 6p state.

$$\ln G^A + 2AG^A = \ln G^0$$

where G^A is the saturated gain, (integrated)

G^0 is the unsaturated (small signal) gain, (integrated)

and A is a factor describing the properties of the ASE flux

$$A = \frac{d\Omega}{4\pi} \cdot \frac{\tau_u}{\tau_s} \cdot \frac{\Delta\nu_n}{\Delta\nu_s}$$

In this expression

τ_u is the excited state lifetime

τ_s is the spontaneous lifetime

$\Delta\nu_n$ is the width of the narrowed ASE line

$\Delta\nu_s$ is the bandwidth of the spontaneous fluorescence

and $\frac{d\Omega}{4\pi}$ is the solid angle contributing to the ASE output.

$$\frac{d\Omega}{4\pi} = \frac{(1 + q - \sqrt{1 + q^2})}{2q}$$

where q is the aspect ratio b/ω_0 relating to the focal volume.

To recap, $\ln G^0 = \sigma_{\text{stim}} \Delta N l$

where σ_{stim} = stimulated emission cross-section

$$= 2.2 \times 10^{-12} \text{ cm}^2 \text{ (see Section 3.2.3.2)}$$

ΔN = population inversion which can be estimated from
rate equation calculations

and l = interaction length = confocal parameter of the
focused beam

Returning to Chapter 3, we then derived a relationship between G^A and G^0 and the expected broadening of the resonance linewidth as a result of the stimulated emission.

$$\frac{\Delta\nu_{\text{stim}}}{\Delta\nu_{\text{spon}}} = \frac{\ln G^0}{\ln G^A} \quad \text{(Equation 3.10)}$$

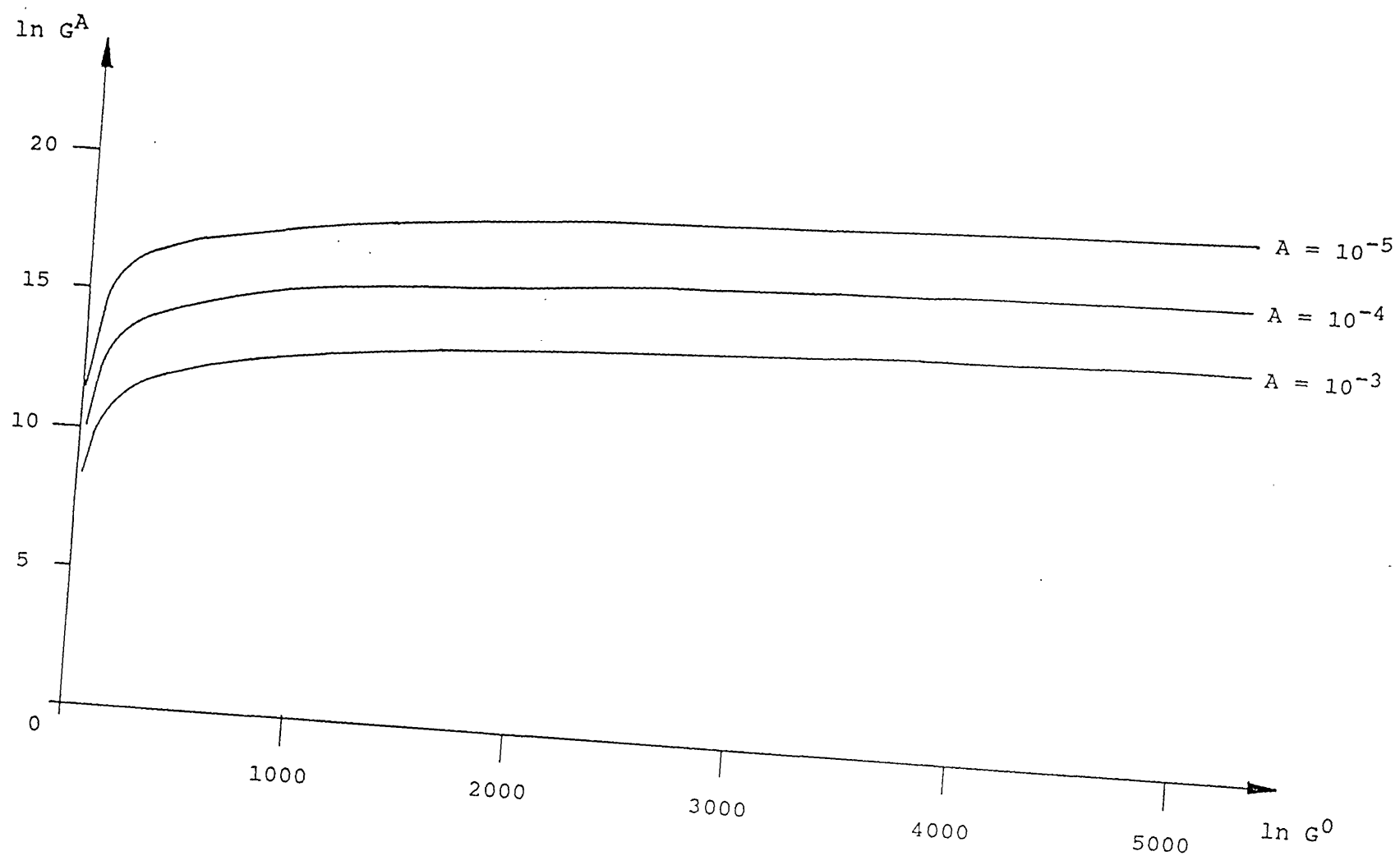


Figure 4.15 Plot of $\ln G^A$ Versus $\ln G^0$
Calculated from Theory Developed in Chapter 3

We now relate this theoretical evaluation to our experimental conditions. Figure 4.15 shows a plot of G^A against G^0 for a range of values of A . There are a number of features of this figure worthy of comment since they impact on the calculations of line broadening based on it.

The major comment relates to the degree of saturation indicated by the curves plotted. Very significant saturation is present for values of $\ln G^0$ greater than approximately 500 to the extent that $\ln G^A$ is only very weakly dependent on $\ln G^0$ for $\ln G^0 > 500$. Since

$$\frac{\Delta \nu_{\text{stim}}}{\Delta \nu_{\text{spon}}} = \frac{\ln G^0}{\ln G^A}$$

and if we consider $\ln G^A \sim \text{constant}$, then

$$\frac{\Delta \nu_{\text{stim}}}{\Delta \nu_{\text{spon}}} \propto \ln G^0$$

Hence any fractional error in $\ln G^0$ is transferred directly to the expected broadening of the linewidth.

Additionally, we make a comment on the parameter A . For $\ln G^0$ greater than approximately 500 and A in the range 10^{-3} to 10^{-5} , we find that

$$\ln G^A \ll 2AG^A$$

Hence, we can say that

$$\ln G^0 \approx 2AG^A$$

For a fixed value of $\ln G^0$ then

$$\ln G^A \propto 1/\ln A$$

This is clear from Figure 4.15. The result of this is that, for a fixed value of $\ln G^0$, the value of $\ln G^A$ is extremely insensitive to the value of A . This relates to an insensitivity in the line broadening factor to A . An error of

+/- one order of magnitude in A introduces an error of only +/-15% in the line broadening factor.

In conclusion, the line broadening factor is, for the parameters considered, directly proportional to $\ln G^0$, but is insensitive to the value of the parameter A.

We now present some calculations of the expected line broadening due to stimulated emission of radiation, for both the high and low intensity regimes considered experimentally.

Low intensity regime

$$I = 10 \text{ MW/cm}^2$$

$$2\omega_0 = 125 \text{ um}, 2b = 3.3 \text{ cm}$$

Then the relevant parameters are

(i) For the calculation of $\ln G^0$,

$$\Delta N = 5 \times 10^{13} \text{ cm}^{-3} \text{ (peak 6p population from rate equation calculations)}$$

$$l = 3.3 \text{ cm}$$

$$\text{Then } \ln G^0 \approx 370$$

(ii) For the calculation of A,

$$q = 270$$

$$\tau_s = 30 \text{ ns [Verolainen and Osherovich, 1969]}$$

$$\tau_u = \tau_s \text{ since upper state lifetime is dominated by spontaneous decay in this intensity regime}$$

$$\Delta\nu_n / \Delta\nu_s \text{ is not known but is assumed to be } = 1$$

$$\text{Then } A \approx 10^{-3}$$

From Figure 4.15, we see that for these values of $\ln G^0$ and A, $\ln G^A \approx 12$, and hence

$$\begin{aligned} \Delta\nu_{\text{stim}} &\approx 31 \times \Delta\nu_{\text{spon}} \\ &= 93 \text{ GHz} \end{aligned}$$

where $\Delta\nu_{\text{spon}}$ = linewidth at zero intensity = 3 GHz (see Section 3.2.1). Experimentally, a linewidth of approximately

80 GHz was observed at these intensities.

High intensity regime

$$I = 1 \text{ GW/cm}^2$$

$$2 \omega_0 = 25 \mu\text{m} ; 2b = 0.15 \text{ cm}$$

Then the relevant parameters are

(i) For the calculation of $\ln G^0$,

$$\Delta N = 1.2 \times 10^{16} \text{ cm}^{-3}$$

$$l = 0.15 \text{ cm}$$

$$\text{Then } \ln G^0 \approx 4000$$

Note: estimation of the population inversion for high intensities from rate equation calculations is most probably inaccurate, as the expected inversion is unlikely to be reached in the presence of such intense stimulated emission. As an estimate we have used the maximum 6p population for a reduced 6p lifetime of 0.5ns (see Figure 3.11)

(ii) For the calculation of A,

$$q = 60$$

$$\tau_s = 30 \text{ ns, as before}$$

$\tau_u = 1 \text{ ns}$, since the upper state lifetime is dominated by the ionisation loss at these high intensities

$$\Delta \nu_n / \Delta \nu_s = 1, \text{ as before}$$

$$\text{Then } A \approx 3 \times 10^{-4}$$

From Figure 4.15, we see that for these values of $\ln G^0$ and A, $\ln G^A \approx 16$, and hence

$$\begin{aligned} \Delta \nu_{\text{stim}} &\approx 250 \Delta \nu_{\text{spon}} \\ &= 750 \text{ GHz} \end{aligned}$$

The experimentally observed linewidth of 160 GHz at this intensity, is a factor of approximately four less than this calculated width. However, in view of the comments above on uncertainties in the value of $\ln G^0$ at high intensities, this

is considered to be reasonable agreement.

In these calculations, the effect of the difference in divergence of the beams at 249.63nm and 828nm due to the difference in wavelengths, has not been included in the model. We postulate that in such a heavily saturated regime, the fact that stimulated emission photons are lost from the pumped region due to divergence as the beams propagate, is not significant in determining the integrated saturated gain G^A .

Hence we have calculated that, for our experimental parameters, the effect of stimulated emission from the two-photon-resonant state is to broaden substantially the linewidth of the resonant state, leading to associated saturation of two-photon-resonant processes. We have calculated broadened linewidths, for both high and low intensity regimes, which are comparable with our experimental observations. This is substantially better agreement than for any other mechanism considered.

The agreement between the theoretical predictions and observed experimental results substantiate the hypothesis that the dominant mechanism leading to saturation of two-photon-resonant processes in Xenon, both at low and high intensities, is lifetime broadening due to the stimulated emission of radiation from the two-photon-resonant state.

4.4.5 Stark Broadening by Photoelectrons

As discussed in Section 3.2.4., the approximations made in the usual evaluation of Stark broadening due to photoelectrons may not be valid for Xenon.

However, the results of our rate equation calculations can be used in assessing the significance of this effect as a

broadening mechanism, particularly in the low intensity ($I \sim 10$ MW/cm²) regime. Rate equation analysis shows that, for an intensity of 10 MW/cm², pumping on resonance, the proportion of the ground state population ionised during the passage of a 10 ns pulse is approximately 5×10^{-10} . Hence, since the resulting broadening must have some dependence on the ion density, we conclude that the contribution to the linewidth by Stark broadening due to photoelectrons at this intensity should be negligible compared with at higher intensities. Even at high intensities (~ 1 GW/cm²) it is not expected that the broadening from this source should be more than a few GHz [Thomas, 1983]. Hence we conclude that this mechanism does not contribute significantly to the saturation observed.

4.5 Conclusions

In this chapter we have presented experimental results on saturation of two-photon- resonant three-photon ionisation in Xenon and the observation of stimulated emission of radiation originating from the two-photon-resonant state. We have reported

- * Over a range of intensities, the dependence of ionisation signal, in the region of the two-photon resonance does not agree with that expected from a simple rate equation analysis.
- * Measurements of the two-photon resonance linewidth which are substantially broadened over a range of intensities (80 - 300 GHz) compared with the Doppler linewidth (2.6 GHz)
- * Observation of stimulated emission of radiation between the two-photon-resonant (6p) and 6s states. Saturation of the stimulated emission process was observed.

We have seen, from our analysis, that the saturation of the two-photon-resonant three-photon ionisation is not thought to be a result of a number of mechanisms, namely power or ionisation broadening, or broadening due to either the a.c. Stark effect or the d.c. Stark effect resulting from the presence of photoelectrons. However, our experimental results indicate substantial stimulated emission of radiation and our analysis of this, based on the theory developed in Chapter 3, shows good agreement between theory and experiment.

The linear dependence of linewidth on intensity, shown in Figure 4.9, has not been explained: it is probably inaccurate to claim a linear dependence due to the relatively small number of data points available.

We conclude that lifetime broadening due to the stimulated emission of radiation is responsible for the observed saturation of two-photon-resonant processes in Xenon, where the resonant state is the $6p, J = 0$ state.

4.6 References

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CHAPTER 5

THEORY OF LASER-INDUCED AUTOIONISING STATES

5.1 Introduction

The aim of this chapter is to describe the theory of laser-induced autoionising states, alternatively known as laser-induced continuum structure (LICS), and the uses of such phenomena in non-linear optics.

A laser-induced autoionising state occurs when the interaction of a laser field with an atom or molecule produces a modification of the atomic or molecular continuum. Anticipating the experimental work reported in Chapter 6, we restrict our treatment here to LICS in atomic systems only.

Laser-induced autoionising states can be described in a manner analogous to real autoionising states, which are well known, by replacing the configuration interaction, caused by a residual electrostatic interaction between electrons, by a radiative interaction, namely a dipole bound-continuum laser coupling. Laser-induced autoionising states do differ, however, from real autoionising states in some respects. One important difference is that while real autoionising states are fixed in energy, the position and width of laser-induced autoionising states is dictated by the laser frequency and power respectively. This property offers a flexible tool for resonant modification of non-linear susceptibilities and transition rates. Other differences arise from the dipole selection rules for radiative interactions and will be discussed further in Section 5.3.3.

This chapter is arranged as follows:-

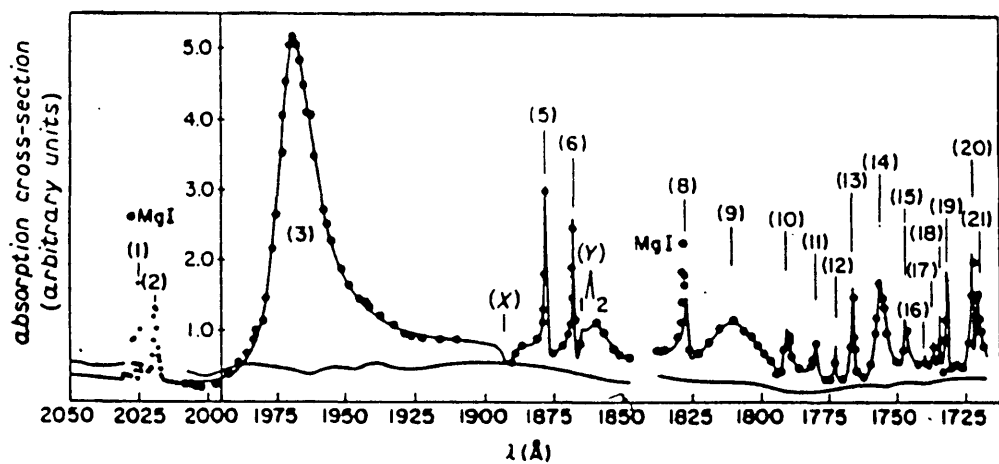


Figure 5.1

Absorption Spectrum of Atomic Strontium in the Vacuum
Ultra-violet (Ionisation Limit is at about 2180 Å)

Section 5.2 is a brief review of the nature of real autoionising states while Section 5.3 describes the Fano theory of autoionising states and its application to the particular case of laser-induced continuum structure. The final section, 5.4, discusses the limitations of the theory when applied to real experimental situations, where both laser field and atomic system are non-ideal.

5.2 Real Autoionising States

Autoionising states are known to give a highly structured character to certain parts of the continuum absorption spectra of many-electron atoms. For example, Figure 5.1 shows the absorption spectrum of atomic Strontium in the vacuum ultra-violet autoionising region. The highly structured nature of the spectrum corresponds to real autoionising states. These structured continua show up strongly not only in single-photon absorption [Garton et al, 1968] but also in four-wave-mixing susceptibilities [Armstrong and Wynne, 1974], and multiphoton ionisation cross-sections [Alber and Zoller, 1983]. The subject has been studied extensively, both theoretically and experimentally.

Before considering the theory relating to laser-induced continuum structure, it is useful to consider the nature and origin of real autoionising states which is, briefly, as follows.

The ionisation limit F_i , of an atom is the energy required to remove the least tightly bound electron. However, it may happen that the energy required to excite two bound electrons to nominally bound one-electron states is greater than the energy required to remove a single electron completely. For

example, [Armstrong and Wynne, 1977], the ground state configuration of Strontium is $5s^2 1S^0$ and the first ionisation limit occurs as the limit of the series $5s^2 1S^0 - 5s np 1P^1_0$ i.e. as the limit of the excitation of one of the 5s electrons into np states with unchanged spin direction. This limit occurs at $45,932\text{cm}^{-1}$ or about 5.69eV. If both the 5s electrons are promoted to 4d states, the configuration $4d^2 3P$ has levels which are bound, although loosely, at around $44,600\text{cm}^{-1}$, below the ionisation limit. However, to excite the $5s^2$ configuration to the $4d4f 1P^0$ configuration requires $53,546\text{cm}^{-1}$ of energy which is well above the ionisation limit at $45,932\text{cm}^{-1}$. Hence we have a degeneracy between continuum states and the two-electron state.

This degeneracy between a nominally bound configuration and a continuum of the same angular momentum, J, is "lifted" by the configuration interaction as was shown by Fano, 1961 and Fano and Cooper, 1963. This interaction mixes the wavefunctions of the bound two-electron state with a band of continuum states and produces new continuum states which constitute the autoionising resonance. Such states are unstable against ionisation with one electron being emitted from the atom.

In the Noble gases, there are also autoionising states which arise from single electron excited states as opposed to two electron states. Strong spin orbit coupling in the noble gases results in two series of excited states, which are well separated in energy. These correspond to two possible configurations of the core electrons (see for example Sobel'man, 1972). This gives rise to two ionisation potentials, one for each core configuration. Hence there may be discrete bound states corresponding to one configuration

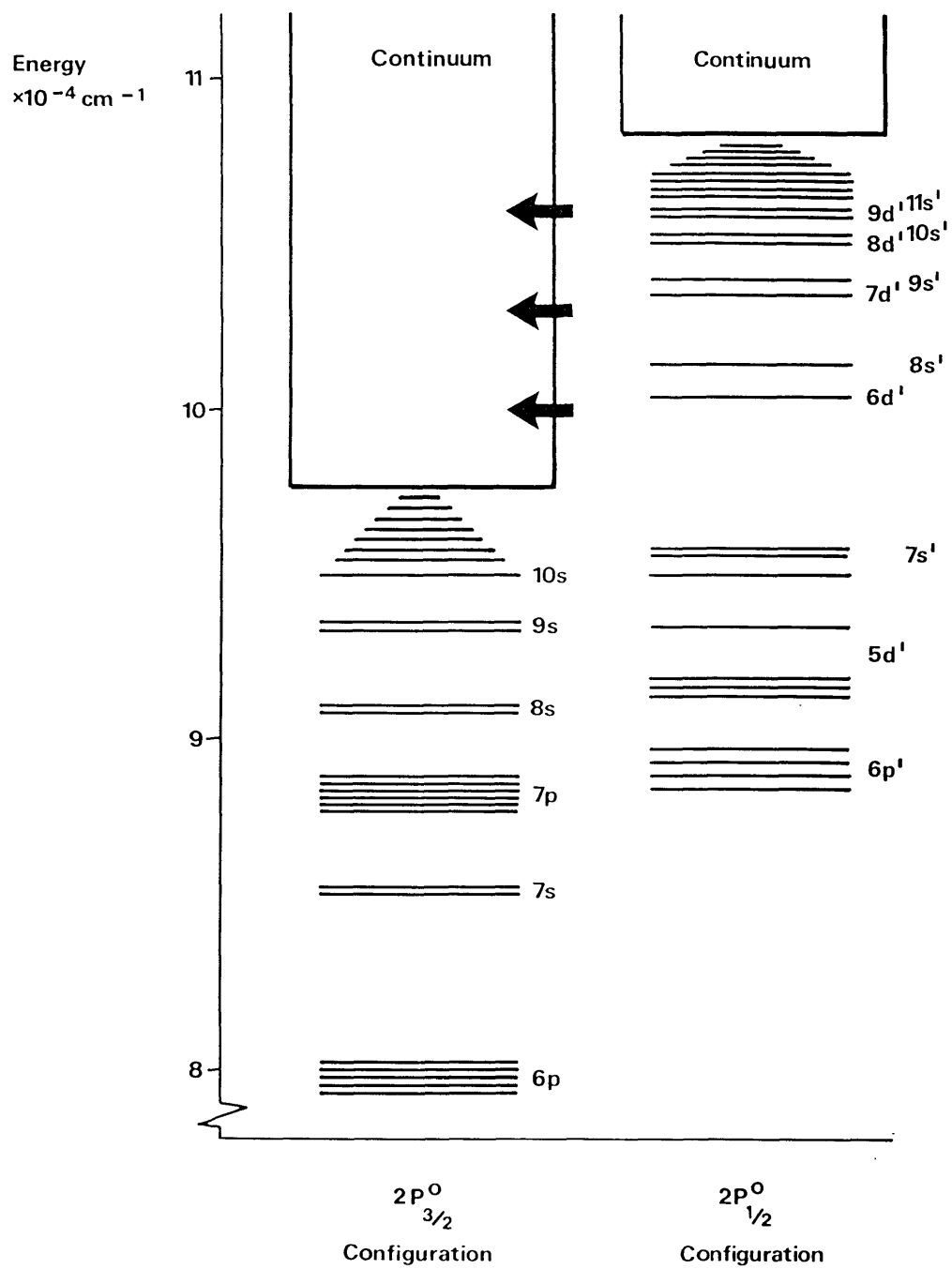


Fig 5.2 Xenon Partial Energy Level Diagram Showing Origin of Real Autoionising States

which have energies above the ionisation limit for the other configuration. This is illustrated for Xenon in Figure 5.2, where the separation of the $2p^0_{1/2}$ and $2p^0_{3/2}$ ionisation potentials, is $10,537\text{cm}^{-1}$. These real autoionising states in Xenon have been investigated and identified experimentally, most recently by Bonin, McIlrath and Yoshino, 1985.

It should be pointed out that the region of the Xenon continuum investigated in the laser induced autoionisation experiments described in Chapter 6, lies well above both ionisation limits, in a region of the continuum where no real autoionising structure would be expected.

When considered in the context of non-linear optics, it is clear that the use of real autoionising states can be of considerable value in the enhancement of non-linear processes which include a continuum contribution. The efficiency of such processes is usually limited by the small value of the bound-free dipole matrix elements.

Experimentally, such enhancement has been observed by, among others, Hodgson et al, 1974, who studied vacuum ultra-violet, (VUV), generation in Strontium via two-photon-resonant four-wave mixing, $\omega_4 = 2\omega_1 + \omega_2$ using two nitrogen pumped dye lasers. ω_1 being two-photon-resonant results in a large enhancement of the non-linear susceptibility. As the second laser was tuned, the sum frequency, ω_4 , was scanned through a region of the continuum containing a real autoionising resonance. In the proximity of this resonance, a large increase in the VUV signal was reported, and a lineshape was observed which was attributed to the autoionising resonance. The theoretical relationship between the observed frequency dependence of the four-wave-mixing signal and the structure of

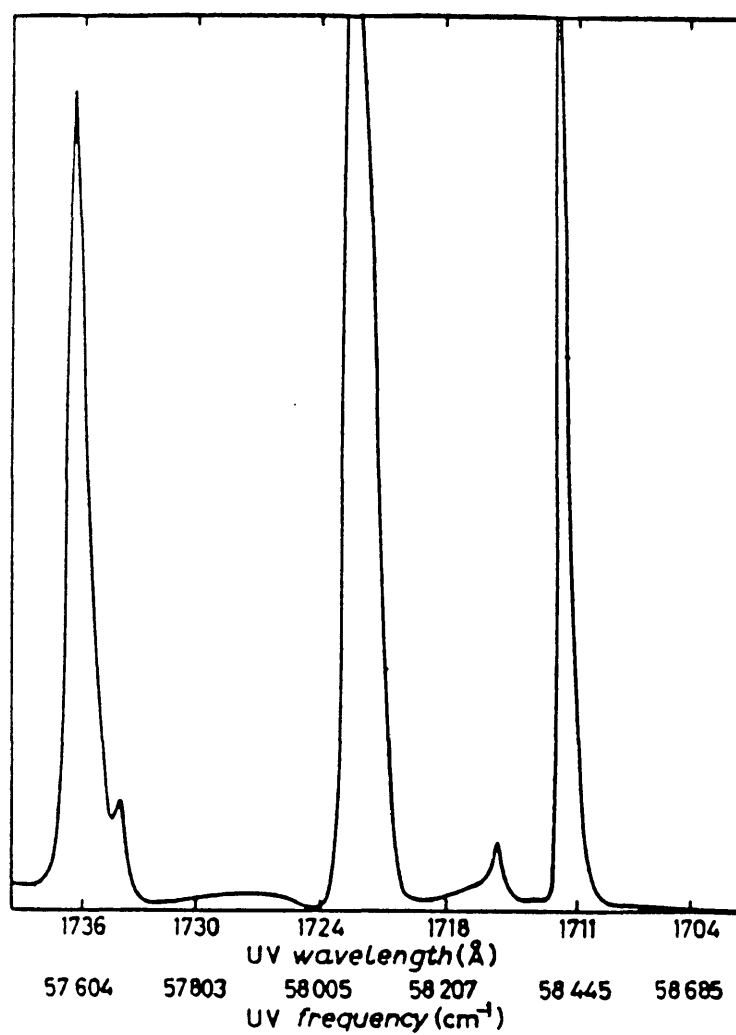


Figure 5.3 Real Autoionising Spectrum in Strontium
Probed via Four-Wave Mixing

the autoionising state has also been calculated by Hodgson et al. One such autoionising spectrum is shown in Figure 5.3 (after Hodgson et al, 1974). Hence the autoionising resonance can be used to enhance the non-linear susceptibility and process efficiency in a manner exactly analogous with resonant enhancement of non-linear processes by tuning close to discrete levels below the ionisation limit.

However, autoionising states, both real and induced, have one characteristic which distinguishes them from bound resonances. As we will see in the following section, the lineshape of an autoionising resonance is asymmetric. In addition to having a maximum, the use of which has already been described for real autoionising resonances, there is also a minimum in the resonance. Theoretically this is a zero. This Fano window, as it is known, is also potentially useful in non-linear optics, as will be discussed in the following section.

5.3 Laser-Induced Autoionising States

As outlined in the introduction to this chapter, laser-induced autoionising states are produced when a radiative interaction replaces the configuration interaction responsible for real autoionising states. This situation can be thought of as a combined atomic state consisting of the atom and the laser field producing an effectively bound state with an energy greater than the ionisation limit of the atom. This state is then degenerate with continuum states in the same way as the two-electron states which are responsible for real autoionising states. Simplistically, one can think of the laser as pumping or embedding a high lying unpopulated state into the continuum. For this reason, we refer to the laser involved as the "embedding" laser or field. A recent review of laser-induced

continuum structure is given by Knight, 1984.

A full theoretical analysis of continuum structure was developed in the classic papers of Fano and his co-workers in the early 1960's [Fano, 1961; Fano & Cooper, 1963]. At that time, early in the history of laser physics and non-linear optics, the purpose of the theory was to gain understanding of real autoionising states; the concept of laser-induced continuum structure had not yet emerged. As will be seen in the theory presented in Section 5.3.2, the work of Fano is general to all continuum structure. Laser-induced structure is described simply by replacing the configuration interaction with a radiative interaction.

Fano's theory considers the atomic wavefunctions resulting from the degeneracy of discrete and continuum states. In its general form, it requires no input from the concepts of modern optics and non-linear optics. However, a simple understanding of the physical interactions leading to laser-induced continuum structure can be gained by considering the interaction in terms of Rabi frequencies, a concept frequently used in analysing non-linear interactions between matter and radiation. This treatment is presented in Section 5.3.1 and is followed by an outline of the Fano treatment with particular emphasis to laser-induced continuum structure in Sections 5.3.2 and 5.3.3. Further comments on the theory are contained in Section 5.3.4.

5.3.1 Concept of Fano Minimum via Rabi Oscillations

The interaction between a radiation field and an atom can be described in terms of the Rabi frequency. This describes the strength of the dipole interaction between states $|i\rangle$ and $|j\rangle$, and is defined as

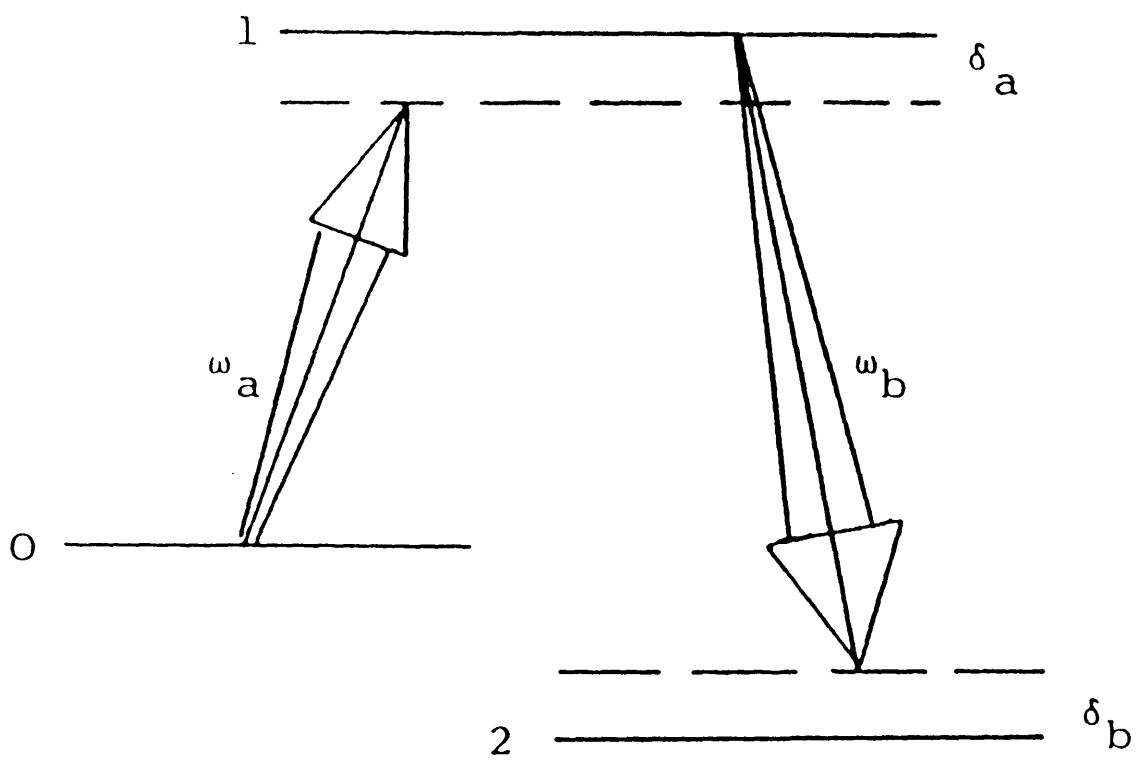


Figure 5.4 Coherently Excited Lambda System

$$\Omega = \frac{\underline{d}_{ij} \cdot \underline{E}}{\hbar}$$

where $\underline{d}_{ij}$ is the dipole coupling between the states and $\underline{E}$ is the electric field strength.

Hence the Rabi frequency gives the strength of the dipole interaction $\underline{d}_{ij} \cdot \underline{E}$ in terms of a frequency. This describes the rate at which population would oscillate between the levels $|i\rangle$ and $|j\rangle$ under resonant excitation by radiation of electric field strength $\underline{E}$ [Knight, 1984]. This concept is extensively applied to multiphoton absorption and ionisation problems [see, for example, Knight and Milonni, 1980].

The approach can also be used to obtain a qualitative understanding of laser-induced continuum structure as follows. Consider the atomic system illustrated of in Figure 5.4. This three-level system shows two discrete states $|0\rangle$ and $|2\rangle$ both radiatively coupled to a common excited state $|1\rangle$. Such a system is known as a Lambda system. In this case it is coherently excited since a coherent field of frequency ω_a and amplitude E_a excites the transition from state $|0\rangle$ to state $|1\rangle$ while another coherent field of frequency ω_b and amplitude E_b excites the transition from state $|1\rangle$ to state $|2\rangle$.

Without reference to the full theoretical analysis of Fano and others, we now consider, by means of the simple system described, why it should be possible to encounter instances when an excitation channel is effectively blocked off, i.e. there is a minimum in the resonance. This "Fano window" is a characteristic unique to autoionising resonance lineshapes.

When the two fields E_a and E_b , are Raman-resonant (i.e. detunings δ_a and δ_b , are equal as shown in Figure 5.4), it can be shown that the coherent superposition of states, excited by approximately equal Rabi frequencies

$$\Omega_a = \frac{d_{01} \cdot E_a}{\hbar} = \Omega_b = \frac{d_{21} \cdot E_b}{\hbar}$$

has an unusual property. The atomic wavefunction can be represented by the antisymmetric superposition state

$$\psi(t) \simeq \frac{1}{\sqrt{2}} (e^{-i\omega_a t} |0\rangle - e^{-i\omega_b t} |2\rangle)$$

For the detuning condition $\delta_a = \delta_b$, it can be shown [see, for example, Dalton and Knight, 1982(a), 1982(b)] that this becomes stable, immune to photoexcitation. From Fermi's Golden Rule the rate of photoexcitation is given by

$$R \simeq \frac{2\pi}{\hbar} |\langle \psi(t) | d \cdot (E_a + E_b) | 1 \rangle|^2 \simeq 0$$

The equal, but opposite, transition moments, corresponding to the $\exp(-i\omega_a t) |0\rangle$ and $\exp(-i\omega_b t) |2\rangle$ terms in $\psi(t)$, interfere destructively, to give no net absorption and consequently $R \simeq 0$. Hence the population is trapped in a non-decaying superposition. The physical interpretation of this is that, should, for example state $|1\rangle$ lie above the ionisation limit as part of the continuum, no ionisation will occur when the appropriate detuning condition is satisfied. A minimum in the ionisation spectrum would be observed. Hence we have a simple explanation of the characteristic minimum observed in Fano-type laser-induced autoionising resonances.

This analysis also leads to a qualitative understanding of the dependence of the laser-induced structure on laser frequency

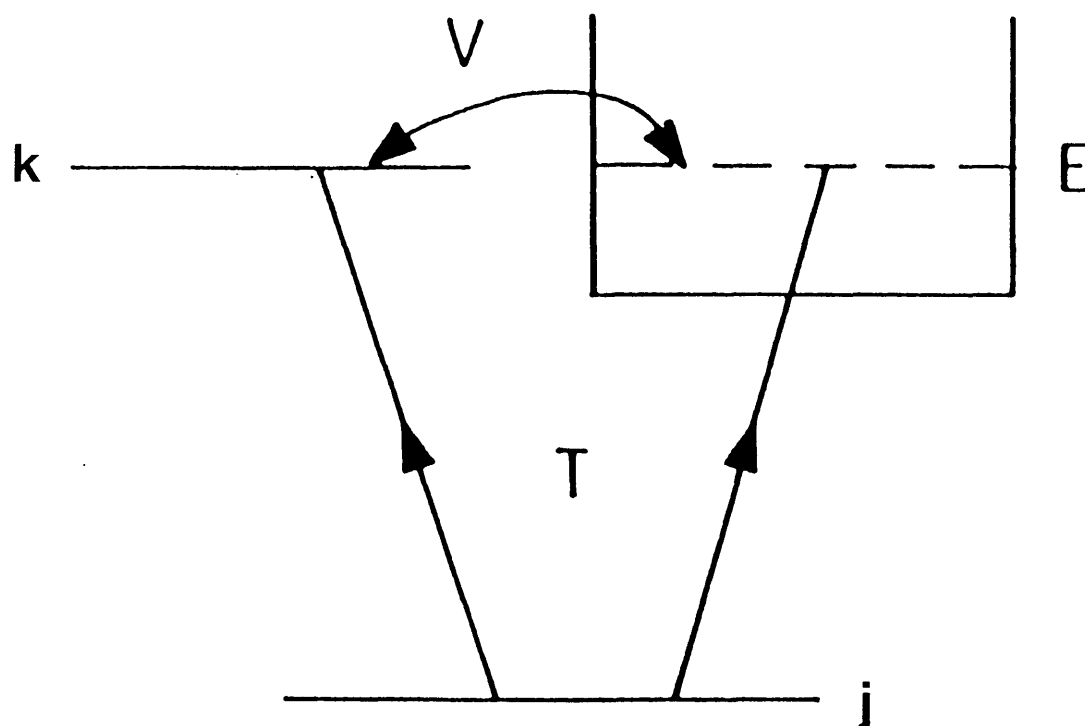


Figure 5.5 Energy Level Diagram showing
Origin of Autoionising State

and intensity. The autoionising level produced by a laser is of adjustable position as this is easily controlled by the frequency of the embedding laser. In addition, the width of the induced structure is controlled by the laser power. This is not immediately obvious in the same way as the frequency dependence of the energy position. However, laser power controls the interaction strength and may be expected to control the fundamental characteristics of the autoionising resonance. The result is that laser-induced autoionising states offer greater flexibility than real autoionising states in terms of position and width.

5.3.2 Fano Theory of Continuum Structure

The theory of autoionising states presented here is quite general as the embedding interaction need not be specified at this stage. As previously mentioned this highlights the similarities between laser-induced and real autoionising states.

The theory presented follows the outline of the theory of Fano and others, and draws heavily on a review article by Knight, 1984.

Consider a discrete state $|k\rangle$ strongly coupled by an interaction V to a flat continuum E , as shown in Figure 5.5.

In the case of LICS, the state $|k\rangle$ describes both atom and radiation field. In the case of real autoionising structure, it describes a discrete excited state above the ionisation limit.

The Fano wavefunction of the closely coupled k - E system of energy $\sum$ can be written [Fano, 1961] as

$$|F(\Sigma)\rangle = a(\Sigma)|k\rangle + \int_0^\infty dE b_E(\Sigma)|E\rangle$$

In this expression $a(\Sigma)|k\rangle$ describes the discrete contribution to the wavefunction and $\int dE b_E(\Sigma)|E\rangle$ the continuum contribution. In addition, $a(\Sigma)$ and $b_E(\Sigma)$ are time-independent amplitudes, and

$$H_e|F(\Sigma)\rangle = \Sigma|F(\Sigma)\rangle$$

where H_e is the total Hamiltonian. The energy Σ of the interacting system is real.

The amplitudes $a(\Sigma)$ and $b_E(\Sigma)$ can be determined by taking matrix elements of H , using orthonormality and solving the coupled time-independent algebraic equations. This has been done by Barton, 1963. It can be shown that

$$|F(\Sigma)\rangle = \frac{1}{((\tilde{E}_k - \Sigma)^2 + (\pi|V_{ek}|^2)^2)^{1/2}} \left\{ V_{ek}(|k\rangle + P \int_0^\infty \frac{V_{kE}|E\rangle dE}{\Sigma - E} \right. \\ \left. - (\tilde{E}_k - \Sigma)|\Sigma\rangle \right\}$$

where $\tilde{E}_k$ is the energy E_k of the discrete state $|k\rangle$ shifted by its interaction with the continuum

$$\tilde{E}_k = E_k + P \int_0^\infty \frac{|V_{kE}|^2 dE}{\Sigma - E}$$

The interaction V , the specific nature of which need not be specified at this point, mixes the original discrete state k with the continuum. This produces a modified or "dressed" discrete state

$$|\phi\rangle = |k\rangle + P \int_0^\infty \frac{V_{kE}|E\rangle dE}{\Sigma - E} \quad (5.1)$$

The complete continuum state $|F(\Sigma)\rangle$ is known as the Fano state and can then be written as

$$|F(\xi)\rangle = \frac{1}{((\tilde{E}_k - \xi)^2 + (\pi |V_{\xi k}|^2)^2)^{1/2}} \left\{ V_{k\xi} |\phi\rangle - (\tilde{E}_k - \xi) |\xi\rangle \right\} \quad (5.2)$$

This comprises a modified discrete state which is proportional to $|\phi\rangle$ and a term proportional to $|\xi\rangle$ which represents the modified continuum. The amplitude of the $|\phi\rangle$, i.e. discrete state, dependent term in the full Fano state has a Lorentzian dependence on energy ξ , whereas the amplitude of the continuum dependent term has a dispersive energy dependence. It is the combination of these Lorentzian and dispersive components which leads to the unique Fano lineshape characteristic of continuum structure.

If we consider probing the dressed state $|F(\xi)\rangle$ from another state $|j\rangle$, as shown in Figure 5.5 by a weak perturbation T , it can be seen that there are now two interfering routes to the old continuum. The transition moment to the new dressed state, $|F(\xi)\rangle$ can be expressed in terms of the undressed states using the expansion for $|F(\xi)\rangle$ in terms of discrete and continuum components (Equation 5.2) as

$$\langle F(\xi) | T | j \rangle = \frac{1}{((\tilde{E}_k - \xi)^2 + (\pi |V_{\xi k}|^2)^2)^{1/2}} \left\{ V_{k\xi} \langle \phi | T | j \rangle - (\tilde{E}_k - \xi) \langle \xi | T | j \rangle \right\}$$

The width of the structure in the continuum (from the embedding of state $|k\rangle$) can be shown to be

$$\Gamma_k = \pi |V_{\xi k}|^2 \quad (5.3)$$

Hence the structure width is dependent on the strength of the embedding interaction through the dipole interaction $V_{k\xi}$. The transition amplitude can be written as the sum of absorptive and dispersive parts,

$$\langle F(\varepsilon) | T | j \rangle = \langle \varepsilon | T | j \rangle \left\{ q \frac{\Gamma_k}{((\tilde{E}_k - \varepsilon)^2 + \Gamma_k^2)^{1/2}} - \frac{(\tilde{E}_k - \varepsilon)}{((\tilde{E}_k - \varepsilon)^2 + \Gamma_k^2)^{1/2}} \right\} \quad (5.4)$$

In this expression, the factor q is the Fano q -parameter and is defined as

$$q = \frac{\langle \phi | T | j \rangle}{\langle \varepsilon | T | j \rangle} \cdot \frac{1}{\pi V_{\varepsilon k}} \quad (5.5)$$

From Equation 5.5, we see that the Fano q -parameter represents the ratio of the transition amplitude from probe state $|j\rangle$ to the dressed discrete state $|\phi\rangle$, to that from $|j\rangle$ to the old continuum $|\varepsilon\rangle$. The proportion of absorptive to dispersive contributions in the total excitation amplitude, from state $|j\rangle$ to the modified continuum including continuum structure, is dictated by q . Analogous with Equation 5.3, $\Gamma_j = \pi |T_{\varepsilon j}|^2$ is the width of $|j\rangle$ due to its coupling to $|\varepsilon\rangle$. Hence substitution for $\langle \phi | T | j \rangle$ and $\langle \varepsilon | T | j \rangle$ in Equation 5.5 leads to

$$q = \frac{\langle \phi | T | j \rangle}{\sqrt{\Gamma_j \Gamma_k}} = \frac{1}{\sqrt{\Gamma_j \Gamma_k}} \left\{ \langle k | T | j \rangle + P \int_0^\infty \frac{V_{\varepsilon k}}{\varepsilon - E} \langle \varepsilon | T | j \rangle d\varepsilon \right\} \quad (5.6)$$

Referring back to Equation 5.4, we arrive at the following expression for the modification of the probe excitation of the continuum from $|j\rangle$ induced by the dressing,

$$R = \frac{\langle F(\varepsilon) | T | j \rangle^2}{\langle \varepsilon | T | j \rangle^2} = \frac{(q + e)^2}{1 + e^2} \quad (5.7)$$

Here e is the detuning of the probe interaction in units of the continuum structure width,

$$e = \frac{(\varepsilon - \tilde{E}_k)}{\Gamma_k}$$

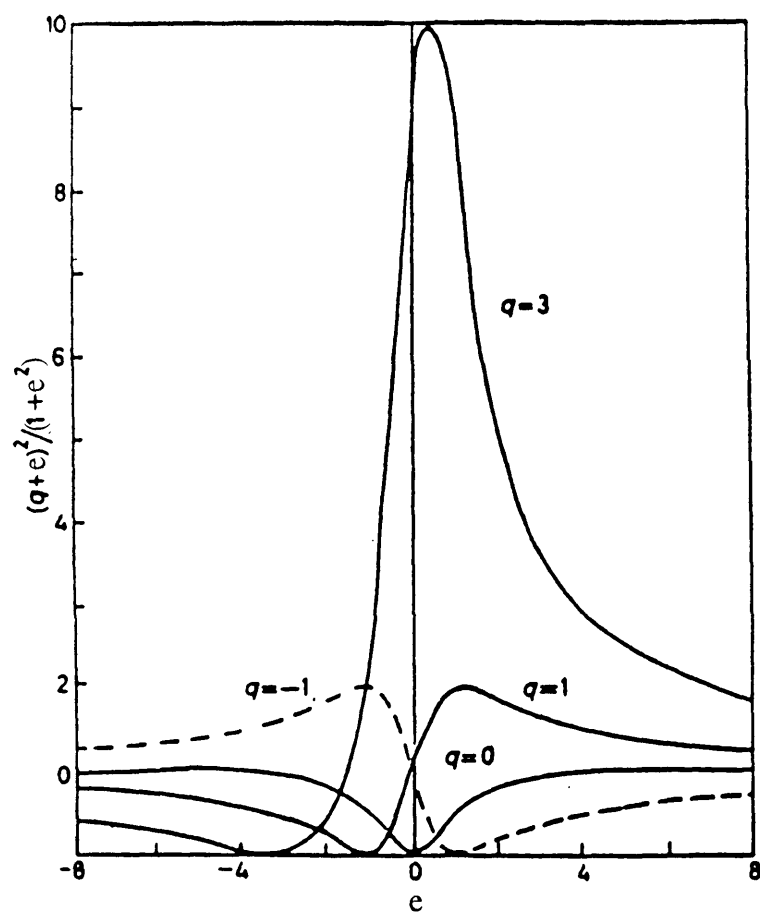


Figure 5.6 Fano Lineshapes for Various Values of q

This detuning is the mismatch in energy between discrete and continuum states. For laser-induced continuum structure, for example, the discrete state $|k\rangle$ includes atom-plus-photon energies and then e can be written as a genuine detuning. The modification factor R gives the lineshape of the induced resonance and is shown in Figure 5.6 for a range of values of q . The physical interpretation of these lineshapes is as follows.

For large values of q , the ionisation channel via the discrete state dominates. Hence the absorptive part of the induced state dominates and a resonance which is almost symmetric results. The maximum enhancement, which occurs at a detuning of $e = 1/q$, is $\approx q^2$. As $q \rightarrow \infty$, the lineshape tends to a symmetric Lorentzian profile with a maximum at zero detuning.

However, if q is small then the direct ionisation channel to the continuum dominates. In this case, the major contribution to the induced state arises from the dispersive part and an asymmetric enhancement of ionisation as a function of detuning results. The zero in R at $e = -q$ now becomes a prominent feature of the resonance lineshape. At this detuning, the decay channel of ionisation closes down, i.e. the two transition moments to the continuum, via the discrete and continuum states, cancel.

5.3.3 Fano Theory Applied to Laser-Induced Continuum Structure

Throughout this discussion, the exact nature of the interaction V coupling the discrete states to the continuum has not been exactly specified. This fact highlights the similarities between real and induced autoionising states. As previously mentioned, the only difference is in the origin of the

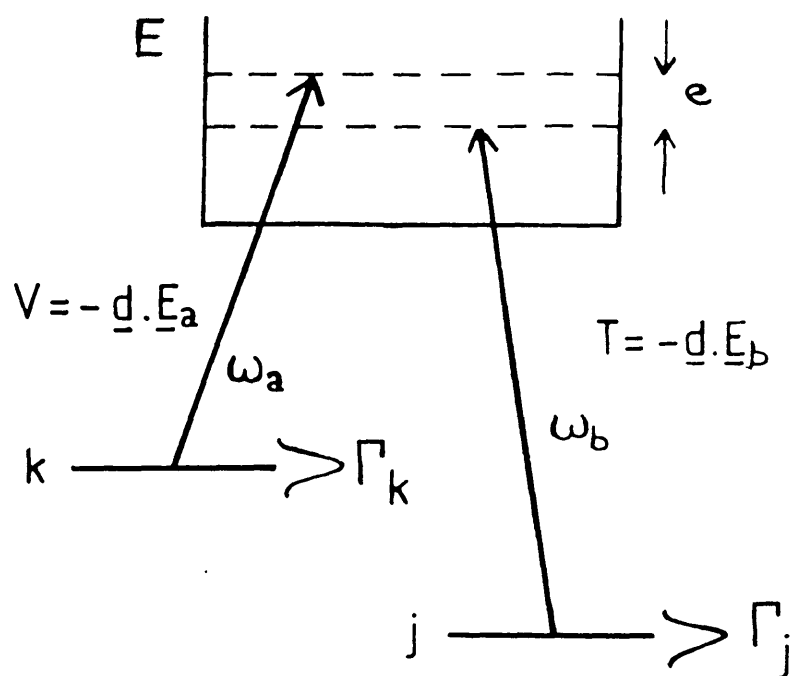
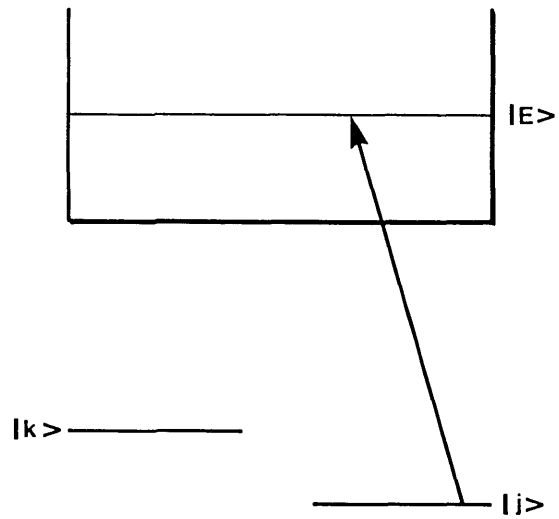


Figure 5.7 Energy Levels for Laser-Induced Autoionising State

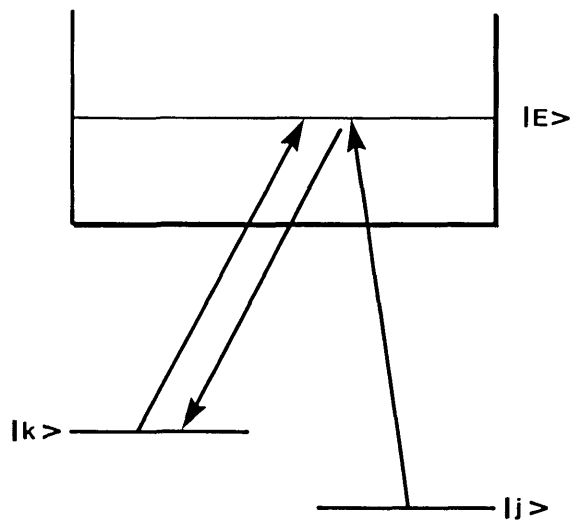
interaction, V , causing the discrete state to be mixed with the continuum. In the case of real autoionising states, this arises from the internal configuration interaction resulting from residual Coulomb interaction between electrons, while in the case of laser-induced autoionising states, it arises from the external interaction of dipole bound-continuum laser coupling.

The concept of laser-induced continuum structure was first introduced by Armstrong, Beers and Feneuille in 1975. The advantages of LICS over real autoionising states in terms of flexibility position and width have been described in Section 5.3.1. Armstrong and co-workers recognised the opportunities for resonant enhancement of non-linear processes. However, LICS offer the additional possibility of impeding processes which involve a continuum contribution, via the minimum in the Fano lineshape. It is this particular property which lead to the experimental work described in Chapter 6.

Let us now consider, in particular, the development of the Fano theory for the case of laser-induced continuum structure. Consider photoionisation into a continuum structured by a laser interaction. As shown in Figure 5.7, the dipole interaction V embeds state $|k\rangle$ into the continuum and this LICS is probed from another discrete state $|j\rangle$ by a second dipole interaction T . As we have seen, Fano theory gives the modification to the transition rate due to the continuum dressing. However, in the case of LICS, the q -value is different from that given in Equation 5.6 due to angular momentum selection rules. There is no direct coupling between states $|j\rangle$ and $|k\rangle$, since if V and T are both single-photon dipole interactions and both $|j\rangle$ and $|k\rangle$ are coupled to the continuum, then there can be



(a) Single-Photon Ionisation Channel



(b) Three-Photon Ionisation Channel

Figure 5.8 Ionisation out of State $|j\rangle$
via a Laser-Induced Autoionising State

no single photon coupling between them. Hence $\langle k | T | j \rangle = 0$.

There is, however, interference between ionisation pathways because of the principal part term in $|\phi\rangle$ (or q). The two channels which interfere are the direct $\langle E | T | j \rangle$ amplitude and the indirect, Raman-excited amplitude which couples $|j\rangle$ to $|k\rangle$ via the continuum and which can then be excited out of $|k\rangle$ into $|E\rangle$. This indirect Raman coupling is given by the principal part term. The interference of the single and three-photon, processes as shown in Figure 5.8 is a useful concept when analysing laser-induced continuum structure processes.

Hence for LICS

$$q = \frac{\langle \phi | T | j \rangle}{\sqrt{\pi_j \pi_k}} = \frac{\mathcal{P} \int_0^\infty dE \frac{T_{jE} V_{Ek}}{\varepsilon - E}}{\pi T_{j\varepsilon} V_{\varepsilon k}} \quad (5.8)$$

This leads to an alternative interpretation of the factor q . Consider the two-photon Rabi frequency $\Omega^{(2)}$, linking states $|k\rangle$ and $|j\rangle$ via the continuum, which is, by analogy with the single photon Rabi frequency,

$$\Omega^{(2)} = \oint \frac{\langle j | T | E \rangle \langle E | V | k \rangle}{\varepsilon - E + i\varepsilon} \quad (5.9)$$

This is complex because it involves contributions from continuum states. It can be decomposed into real and imaginary parts using

$$\lim_{\varepsilon \rightarrow 0^+} \frac{1}{x + i\varepsilon} = \mathcal{P}\left(\frac{1}{x}\right) - i\pi\delta(x)$$

i.e.

$$\Omega^{(2)} = \mathcal{P} \int dE \frac{T_{jE} V_{Ek}}{\varepsilon - E} - i\pi T_{j\varepsilon} V_{\varepsilon k}$$

Hence, by comparison with Equation 5.8,

$$q = \frac{\text{Re } \Omega^{(2)}}{\text{Im } \Omega^{(2)}}$$

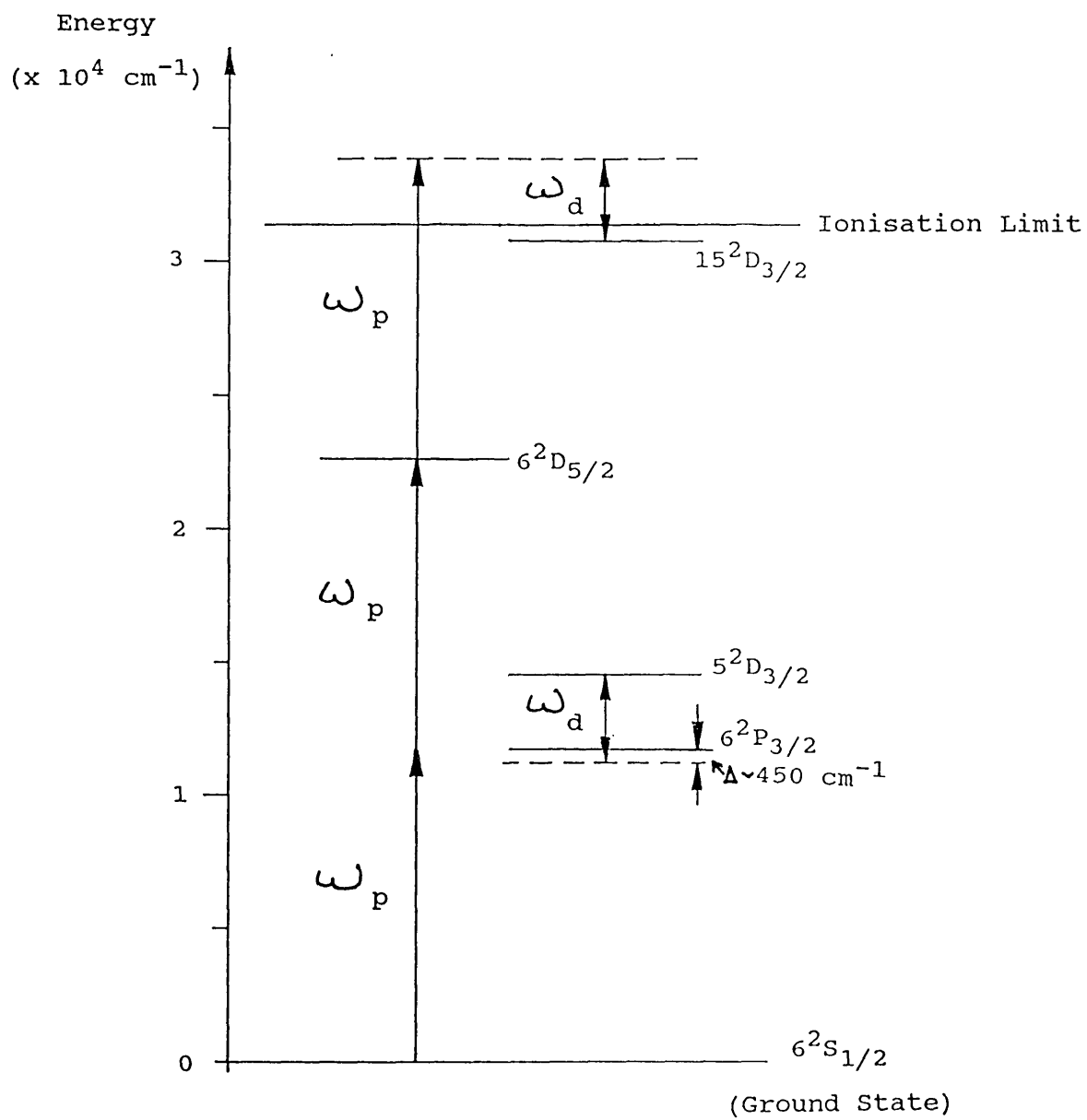
i.e. q is the ratio of the real to imaginary parts of the two-photon Rabi frequency. Again this can be interpreted in terms of discrete and continuum contributions of the transition rate.

This interpretation of q can be useful as the complex Rabi frequency occurs in other contexts; for example, in multiphoton physics it appears as a damping term [see, for example Knight, 1979] and it also plays an important role in photoionisation quantum beats [see, for example Knight, 1980].

5.3.4 Further Comments on the Fano Asymmetry Parameter in LICS

The Fano asymmetry parameter q is a property of the atom and fields involved, and can be resonantly tuned by altering the embedding laser frequency, [Alber and Zoller, 1983].

To understand this, the expression for q in terms of the two-photon Rabi frequency is a good starting point. However, a more general expression for this two-photon or Raman coupling Rabi frequency, $\Omega^{(2)}$, between the probe and embedding states, is required. In the form of the two-photon Rabi frequency given in Equation 5.9, only the continuum is shown as a virtual intermediate state. In reality, all the states of the atom, discrete and continuum, accessible by dipole selection rules will contribute as virtual intermediate states. States lying below the embedding state can participate by stimulated emission processes as opposed to absorption. To describe these, the rotating wave approximation must not be made. Hence both slowly and rapidly varying components of $\Omega^{(2)}$ must be considered. The resulting generalisation of $\Omega^{(2)}$ is given by [Alber & Zoller, 1983]



(a) Cesium Partial Energy Level Diagram

Figure 5.9 Resonant Tuning of the Fano q-parameter

$$\Omega^{(2)} = \langle j | V \frac{1}{E_k + \hbar\omega_p - H_A + i\varepsilon} T | k \rangle + \langle j | T \frac{1}{E_k - \hbar\omega_d - H_A} V | k \rangle \quad (5.10)$$

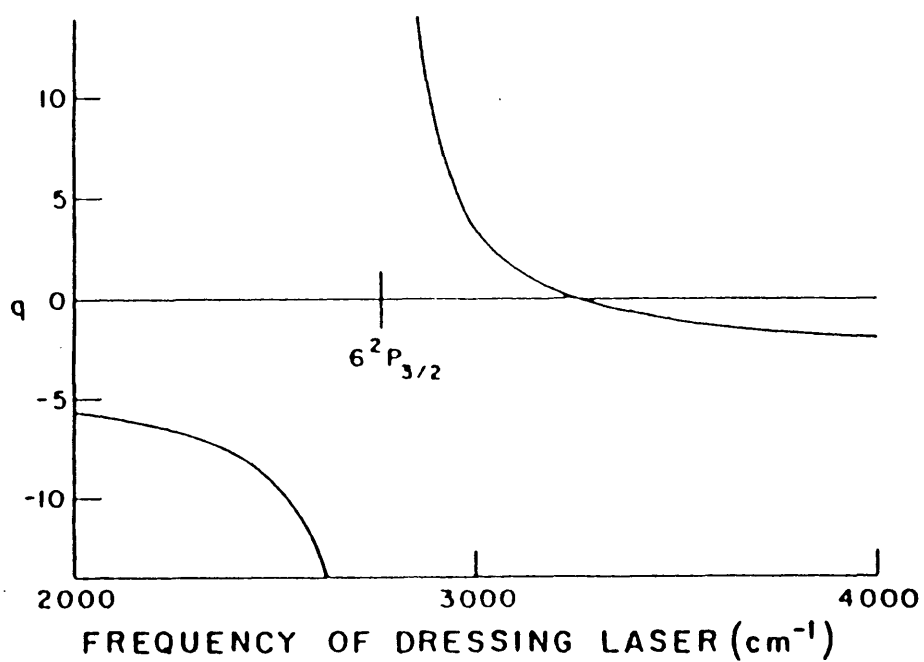
where H_A is the atomic Hamiltonian,

ω_p and ω_d are the probe and embedding (or "dressing") laser frequencies,

and T and V are the probe and embedding dipole interactions respectively, as before.

The first term in Equation 5.10 corresponds to the continuum coupling of Equation 5.9, while the counter-rotating second term corresponds to coupling between states $|k\rangle$ and $|j\rangle$ via lower-lying bound intermediate states. This term is generally small in comparison with the first term, but it can be tuned to resonance. In these circumstances the denominator $E_k - \hbar\omega_d \rightarrow 0$ and this counter-propagating term can dominate $\Omega^{(2)}$. This second term contains no continuum contribution and is therefore entirely real, leading to resonant enhancement of the Fano asymmetry parameter q , as the photon energies are tuned close to a real bound intermediate state.

Alber and Zoller, 1983 have calculated the effect of a lower lying resonance on the value of q for atomic Cesium. As shown in Figure 5.9(a), they consider embedding the $15^2D_{3/2}$ state into the continuum, this structured continuum being probed by a two-photon resonant three-photon process from the $2S_{1/2}$ ground state. For the laser frequencies involved there is a $6^2P_{3/2}$ virtual intermediate state which makes a major contribution to the value of the q -parameter, and can produce a resonant enhancement of q as ω_d is tuned through the $5^2D_{3/2} - 6^2P_{3/2}$ resonance frequency. As shown in Figure 5.9(b), this



(b) q -parameter Enhancement as Embedding Laser Frequency is Tuned Through Virtual Bound Intermediate Resonance

Figure 5.9 Resonant Tuning of the Fano q -parameter

enhancement has a dispersive nature as would be expected from Equation 5.10. Hence in Cesium, close to such a resonance $|q| \sim 10$ should be possible with a resultant ionisation rate enhancement of the order of $q^2 \approx 100$.

5.4 Application of Theory to Experimental Conditions

The theory of laser-induced continuum structure which has been presented in the previous sections forms the basis for an understanding of the physical processes involved in the production of laser-induced autoionising states. However, there are a number of assumptions in the theory which may not apply experimentally.

In this section we discuss the limitations in the theory as it stands, together with some modifications which can be made to make the theory more relevant to real experimental conditions. It should be pointed out that such modifications to the theory are non-trivial and are the subject of current research in the Laser Theory Group at Imperial College [Lauder, 1985]. Much of the theoretical modification cannot be done analytically but must rather be approached by numerical calculation.

5.4.1 "Embedding" and "Probe" Field Strengths

The theory as it has been presented in Section 5.3 is a weak field theory. Although there is no restriction placed on the strength of the embedding interaction, V , by the theory, the probing interaction T must be treated as a perturbation to the system i.e. it is a weak interaction. Since both V and T are laser dipole interactions, the strength of the interaction is determined by the electric field strength, or intensity, of the laser involved. Experimentally however, the electric field strength of the probe laser may be such that perturbation

theory cannot be used. In many experimental situations both embedding and probe lasers are likely to be of comparable intensity. Clearly if "embedding" and "probe" lasers are of similar power then the distinction between the two fields becomes artificial. The system should then be considered as a single unit involving the interaction of two strong fields with "embedding" field being interrogated by the second "probe" field.

When the constraint that the probe field should be weak is lifted, then it is found that, while the lineshape of the embedded state retains the features of a Fano profile such as asymmetry and a minimum, the shape is no longer described by Equation 5.7,

$$R = \frac{(q + e)^2}{1 + e^2}$$

A q-parameter still exists for the system; however the simple relationship above for transition rate, no longer applies. Hence assigning a q-parameter is no longer easily possible nor meaningful. Lineshapes can only be found by lengthy computation. It is found, however, that the closing down of, for example, ionisation channels and associated population trapping, still occurs.

5.4.2 Time-dependent Laser Fields

Until now it has been assumed that both the embedding and probing interactions, V and T, are constants in time. This corresponds to non time-dependent laser intensities. The theory can relatively easily cope with pulsed fields, as long as the pulses are "top-hat" in form. Obviously, the pulsed lasers used experimentally in this type of work, do not have this time dependence. Ideally, the temporal profile of the

Page 265 - Corrigendum

The case of two independent lasers pumped by a single pump laser would not be expected to lead to correlated phase outputs. Rather, phase correlation may be expected between two lasing outputs derived from a single laser cavity. Hence, for two independent lasers, dephasing time will be determined by independent laser coherence. The optimum for lack of dephasing is bandwidth limited pulses.

[delete final sentences in paras of 5.4.3]

pulse may be Gaussian, while in practice it may be rather more complicated than this, particularly in the case of multi-mode lasers.

Time dependent laser intensities in the form of Gaussian pulses have been included in the theory by numerical evaluation [Lauder, 1985]. The results agree with what may have been expected intuitively. Since the width of the laser induced state is controlled by the strength of the two dipole interactions, it may be deduced that a pulsed interaction would produce continuum structure, the width of which varies during the passage of the laser pulses. It could be expected that this would cause "smearing out" of the detected time-averaged structure.

This is indeed the result of the calculations by Lauder, 1985. These calculations showed that Gaussian pulse excitation had the effect of broadening the width of the maximum and while the minimum remains, it becomes wider and is no longer an exact zero.

5.4.3 Laser Coherence

The coherence of the fields involved in the interaction, is also an important parameter. This may be difficult to assess experimentally. The most extreme case of mutually incoherent lasers is when the beams are incoherent and totally uncorrelated as in two completely independent lasers. On the other hand, the two interaction beams might result from separate lasers pumped however, by a single pump laser. ~~In this case they may be mutually incoherent but mutually correlated.~~

Such conditions can be included analytically in an analysis of

the problem using the density matrix formalism. This has been done by Lauder, 1985, and Knight et al, 1984. In summary the conclusions of their work are that if the lasers are incoherent but correlated then the embedded structure will be the same as for mutually coherent laser fields. ~~This situation could occur if the two lasers are both pumped by the same laser, as in the experiments described in the following chapter.~~

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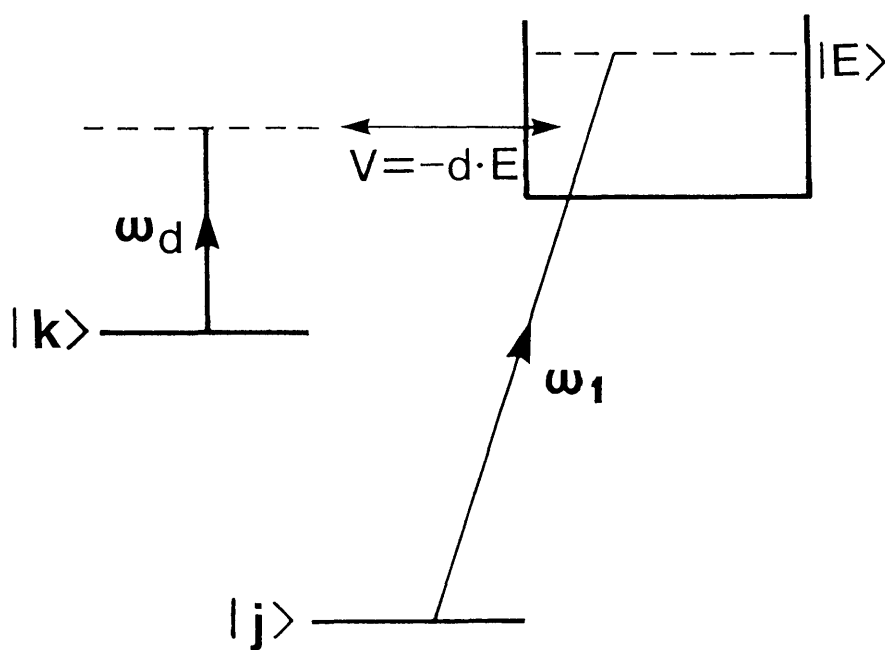


Figure 6.1 Embedding and Probing of a Laser-induced Autoionising State

CHAPTER 6

EXPERIMENTAL STUDY OF A LASER-INDUCED AUTOIONISING STATE.

6.0 Terminology

Throughout this chapter, the following terminology will be adopted:

Embedding field frequency	- ω_d
Embedding state	- $ k\rangle$
Probing field frequency	- ω_1
Probing state	- $ j\rangle$

6.1 Introduction

The detection and monitoring of a laser-induced autoionising state requires the probing of the structured continuum by some process, the efficiency of which contains a continuum contribution. In the simplest example of this, shown in Figure 6.1, the structured continuum is probed by a second laser causing ionisation from state $|j\rangle$ which may be either a populated excited state or the ground state.

The more complex process of multiphoton ionisation, (MPI) resonant or non-resonant, can also be used to probe the structured continuum. However, in the case of resonant MPI care must be taken to ensure that the resonant nature of the process does not mask the effect of the induced structure. This can be achieved by keeping the frequency of the MPI laser fixed and tuning the embedding laser to track the embedded structure through the continuum in the region of the multiphoton energy. This technique is used in the experimental work described in this chapter.

In addition, parametric non-linear processes, such as four-wave mixing, which involve a continuum contribution, can also be used as probes [Dimov et al, 1982, 1983(a), (b), (c)]. The induced structure can be used to achieve increased efficiency of such a process in a manner analogous to enhancement by real states. Again, care must be taken to eliminate the effect of other resonances.

While the terminology of "embedding" and "probe" fields is useful for identifying the various laser fields involved in the process, one must remember that in some cases the distinction is artificial. When both fields are of similar intensity, as is the case for the experimental work described in this chapter, then the concept of a non-perturbing probe field is not applicable. One must then consider the interaction of both fields with the atom. This is considered in more detail in Section 5.4.1.

In our experiments described in this chapter, we studied the effect of a laser-induced autoionising state on the two-photon-resonant, three-photon ionisation yield. The two-photon-resonant three-photon ionisation process is that studied in Chapter 4 when considering saturation of the process. To recap, laser radiation at $\lambda = 249.63\text{nm}$ is two-photon-resonant with the 6p ($J=0$) state in Xenon. One additional UV photon is sufficient to ionise the atom.

Bearing in mind the earlier comments regarding the use of resonant probe processes, the frequency of the three-photon ionisation laser was kept fixed on the two-photon resonance while the embedding laser frequency was tuned, moving the position of the embedded state through the continuum in the region of the three-photon energy. The partial energy level

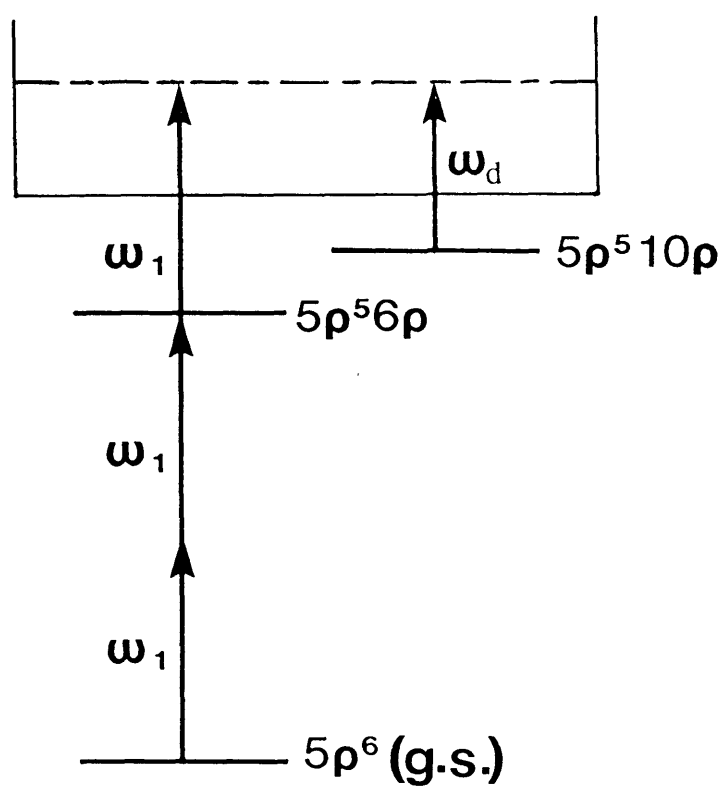


Figure 6.2 Xenon Partial Energy Level Diagram showing
LICs Embedding and Probing Configuration

diagram for Xenon showing two-photon-resonant three-photon ionisation and embedding configuration are shown in Figure 6.2. The $10p$ ($J=0$) state at $95,287\text{cm}^{-1}$ was coupled into the continuum. This state was chosen because it is a singlet state, well isolated from other states.

The condition that a bound state should be mixed with the continuum at energy $3\omega_1$ by a dressing field of photon energy ω_d is given by

$$\hbar\omega_{IP} > 3\hbar\omega_1 - \hbar\omega_d$$

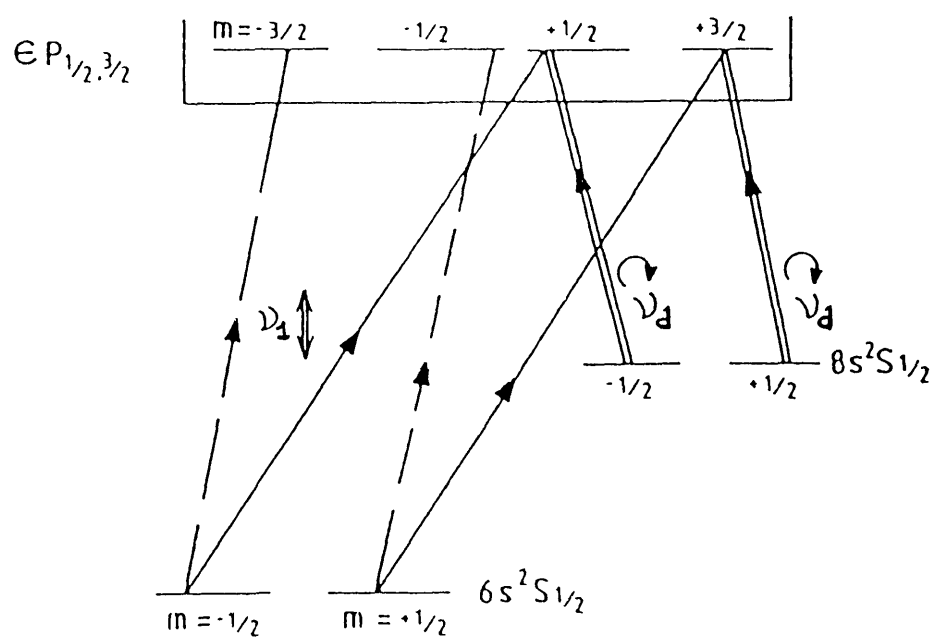
where $\hbar\omega_{IP}$ is the ionisation potential of the atom.

If, in addition, $2\hbar\omega_1 + \hbar\omega_d > \hbar\omega_{IP}$, non-degenerate two-photon-resonant three-photon ionisation is possible and irradiation of the atom by both optical fields will produce a net increase in the total ionisation, compared with that obtained with only ω_1 present, i.e., if $\omega_{IP} < 5/2 \omega_1$, the induced continuum structure will be superimposed on an enhanced background due to $2\omega_1 + \omega_d$. The fact that all the possible two-photon-resonant states in Xenon are high-lying in energy result in this increase of the total background ionisation signal for our experimental arrangement.

Before describing experimental details, procedures, results and conclusions, we first review the current status of experimental work on laser-induced continuum structure by other researchers.

6.2 Previous Experimental Work on Laser-Induced Autoionisation

Despite extensive theoretical work [Knight, 1984 and references therein] on laser-induced autoionising states by many researchers, there have been relatively few experimental tests of the theories developed.



(a) Circularly Polarised Embedding (ν_d) and Linearly Polarised (ν_1) Transitions in Cesium employed by Heller et al, 1981

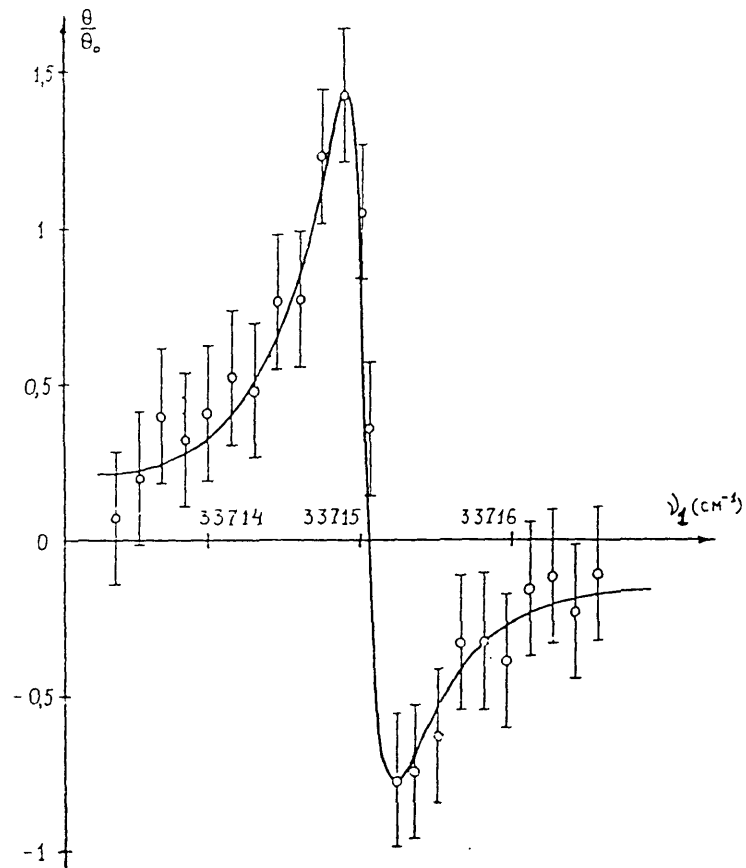
Figure 6.3

The two main forces in experimental work in this field have, to date, been the Bulgarian group of Dimov and co-workers at the University of Sofia and some Russian researchers at the L.V. Kirensky Institute of Physics, Krasnoyarsk, USSR. Independent work has been published by these two teams, together with some collaborative studies. They have concentrated on the observation of laser-induced continuum structure via photoionisation and non-linear mixing in alkali metals such as Cesium and Sodium.

The first observation of a laser-induced autoionising state was made by Heller et al, 1981, who studied photoionisation of Cesium in the presence of induced continuum structure. This followed a theoretical paper by Heller and Popov published in 1976, in which they considered the control of parametric generation and absorption of tunable vacuum ultra-violet radiation by laser-induced autoionising-like resonances in the continuum. In that paper, the authors derive theoretical relationships between the non-linear susceptibility and hence efficiency of a non-linear process and the structure of the induced autoionising state, in particular the Fano q -parameter.

The relevant energy level diagrams for the experimental work described by Heller et al, 1981 is shown in Figure 6.3(a). A right hand circularly polarised (σ_+) Nd:YAG laser (λ_d) of intensity $\sim 100 \text{ MW/cm}^2$ was used to embed the $8s^2 S_{1/2}$ excited state into the $\sum P_{1/2,3/2}$ continuum of Cesium. The probe field used was a frequency-doubled tunable dye laser at a wavelength of 296.6nm (λ_1) and was linearly polarised. The probing transition was from the $6s^2 S_{1/2}$ ground state. Both lasers had linewidths of 6GHz.

The linearly polarised light can be considered as an equal



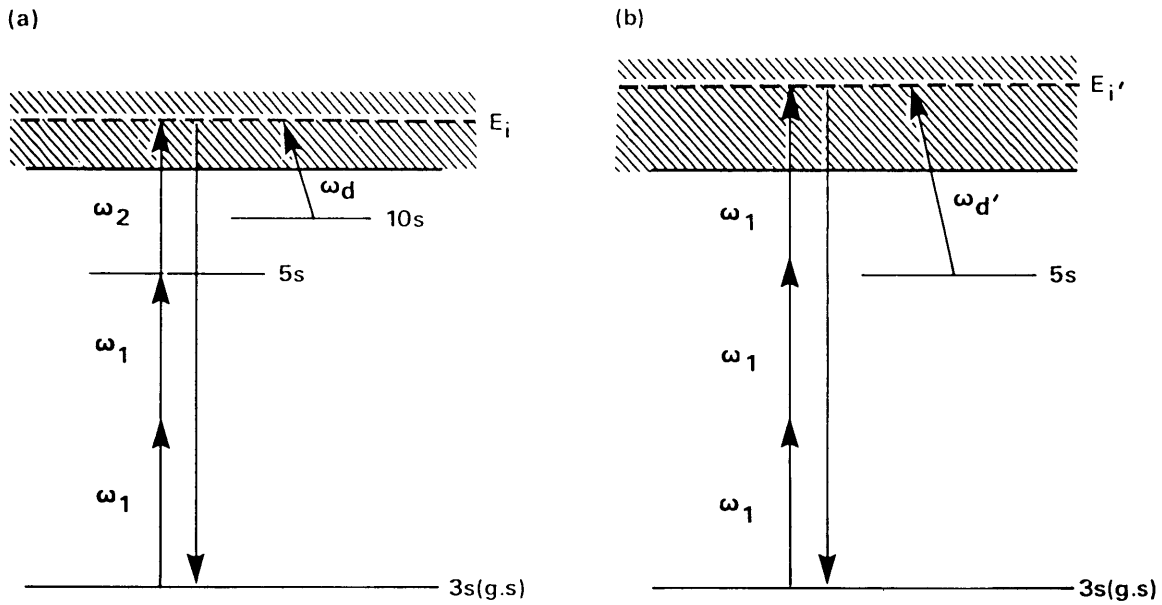
(b) Polarisation Rotation Angle, θ , (in units of initial angle, θ_0) versus Detuning of Probe Frequency, ν_1 , in the Region of the Laser-Induced Autoionising State (after Heller et al, 1981)

Figure 6.3

superposition of left (σ_-) and right (σ_+) circularly polarised light. As a result of angular momentum selection rules, the σ_+ component of the probe causes photoionisation into a structured continuum, while the σ_- component sees an unperturbed continuum. This leads to unequal absorption of the two circular polarisations as the probe field is tuned through the autoionising resonance. Hence the plane of polarisation of the light is rotated as it is transmitted through the Cesium cell. Figure 6.3(b) shows Heller et al's results [Heller et al, 1981] from which the authors calculated an enhanced absorption of a factor of 6 at the peak of the resonance and a reduced absorption of 10% in the "Fano window". The polarisation rotation is in opposite senses on the peak and minimum of the autoionising resonance. From these results, a q-value of 6.8 was calculated and compared favourably with theoretical predictions.

More recent observations of laser-induced continuum structure have been via non-linear mixing processes (frequency up-conversion) which involve a continuum contribution. The investigation of the nature of the induced resonance by the monitoring of the efficiency of the non-linear mixing is a rather more direct measurement than via the polarisation rotation effects used in Heller et al's earlier experiment.

The use of real autoionising states in the enhancement of non-linear mixing processes such as frequency up-conversion which involve a continuum contribution is well known. See, for example, Hodgson et al, 1974, who observed a large resonant enhancement of a two-photon-resonant four-wave mixing signal (sum frequency generation) when tuning close to a real autoionising state in Strontium vapour. The frequency



(a),(b) Energy Level Diagrams Showing Embedding and Probing Configurations

Figure 6.4 Experimental Investigation of LICS, via
Four-wave Mixing Processes in Sodium, by Dimov and co-workers

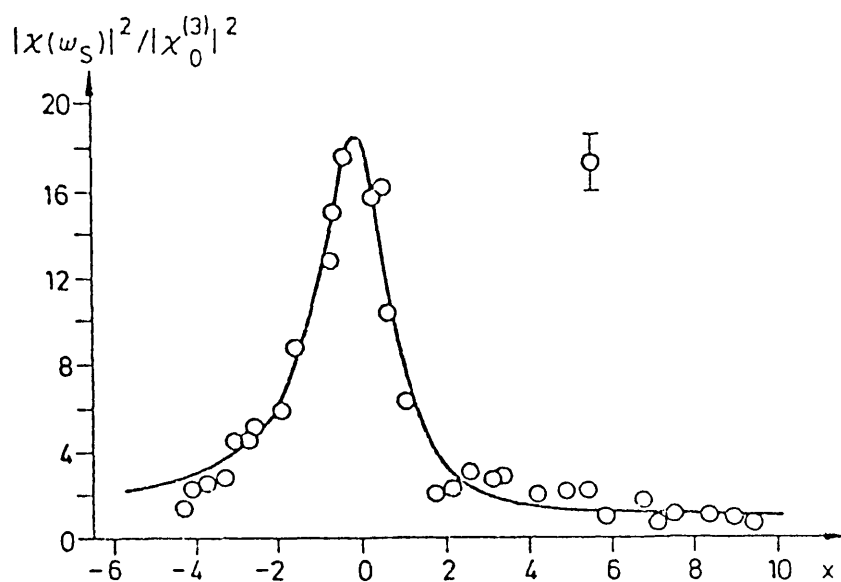
dependence of the generated signal can be used to derive the structure of the autoionising state.

Studies of laser-induced autoionising states via non-linear mixing processes have been carried out by the group at the University of Sofia, Bulgaria. Using Sodium as the non-linear medium, they have observed third order non-linear mixing processes such as two-photon-resonant four-wave mixing, sum frequency generation [Dimov et al, 1982, 1983(a), 1983(c)] and non-resonant third harmonic generation [Dimov et al, 1983(b), 1983(c) Pavlov et al, 1982].

Narrow bandwidth ($\Delta\omega = 3\text{GHz}$) dye lasers, pumped by the second harmonic of a Nd:YAG laser, were employed in the up-conversion schemes. Either the Nd:YAG fundamental frequency or second harmonic was used to mix suitably placed states into the continuum. Intensities in the region of $1\text{GW}/\text{cm}^2$ were attained in the focal region of a 30cm focal length lens. Processes studied included two-photon-resonant four-wave mixing, frequency up-conversion i.e. $\omega' = 2\omega_1 + \omega_2$ where ω_1 is two-photon-resonant with the 5s state in Sodium. In this case the 10s state was embedded into the continuum by the Nd:YAG fundamental (see Figure 6.4(a)).

An alternative experiment, also in Sodium, considered non-resonant third harmonic generation in the presence of a laser induced autoionising state resulting from the embedding of the 5s state into the continuum. The embedding laser in this case was the second harmonic of the Nd:YAG laser. This scheme is shown in Figure 6.4(b). Phase matching was achieved for this process by using Xenon as a buffer gas.

In both these experiments, Dimov and his co-workers observed a



(c) Laser-induced Autoionising Resonance measured via Third Harmonic Generation

Figure 6.4 Experimental Investigation of LICS, via Four-wave Mixing Processes in Sodium, by Dimov and co-workers

non-linear mixing signal with a frequency dependence which could be attributed to the presence of induced continuum structure. In the four-wave mixing experiment, the non-resonant laser frequency ω_2 was tuned, while in the third harmonic experiment the fundamental frequency was varied. In both cases, the frequency of the embedding laser was fixed.

The dependence of the generated intensity on fundamental intensity(ies) in both THG and four-wave mixing schemes was found to obey the expected power laws at low intensities. However, some saturation of the two photon-resonant four-wave mixing signal was observed at input intensities greater than 500 MW/cm². [Dimov et al, 1982].

Enhancements of a factor of around 20 were observed in the non-linear mixing signals and reductions of approximately 20% were observed at the Fano window positions. Figure 6.4(c) shows an induced autoionising resonance measured via third harmonic generation [Dimov et al, 1983(b)]. The solid line is theoretically calculated. From this data, values for q , the Fano asymmetry parameter, were derived.

Further work is planned in this area. One known experiment involving laser-induced autoionisation in Krypton is to be carried out at Australian National University, Canberra, Australia [Baldwin, 1985]. No doubt, other work will follow as the application of laser-induced continuum structure in non-linear optics develops further.

Note added in proof to Section 6.2

Recent experimental work on LICS in Sodium has been reported by Feldmann et al, 1986. These workers have made a systematic investigation of resonances induced in the multiphoton ionisation spectrum of Sodium by a second strong laser field. They found in their experiments that a Raman coupling between the initial and 'embedded' states through low-lying discrete states dominated their ionisation spectrum. As shown by Alber and Zoller, 1983, and described in Section 5.3.4, such bound-bound Raman coupling can lead to substantial enhancement of the Fano q-parameter. For large q-values, symmetric line profiles are generated (Section 5.3.2). Hence the Raman resonances obscured the asymmetric nature of the induced resonances and symmetric lineshapes were observed by Feldmann and his co-workers.

It should be noted that in Xenon there are no low-lying states in the neighbourhood of a Raman resonance for our experimental conditions. The Raman coupling, therefore, does not make a significant contribution and asymmetric resonances, associated with small q-values, would be expected.

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UV peak power = $100\text{MW}/\text{cm}^2$; blue peak power = $100\text{MW}/\text{cm}^2$

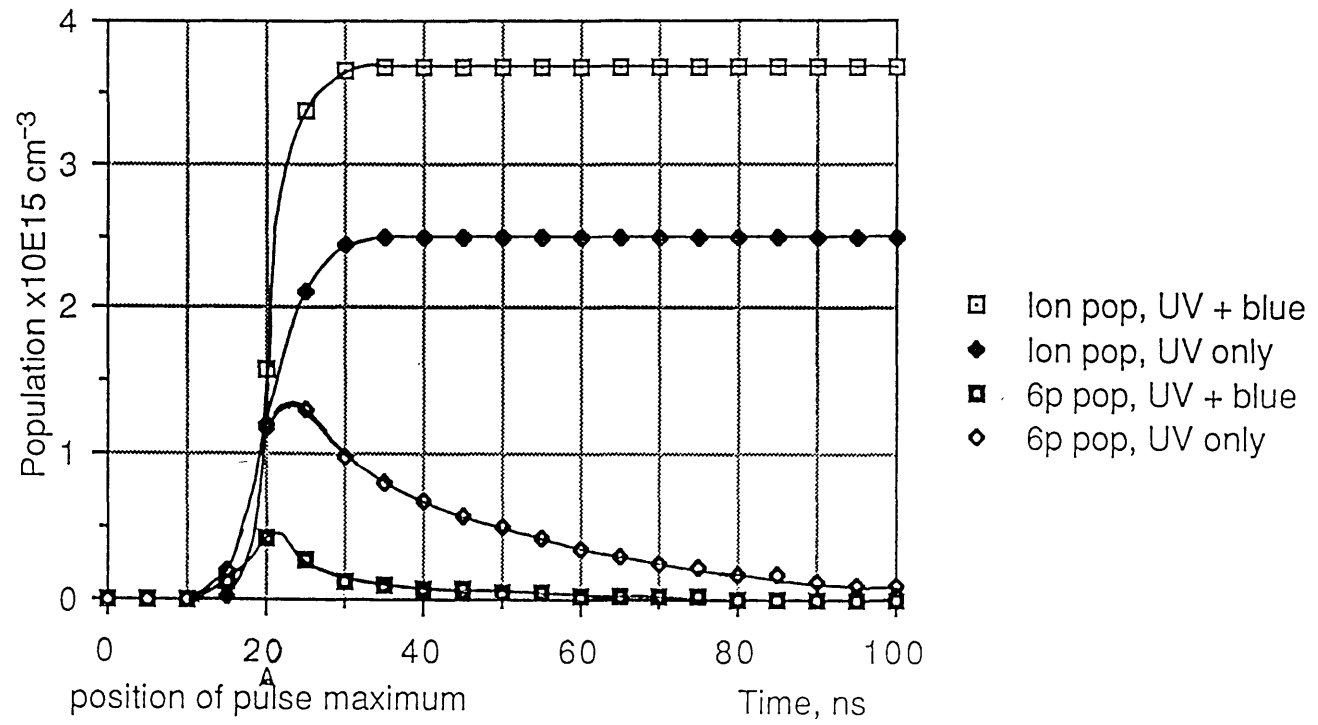


Figure 6.5 Result of Rate Equation Calculation showing
Effect of Presence of Embedding (blue) Field
on Total Ionisation Signal

$$\frac{dN_2}{dt} = - \frac{\sigma_d I_d}{\hbar \omega_d} N_2$$

where the ionisation cross-section, σ_d , angular frequency, ω_d , and intensity, I_d , all relate to the embedding (blue) laser. Pindzola, 1981, gives a figure of $4.8 \times 10^{-18} \text{ cm}^2$ for the photoionisation cross-section out of the 6p ($J=0$) state at a wavelength of 390 nm.

The results of the calculation for a UV intensity of 100 MW/cm^2 and a blue intensity of 100 MW/cm^2 is shown in Figure 6.5. One example only is included as the results merely confirm what would be expected intuitively, namely the ion population is increased: in this example by approximately 50%. In the saturated region where total ionisation occurs before the complete transit of the laser pulse(s), the effect of the presence of the blue laser field is merely to produce complete ionisation in a shorter time.

In the work carried out, the intensities of both lasers were limited to the range 10's - 100's MW/cm^2 , i.e. intensities below the saturation intensities for ionisation from the 6p state. In all experimental work, the "embedding" (blue) and "probe" (UV) beams were of similar intensities.

6.4 Experimental Details

6.4.1 Blue Dye Laser

The scheme described for the embedding of an autoionising state in the continuum of the Xenon atom required that the wavelength of the embedding laser be 401.73 nm for the chosen energy levels. The visible dye laser was installed to operate in this region of the spectrum. The oscillator design was as that described in Section 2.4.2 and both Lambda Physik and Lumonics

XeCl* excimer pump lasers were used. However, the operation of the blue dye laser presented some difficulties: its operation was not identical to the green dye laser ($\lambda = 499\text{nm}$) and is therefore described in this section.

Two dyes were available for this spectral region, namely diphenylstilben (DPS) and PBBO. These have relatively high efficiencies when excimer pumped (7.3% for DPS and 11% for PBBO compared with 16.3% for Coumarin 307 used in the green dye laser) [Lambda Physik, Technical Data] but can be more difficult to operate than dyes in other regions of the visible spectrum. Firstly, solvents compatible with operation in this spectral region, such as dioxan, are more reactive than ethanol or methanol. They require circulation systems made of PTFE tubing which is solid rather than the flexible and more convenient PVC tubing. Secondly, although the dyes are quoted as having stabilities comparable to, or somewhat better than the Coumarins, the solvent dioxan absorbs oxygen easily. This is thought to be responsible for the observed rapid deterioration of the dyes and necessitated frequent replacement of the dye solutions to ensure constant power output.

The wavelength 401.73 nm is somewhat removed from the peak of the lasing output for both PBBO and DPS. The expected performance of the two dyes is shown below:

Dye	Peak (nm)	Tuning Range (nm)
PBBO	390	386 - 420
DPS	406	399 - 415

In initial work DPS was used in preference to PBBO despite the wavelength required being towards the edge of its tuning range because its stability was known to be good. At the time, the

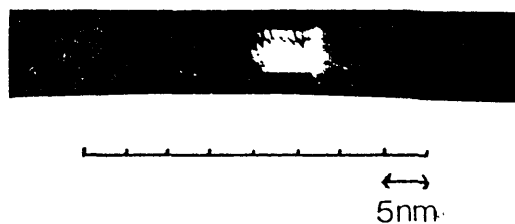


Figure 6.6 Blue Dye Laser:
Spectrograph Photograph of Output after Second Amplifier

stability of PBBO when excimer-pumped was not known.

The dye used in the oscillator and first amplifier was 6×10^{-4} M DPS dissolved in dioxan. Despite the high losses in the dye oscillator, discussed in Section 2.4.2, laser oscillation was achieved although the output energy was low - estimated to be nanojoules. Good amplification was achieved in the first amplifier (~ 400) and amplified spontaneous emission (ASE) was not detected when the signal from the first amplifier was monitored on a 1 m spectrograph.

However, when the signal was amplified in the second amplifier containing 3.5×10^{-4} M DPS in dioxan, it was found that the signal had a large ASE component which was approximately 50% of the total energy output. This was evident from spectrograph photographs such as that shown in Figure 6.6. It is believed that the large ASE component results from the extremely low energy ASE emitted from the first amplifier being amplified in the second in preference to the narrow-band laser signal. This is a problem here because the laser wavelength is at the edge of the gain bandwidth of the dye, so that the ASE, the frequency of which is centred at the peak of the bandwidth, sees a higher gain and is preferentially amplified.

One method of eliminating this problem was to increase the angle between the excimer pump beam and the dye beam to be amplified in the first amplifier, so that the ASE from the first amplifier did not reach the gain region of the second amplifier. Normally, the angular offset between pump and input beams was around 5° , as described in Section 2.4.2 and shown in Figure 2.11. However, the reduction in gain of the first amplifier which this caused due to the reduced signal and pump overlap volume, made it an unacceptable solution.

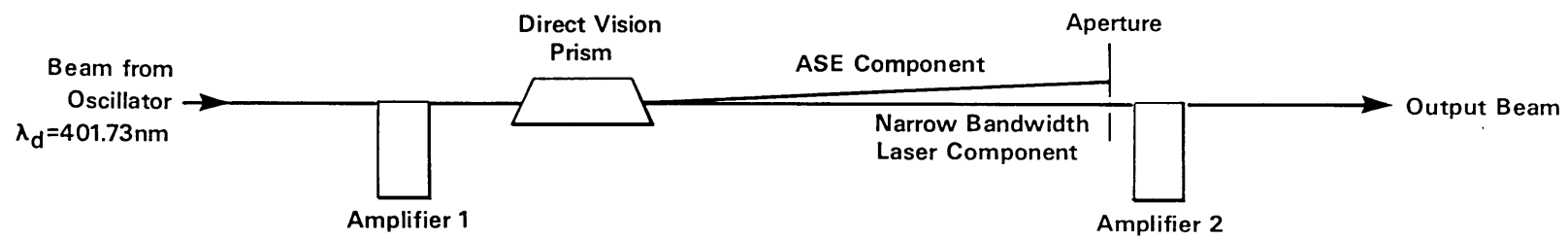


Fig 6.7 Blue Dye Laser: Direct Vision Prism Arrangement

The solution used took advantage of the difference in wavelength between the laser signal and the ASE. By inserting a direct vision prism directly after the first amplifier, as shown in Figure 6.7, the dispersion between the wavelengths was sufficient to spatially separate the signal and ASE and to ensure that no ASE entered the second amplifier. This simple method worked extremely well and the ASE component of the output from the second amplifier was negligible. The output energy was around 1.2 - 1.5 mJ in a 5-7ns pulse using the Lambda Physik EMG101E XeCl* pump laser. Comparable energies in a slightly longer pulse (~ 10 ns) were achieved using the Lumonics 860 XeCl* excimer pump source.

The dye PBBO has a tuning range 386-420 nm indicating that an oscillator at 401.73 nm should be easier to operate using this dye than DPS. Since its stability was not known it was initially used only in the oscillator and first amplifier (10^{-3} M in dioxan) where the pumping power densities are moderate. 3.5×10^{-4} M in dioxan DPS was still used in the final amplifier. With this arrangement, it was then found that the dispersing prism between the amplifiers was no longer needed, due, presumably, to the reduced ASE content of the output from the first amplifier.

The amplification of the two amplifiers for this arrangement was comparable with the system using DPS alone, namely 200 - 400 for the first and 10 - 15 for the second. The pulse energies and durations were also unchanged. However, operation was simpler and more reliable and for this reason was used for the experimental work described.

Compared with the green laser, the lifetime to half-power output of the blue dye laser was short: a few days to a week,

as compared with 4 - 6 weeks. It was sufficiently long, however, to ensure that constant power output over periods of a few hours, the time required to collect one run of data for the laser-induced autoionisation experiment. The blue dyes were replaced every few days to ensure optimum performance.

6.4.2 Beam Combination and Alignment

The performance of the two dye lasers under both Lambda Physik and Lumonics excimer laser pumping is described in Section 2.4.2 (Table 2.4). The spectral characteristics of the dye laser outputs was as that described in 2.4.2. Oscillation occurred in a single longitudinal mode when the oscillators were pumped just above threshold. More typically, two longitudinal modes were present and the average linewidth was 1GHz.

The output of the green dye laser (probe) was then frequency doubled in a Potassium Pentaborate (KB5) crystal and amplified in a KrF excimer amplifier synchronised with the XeCl* excimer pump, as described in 2.4.3 and 2.4.4. The output from the blue dye laser (embedding) passed through a defocused 1:1 telescope before being combined with the UV beam at a dichroic mirror which was 95% transmitting in the blue (neglecting reflection losses) and highly reflective (>95%) at 249.6nm.

The defocused telescope was used to adjust the blue beam divergence to compensate for chromatic aberration in the singlet quartz plano-convex lens used to focus into the ionisation chamber, in order to allow the two beams to be focused at the same axial position. A 1:1 telescope was chosen to give a collimated (or nearly collimated) blue beam of diameter appropriate for the production of approximately equal UV and blue focal spot diameters. This was the most efficient

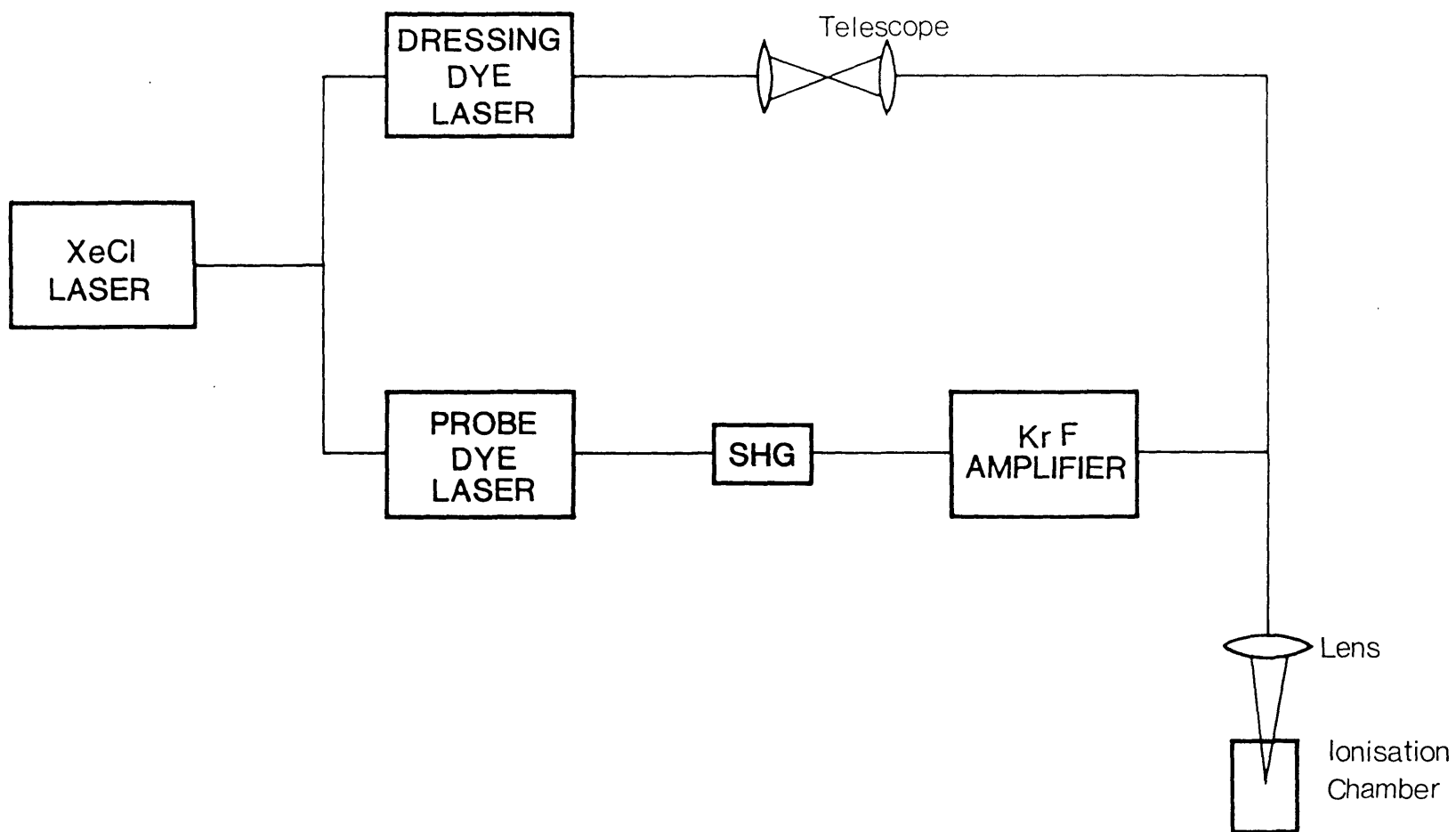


Figure 6.8 Laser-induced Autoionisation Experiment:
Experimental Arrangement Schematic

use of the light if overlapping foci are required. For some experimental arrangements, the telescope was used to provide deliberate separation between the foci. The UV and blue beam paths were approximately equal. The experimental arrangement is shown in schematic form in Figure 6.8. The UV and blue beam diameters at the plano-convex focusing lens were approximately 7 and 10 mm respectively.

As in the experiments investigating two-photon-resonant three-photon ionisation, the ionisation signal was detected using the simple ionisation chamber described in Section 2.4.5. For the effect of the embedded state to be detected it was, of course, necessary that the blue and UV beams overlapped. However, unlike the requirements for a process such as four-wave mixing, exact overlap through focus is not necessary since there are no phase matching requirements for the LICS process.

Two different beam focusing geometries were adopted in the course of the work to achieve the appropriate intensities, as discussed in Section 6.3, for observation of the laser-induced continuum structure. These were

(a) tight focusing with a short ($f=20$ cm) focal length lens. In this arrangement, defocusing and spatial separation of the UV and blue focal spots was used to produce the appropriate power densities.

(b) weak focusing with a long ($f=130$ cm) focal length lens. In this arrangement, conventional overlapping of foci was used.

For the tight focusing configuration, it was necessary to observe the ionisation signal in a region away from the focus of both beams, as the focal power density, which approached GW/cm^2 in focal areas of approximately 25 μm diameter (confocal parameter = 0.15cm), was sufficient to saturate the ionisation

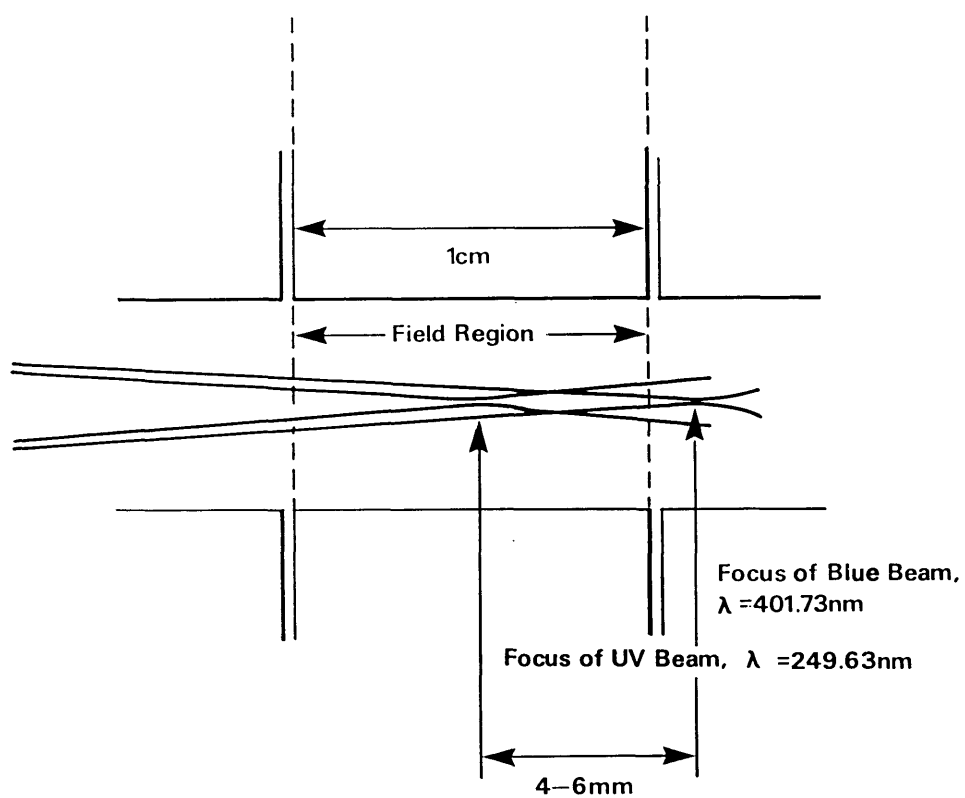


Fig 6.9 Tight Focusing Configuration

process. The arrangement used did not require that the foci of the two beams overlap, in fact, the spatial separation of the foci was used to advantage to ensure a tight control over the intensities in the field region of the ionisation chamber. A typical geometry used is shown in Figure 6.9.

For the weak focusing configuration, spot sizes of approximately 125 μ m were produced at the focus of the 130 cm focal length lens with a calculated confocal parameter of the order of 3.5cm. In this case, no spatial separation of the UV and blue focal spots was required. As previously noted (Section 4.2.3), the beams were effectively collimated in the field region of the ionisation chamber for this arrangement.

With both focusing arrangements, power densities for both beams of 10's - 100's MW/cm² were produced in the field region of the ionisation chamber. The results presented in Section 6.5 were obtained using the weak focusing arrangement, which was found to give more consistent results. Difficulties with the tight focusing, separated foci, arrangement can result from non-uniformities in power density in the ionisation chamber field region due to beam convergence. This causes the ion signal to be integrated over a range of intensities. It was also difficult to ensure accurate placement of the required intensity regions within the ionisation chamber. These problems were overcome by the weak focusing arrangement.

It was advantageous to arrange that within the region of the electric field of the ionisation chamber the volume irradiated by the UV laser alone was minimised. Ion signals resulting from three-photon ionisation to an unstructured continuum from such volumes were detected as increased background to the signal produced by ionisation to a structured continuum in the

presence of both ultra-violet and blue photons. This need not be considered for non-linear processes such as four-wave mixing. Regions irradiated by the blue beam alone were not critical as the efficiency of non-resonant five-photon ionisation by the blue beam was experimentally found to be negligible. The ionisation processes possible are summarised in Table 6.1. Clearly, measurement of the photoelectron energies would allow one to distinguish between the different ionisation processes.

The effect of ionisation from the 6p state by blue photons is not entirely detrimental; the increased background ionisation signal resulting from the combined effect of both laser fields was a useful monitor of the alignment of the two beams.

Co-linearity of the beams and foci was achieved as follows. The beams were aligned by eye to be co-linear over a large distance (few metres) and the focusing lens was then inserted on axis, to avoid chromatic effects resulting from off-axis focusing. The required defocusing of the telescope in the blue beam was calculated from simple geometrical optics and adjusted to give the appropriate focusing conditions.

Two methods were used to ensure axial colinearity and relative axial positions of the foci. These were:

- (i) knife edge test
- (ii) pinhole

It was found that these methods were complementary to each other and the method used was dependent on the focusing arrangement used. They are now considered in detail:

- (i) Knife edge test

Use of this technique in non-linear optics is described by

<u>Beams Present</u>	<u>Ionisation Processes</u>
Blue beam (ω_d) alone	Non-resonant five-photon ionisation to unstructured continuum ($5\omega_d$)
UV beam (ω_1) alone	Two-photon-resonant three-photon ionisation to unstructured continuum ($3\omega_1$)
UV (ω_1) and blue (ω_d) overlapping	Non-resonant five-photon ionisation to unstructured continuum ($5\omega_d$) Two-photon-resonant three-photon ionisation to unstructured continuum ($2\omega_1 + \omega_d$) Two-photon-resonant three-photon ionisation to structured continuum ($3\omega_1$)

Table 6.1 Ionisation Processes

Chabay et al, 1976, and is most useful for overlapping foci, or alignment of the beams with only a small axial separation of the foci. Its use involves the insertion at the focal position of two perpendicular knife edges lying in the plane perpendicular to the beam propagation directions. As the knife edges are moved individually across the beam, the observation of the beams on a screen some distance away shows the degree of beam overlap. For exactly overlapping foci, both beams disappear together. Identification of the axial position of the focus can also be determined since the most rapid disappearance occurs exactly at the focus.

It was found that although this method appeared to work well, it was not sufficiently accurate, particularly with tight focusing arrangements. It is clear that, for example, in non-linear mixing experiments, where exact focal overlap is required, alignment can be optimised to maximise the generated signal once approximate alignment has been achieved. This method can be used in the ionisation experiment by maximising the background ionisation caused by the absorption of two ultra-violet photons and one blue photon. However, this is not always applicable to the separated foci configuration shown in Figure 6.9. In that case, good alignment must be achieved without the option of tweaking. Experimentally, it was found that sufficiently good alignment was not achievable using the knife edge technique.

(ii) Pinhole.

The use of a pinhole was found to be the most convenient alignment method for tight focusing with axially separated foci. It was also used for weak focusing with overlapping foci. Choosing, by experiment, a pinhole to match the focal

spot size, 25 μm in the case of 20 cm focal length lens or 125 μm in the case of the 130 cm focal length lens, this was positioned at the focus of one beam, typically the ultra-violet beam.

In the case of weak focusing, small adjustment of one of the beam steering elements in the other beam was usually sufficient to ensure that it also passed through the pinhole. Some small adjustment of the spacing of the lenses in the 1:1 telescope from their calculated separation was also sometimes required, although the long confocal parameter ($\sim 3.5\text{cm}$) meant that this was rarely necessary.

For tight focusing with axially separated foci, a uniform intensity distribution in the Airy pattern generated by the other beam impinging in the pinhole was used as an indication of colinearity of the beams. Usually the axial positions of the foci could be set with sufficient accuracy by eye, but if necessary the pinhole could be moved axially on a calibrated translation stage to find the exact position of the other focus.

The final alignment, using either knife edge test or pinhole as described above, was always carried out with the focusing lens in the exact position for launching the beams into the ionisation chamber. A mirror was used to reflect the beams to an accessible position for alignment. Hence no further movement of the focusing lens was required after alignment. Any axial movement of the focusing lens would have to have been exactly perpendicular to the beam direction to avoid misalignment. It was felt that this could not be done with sufficient accuracy to avoid misalignment of the foci.

6.4.3 Data Collection and Analysis

In this section we describe the procedure used for each experimental run of the laser-induced autoionisation experiment.

From time to time, both green and blue dye lasers were tuned to approximately the required wavelengths of 499.62 nm and 401.73 nm respectively using a 1m spectrograph and a He-Ne laser for calibration. This procedure was only repeated if required and not on each run.

For each run, the UV beam alone was firstly focused into the field region of the ionisation chamber, and the lens adjusted axially to produce a maximum ionisation signal. For these purposes it was most convenient to monitor the ionisation signal using an oscilloscope. For data collection an electrometer was usually used as an alternative to the oscilloscope. The green laser was then tuned to the centre of the two-photon resonance by maximising the ionisation signal.

Due to the temperature changes in the laboratory, the alignment of the optical system and in particular the stabilisation of the dye laser wavelengths could not be maintained over long periods. To compensate for this effect the UV laser was re-tuned to the peak of the two-photon resonance before each experimental run.

Secondly, the blue and UV beams aligned as described in Section 6.4.2.

The method of data collection was dictated, as for the three-photon ionisation experiments, described in Chapter 4, by the behaviour of the excimer amplifier, and by the tuning performance of both dye lasers and the effect of the temperature

fluctuations already mentioned, on the wavelength of the blue laser. Firstly, the fluctuations in the output of the amplifier required that for each blue tuning position a set of data points of UV intensity and corresponding ionisation signal were measured simultaneously. The method employed for this has already been described in Section 4.2.1. In general about 20 data points were collected at each tuning position. Secondly, while the lifetime of a gas fill in the amplifier was of the order of a day, the amplification available decreased monotonically during this time. Thirdly, due to backlash on the fine tuning control of the blue laser, it was necessary to acquire data while tuning in one direction only and consequently it was difficult to combine data from two or more runs.

In conclusion, as in the three-photon ionisation experiments, each data collection run, scanning the complete blue spectral region of interest had to be completed in a period of 2 hours maximum. Thereafter the UV intensity had changed so that it was impossible to extract information about the ionisation signal at a constant UV intensity over the whole blue frequency range scanned.

The output of the blue laser could be assumed to be constant within the timescale of one experimental run: shot-to-shot fluctuations were typically $\pm 3\%$ under optimum operation of the lasers. Pulse height and duration were measured before and after each run using a beam splitter immediately after the dye laser and a fast rise time vacuum photodiode with S1 photocathode. The pulse was displayed on the Tektronix 7912AD digitiser. This arrangement was calibrated in the same way as the UV monitoring system described in Section 4.2.1. Again losses down the system to the ionisation chamber were measured

or estimated and included in power density calculations.

Equipment used to monitor both ionisation signal and UV intensity has been described in Chapter 4 and is summarised in Table 4.1. Data collection via the Tektronix digitiser was under control of a PDP-11 computer. Pairs of data points of UV intensity and corresponding ionisation signal were stored in sets of approximately 20 for each tuning position of the blue laser. These were later analysed, as described in Section 4.2.2, to produce plots of ionisation signal, for fixed UV intensities, versus blue laser frequency i.e. plots of the laser-induced autoionising structure.

It was found that data for a maximum of 12-15 tuning positions could be acquired on each run. The percentage change in ionisation signal caused by the presence of the embedded state was found to be small ($\sim 20\%$ maximum). This made it difficult, in view of the fluctuating UV power, to locate the autoionising resonance by eye, i.e. by scanning through the blue frequency around the expected position and observing the ionisation signal on an oscilloscope. Consequently the following strategy was adopted and this is reflected in the results presented.

Firstly, a coarse frequency scan was carried out. The scan step was chosen from experimental experience to be large enough to cover a wide range of frequency but small enough so that the feature was not missed. Once the position of the resonance was found by this procedure, it was possible to scan this area more finely. Backlash and temperature fluctuations in the laboratory, however, meant that, in terms of the blue laser tuning micrometer position, the resonance position did fluctuate slightly. This fluctuation was not more than about

Embedding laser intensity = 65 MW/cm^2

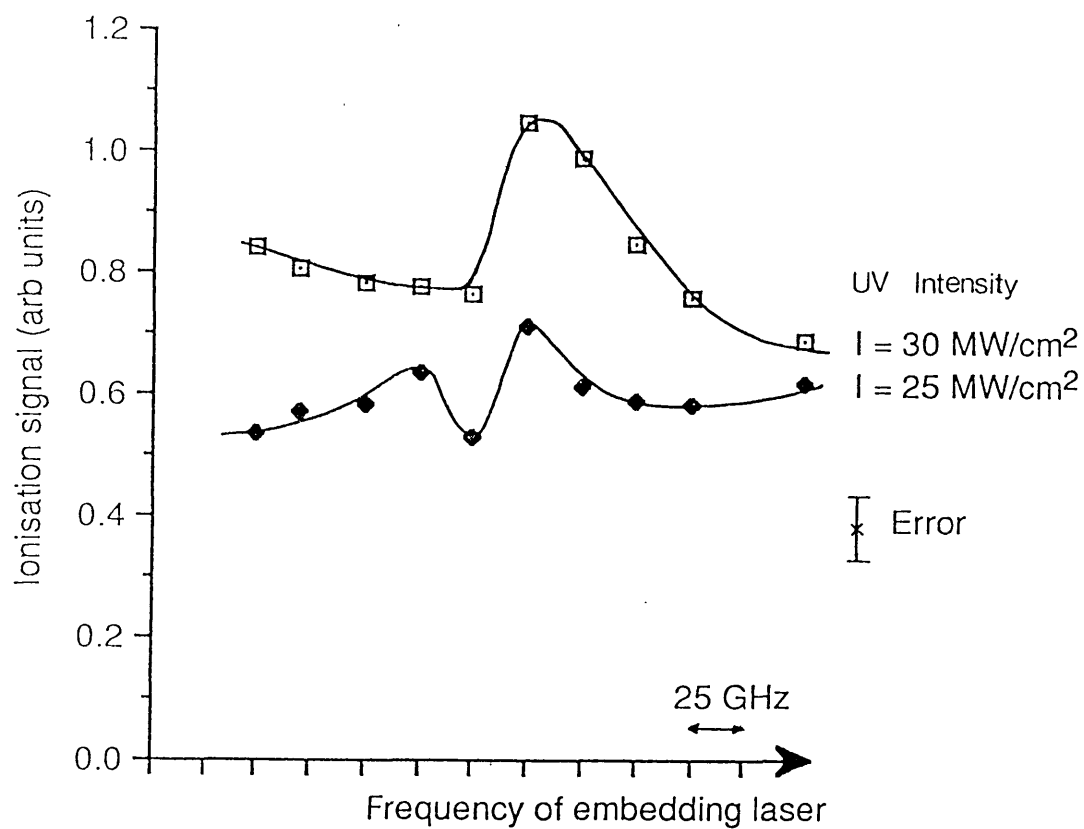


Figure 6.10 Laser-induced Autoionising Feature:
Low Resolution Frequency Scan

one tenth of the feature width. Therefore, to eliminate stitching errors between separate experimental runs, all the data presented on each experimental lineshape and set of lineshapes was collected on single runs.

Unfortunately, the experimental system used did not allow for absolute frequency measurement. Had this been available, it would have been useful in quantitative assessment of phenomena such as a.c. Stark shifting.

6.5 Results and Discussion

Figure 6.10 shows a plot of three-photon ionisation signal versus embedding laser frequency in the region of the laser induced continuum structure. The spectral region scanned is quite broad (approximately 300GHz), with a correspondingly large frequency step (25 GHz) between data points. However, this scan serves to identify the laser-induced autoionising state. The results for UV laser intensities (25 and 30MW/cm²) are shown; in both cases the blue laser intensity was 65MW/cm².

The error in ionisation signal shown is estimated from the plots of ionisation signal against UV laser intensity, as described in Section 4.2.2. Factors contributing to the error include blue (embedding) laser intensity and frequency fluctuations, and UV (probe) laser frequency fluctuations. The frequency fluctuations could possibly result from temperature instabilities in the laboratory, which can affect dye laser cavity lengths. Additionally, variations in longitudinal mode structure and hence linewidth of the dye lasers could also affect ionisation signals.

A higher resolution scan is shown in Figure 6.11 for UV intensities of 30 and 35MW/cm². The blue laser intensity was

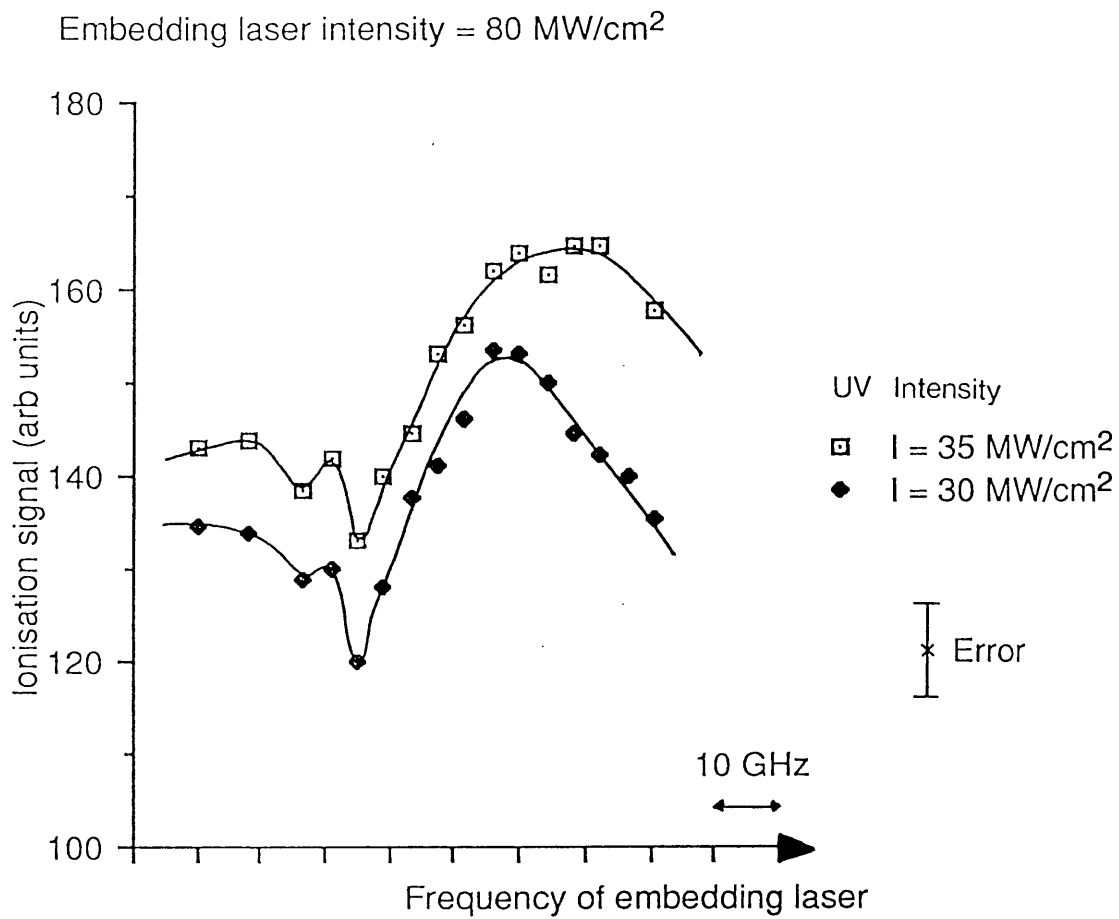


Figure 6.11 Laser-induced Autoionising Feature:
Higher Resolution Frequency Scan

80 MW/cm². Here a 90GHz frequency band was scanned. While autoionising structure is observed, the lineshape is not a classic Fano profile. In particular, a secondary resonance is evident on the lower embedding laser frequency side of the main resonance. This feature was observed on repeated experimental runs and was not thought to arise from a systematic error.

This secondary resonance was investigated in more detail by higher resolution scanning of the region. These results are shown in more detail in Figure 6.12. This data confirms the existence of the secondary resonance. Plots are shown for slightly higher laser intensities. The UV intensities were 35 and 40MW/cm² and the embedding laser intensity was 100MW/cm².

These plots include the background ionisation signal due to two-photon-resonant three-photon ionisation by 2 UV photons and 1 blue photon i.e. $2\omega_1 + \omega_d$. To assess the contribution from this ionisation channel and also to investigate the process further, the blue laser was tuned so that three-photon ionisation ($3\omega_1$) occurred in the wings of the autoionising resonance and the dependence of the ion signal on blue intensity was measured. The results are shown in Figure 6.13.

The linear dependence of ionisation signal on blue intensity shows that ionisation from the two-photon-resonant state (6p) by a blue photon is unsaturated. From the ionisation signal when the blue beam was not present, we see that the contribution to the background signal by the $2\omega_1 + \omega_d$ process is approximately 35% at a blue intensity of 70 MW/cm². This factor should be taken into account in calculating the percentage change in ionisation signal at the minimum and maximum of the autoionising resonance.

Embedding laser intensity = 100 MW/cm²

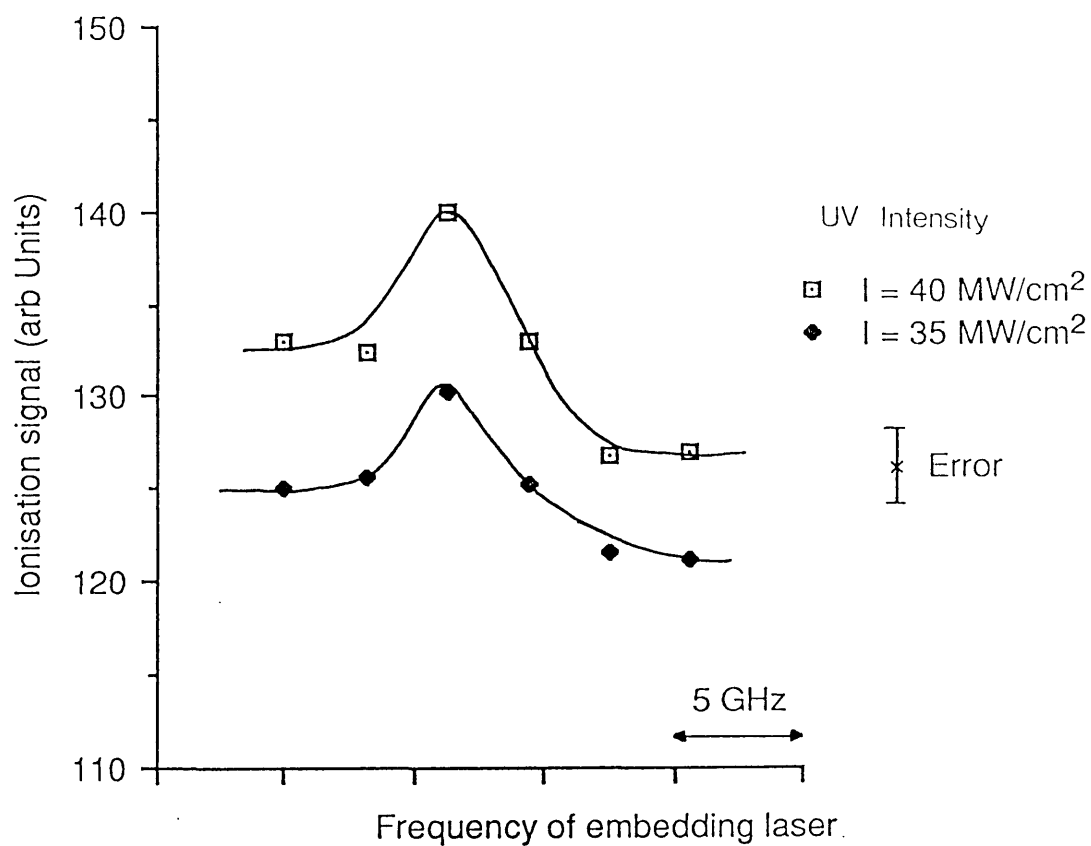


Figure 6.12 Laser-induced Autoionising Feature:
High Resolution Frequency Scan of Subsidiary Resonance

Hence, from Figure 6.11, we calculate a reduction in ion signal of 20% at the resonance minimum and an enhancement of 20% at the resonance maximum for a UV intensity of 30 MW/cm^2 . These figures should be treated as crude estimates only, in view of the likely compound error in the calculation.

Qualitatively, the results obtained show very good agreement with the form of asymmetric Fano lineshapes which would be expected from this type of coherent interaction. In view of the inherent instabilities in the laser system used and the difficulties associated with running such an experiment, the profiles obtained were remarkably repeatable over long periods of time.

There were problems associated with extracting quantitative information from the results collected which arise from two sources. Firstly, the experimental arrangement and method used, and secondly, the physical system consisting of atom and photons of appropriate intensity.

Considering firstly the experimental arrangement and method as has been detailed in Sections 4.2 and 6.4.3, the system used was such that only a limited amount of data could be collected in a single run of the experiment and the degree of correlation between data from different runs is severely limited. The result of this was clear in that the volume of useful data which could be amassed was small in relation to the time invested.

In addition, the number of variables such as laser intensities was large and control of some of them, such as the UV laser intensity was difficult. The behaviour of the lineshape over a wide range of UV intensity, such as several orders of

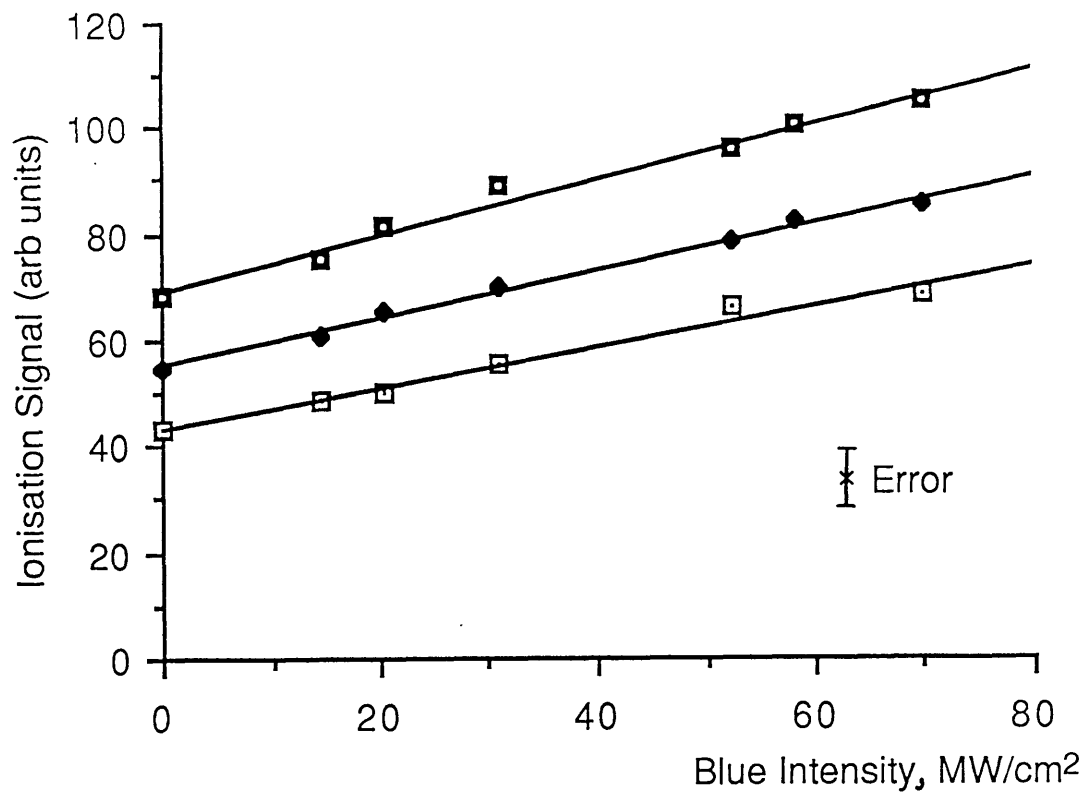


Figure 6.13

Dependence of Ionisation Signal on Intensity of Blue
(Embedding) Laser in the Wings of the Autoionising

Resonance

magnitude, would have produced a wealth of information but was impossible to carry out with the system used. There was some indication from the experimental results that the a.c. Stark effect shifted the lineshape in frequency. The resonance position seemed from results collected possibly to be dependent on the UV laser intensity. It was difficult, however, to collect sufficient data to give any conclusive results.

While the results obtained do show the qualitative behaviour expected of a Fano profile, i.e. asymmetric profile characteristic of coherent interference with minimum as well as maximum in the resonance, the physical regime involved make it difficult to assign, for example, a value of the asymmetry parameter q to the profile obtained. The theory discussed in Chapter 5 relates to an embedding laser field of any intensity but since the probing interaction is treated by perturbation theory, it must be weak. The formula for the shape of the Fano profile

$$R = \frac{(q + e)^2}{1 + e^2} \quad (\text{Equation 5.7})$$

relates to this case.

It has been shown that when this condition is relaxed, and both embedding and probe fields are strong fields, the shape of the Fano profile changes quite dramatically. In this case, perturbation theory can no longer be used and the distinction between embedding and probe fields becomes completely artificial. The system must now be considered as a single entity consisting of the interaction of the two laser fields and the atom. This is discussed in 5.4.1.

The structure observed is not exactly as would be expected for an autoionising resonance. The secondary resonance observed is

a departure from the classic Fano profile and has not been satisfactorily explained. Both embedded and probe states (the $^2P_{3/2}$ $10p(J=1)$ and $6p(J=0)$ are singlets well separated in energy from other energy states including these corresponding to the $^2P_{1/2}$ core electronic configuration. Hence is it unlikely that the observed structure is due to the influence of a second energy level.

Our experimental configuration differs from other reported experiments in that we have scanned the embedded structure through the continuum and probe that structure with a fixed probe frequency. This is in contrast to the conventional arrangement of embedded structure fixed in energy probed by a tunable source. It could be postulated that some non-flatness of the continuum resulting for example from either real autoionising structure or a more slowly-varying non-uniformity of photoionisation cross-section could be responsible for the secondary resonance structure observed.

As has already been discussed, (Section 5.2), the region of the Xenon continuum probed is well-removed from known single and two-electron real autoionising states. Additionally the photoionisation cross-section shows no structure on the frequency scale of the experimental scans [Aron and Johnson, 1977]; the photoionisation spectrum is flat over the frequency region probed. Hence, the sub-structure observed is not understood and cannot be adequately explained.

6.6 Further work

There is still much to learn about the physics of laser-induced continuum structure and much theory which could be tested by a rather more sophisticated version of the experiment described

here. Better control and stability of the lasers used, including perhaps the replacement of the KB5 doubling crystal and excimer amplifier by a more efficient doubling crystal alone e.g. urea, would eliminate the difficulties encountered as a result of the fluctuating output from the excimer amplifier. Improved frequency control of the dye oscillators in terms of temperature stabilisation and a wave meter to give absolute frequency measurements would allow for much better correlations of results. These modifications would greatly improve both the speed of data acquisition and the quality and quantity of information which could be extracted from the data collected.

While the detection system employed was adequate for the measurement of ionisation signals, the data collected is integrated both in time and in photoelectron electron energy. Further refinement would offer much greater insight into the physical processes involved. For example, by measuring the photoelectron energies it would be able to distinguish between ionisation from the 6p state by blue as opposed to UV photons. It is clear that the process of embedding a laser-induced autoionising state must also be accompanied by a variety of other processes mainly due to the populating of high lying levels. The study of such processes would serve to clarify substantially the physical mechanisms involved .

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CHAPTER 7

CONCLUSIONS

7.1 Introduction

This thesis has described two experiments used to investigate the non-linear optical properties of Xenon. These experiments were:

- (i) investigation of mechanisms leading to saturation of two-photon-resonant non-linear processes. The two-photon-resonant state was the $5p^5 (2P^0_{3/2}), 6p, J = 0$ state and the investigation was carried out via monitoring of the three-photon ionisation signal.
- (ii) study of a laser-induced autoionising state.

Additionally, the laser system used to carry out the experiments has been described, with details of the techniques used for the production of narrow-bandwidth radiation at 249.63nm.

The conclusions drawn from each experiment are presented in the following sections, together with a discussion of possible refinements to the experimental system, future experiments that such refinements could make possible and applications of the work carried out.

7.2 Investigation of Saturation Mechanisms in Two-Photon-Resonant Non-Linear Processes

The linewidth of the two-photon-resonant state was measured, under various experimental conditions, via detection of the three-photon ionisation signal. Stimulated emission between the two-photon-resonant state and the initially unpopulated $6s$,

$J = 1$ state was also monitored.

As a result of the experimental work carried out, together with a theoretical assessment of the possible mechanisms leading to saturation, we were able to identify the mechanism thought to be responsible for the saturation observed. This is believed to be lifetime broadening due to the stimulated emission of radiation from the two-photon-resonant state. This process dominates due to the significant population inversion achievable even under modest two-photon pumping conditions and a large stimulated emission cross-section.

Theoretical analysis (Section 3.2.3.2) indicated that stimulated emission could be responsible for the large linewidths (100 - 200 GHz) observed (Chapter 4). Calculations of the effect of other possible mechanisms, namely a.c. Stark broadening, power and ionisation broadening and Stark broadening due to photoelectrons were carried out. The results of these showed that, for the experimental conditions employed, these mechanisms could not be responsible for the heavy saturation and associated large linewidths observed.

These conclusions differ from those of Thomas, 1983, who studied a related non-linear process utilising the same two-photon-resonance employed in this work. Thomas postulates that saturation observed in his experiment, on four-wave mixing, difference frequency generation, could be caused by ground state depopulation resulting from a number of processes such as photoionisation. This does not, however, explain the large linewidths observed in the present work at lower intensities, where, from rate equation calculations, we have seen that ground state depopulation does not occur to any significant extent.

In addition, our calculation of the two-photon-resonant state population indicates that this does not significantly contribute to saturation, as previously suggested by Thomas.

7.3 Study of a Laser-Induced Autoionising State

It has been demonstrated that a laser-induced autoionising state can be produced in Xenon using an excimer-pumped dye laser as the pumping or "embedding" field, and a similar dye laser, frequency doubled, as the probe field. Measurement of the probing two-photon-resonant three-photon ionisation signal, as the frequency of the embedding laser was scanned through the continuum, has indicated the presence of a laser-induced autoionising state, the shape of which exhibits qualitative agreement with a Fano profile. In particular, a minimum in the resonance has been observed, with a reduction in the ionisation signal of 20%: this feature is unique to autoionising resonances.

Theoretically, the minimum in the resonance should be a zero. A number of factors of our experiment, relating to both the laser system and the physical system itself, prevent this occurring in our case. Factors related to the laser system include the pulse shapes, degree of mutual coherence, temporal jitter, and to a lesser extent laser spectral linewidth, which will result in a diffuse resonance. This would prevent an absolute zero ionisation signal from being obtained. Additionally, the energy position of the state used as the embedding state ($10p, J = 0$) and the wavelengths of the lasers used in the interaction result in a d.c. increase in ionisation signal in the presence of both the embedding and probe fields. This prevents attainment of a zero ionisation signal at the resonance minimum. Using three-photon ionisation with a two-

photon resonance with the $6p, J = 0$ state as a probe, this situation cannot be avoided for any embedding state (Section 6.1).

Hence with the system used, a closing down of the ionisation channel via the induced autoionising resonance cannot be achieved. Consequently, the effectiveness of the laser-induced autoionising resonance in the reduction of saturation of two-photon-resonant frequency mixing processes due to ionisation broadening is limited. Another state could be used as the two-photon-resonant state, but the attractiveness of the resonance at 249.63nm would be lost. Four-photon-resonant five-photon ionisation at 499.92nm may be a possibility, but one would then be embedding a laser-induced autoionising state in a region of the continuum where real autoionising states exist.

The dependence of the induced autoionising resonance on probe intensity has been investigated within the capabilities of the experimental system. While qualitatively in agreement with Fano theory, the resonance observed exhibits a subsidiary minimum on the low frequency side of the main resonance, as the embedding laser is scanned through the continuum in the region of the three-photon energy. This feature cannot be explained at present.

7.4 Possible Refinements to the Experiment

The volume of useful data which can be extracted using the current experimental system is limited by two factors. These are

- (i) speed of data acquisition
- (ii) laser system performance - repeatability of laser power output, spectral jitter, laser longitudinal mode control,

whiplash in dye laser tuning mechanisms etc.

The data acquisition problem could be addressed by increasing the degree to which the experiment is computer controlled. For example, control of laser tuning via stepper motors would allow scanning of resonance regions under computer control, and data analysis could also be more rapidly handled using microprocessing.

The poor wavelength calibration of the dye lasers could be improved by maintaining a constant temperature and pressure laser environment and eliminating the mechanical components responsible for the whiplash in the laser tuning. Such environmental control would probably improve the longitudinal mode stability and repeatability of single mode operation. An on-line wavemeter could provide accurate absolute wavelength calibration. Ultimately however, improved longitudinal mode control and the elimination of mode hopping as the lasers are tuned can only be achieved by replacement of the dye lasers by, for example, the travelling wave oscillators of Wells and Zhou, 1985, and Ewart, 1985, used with appropriate line narrowing techniques.

Further modifications to the dye lasers could include revision of the amplifier design to allow transverse pumping all round (360°) the input beams to provide output beams with spatial characteristics which better approach Gaussian profiles. This improved transverse mode quality would enable the beams to be focused to (nearly) diffraction-limited focal spots, with an associated increase in the focal spot power densities achievable. Additionally, simple modifications to the excimer pump beam optics, including the use of anti-reflection coatings would increase the efficiency of transfer of pump energy to the

dye lasers.

Improved shot-to-shot repeatability of the ultra-violet source could be achieved by the use of a higher efficiency second harmonic crystal. This would provide sufficient energy input to the excimer amplifier to ensure saturation and hence a more repeatable output. Alternatively, the ultra-violet output from the second harmonic crystal may be sufficiently high energy to allow elimination of the excimer amplifier, particularly if used in conjunction with a higher power dye laser, possibly with the dye amplifier modifications suggested.

In summary, the modifications suggested would result in more accurate control of the system operating conditions in terms of laser frequency calibration, shot-to-shot repeatability and beam quality, and also lead to a significant increase in the speed at which experimental data could be collected and processed. These changes would have an impact on the volume and types of experiments which could be carried out.

Shot-to-shot repeatability of power output would remove the need for single shot data collection. With the introduction of signal averaging there would also be the opportunity for more sophisticated signal processing and detection of smaller signals. The higher level of control may also permit operation over an extended range of laser output powers, allowing more comprehensive experimental investigation.

Laser frequency calibration would allow one to correlate data from separate experimental runs and to investigate effects such as a.c. Stark shifting of the laser-induced autoionising state.

7.5 Applications

Of the two experiments carried out, the study of saturation mechanisms is mostly of academic interest, although the results are of relevance in the design of non-linear optics experiments involving, for example, the production of coherent vacuum-ultra-violet sources via two-photon-resonant four-wave mixing.

The laser-induced autoionisation experiment is a useful verification of the theory of such phenomena. On the practical side, laser-induced autoionising states could find application in a number of non-linear optics processes. The efficiency of four-wave mixing processes where the generated photon energy lies above the ionisation potential, could be enhanced by the embedding of an appropriately positioned autoionising resonance. As previously mentioned, this has been observed, for third harmonic generation in Sodium, by Dimov et al, 1983.

For the above effect, the maximum of the autoionising resonance is used to achieve enhancement. Alternatively, the Fano minimum of the induced state could be used to reduce to zero the efficiency of some process with a continuum contribution. One can imagine the situation where photoionisation or some other parasitic non-linear process could be controlled in this way to ensure maximum efficiency of, for example, VUV generation via four-wave mixing. This was the initial objective of the work presented here (Section 7.3), although it has been found, for reasons discussed previously, that complete closing down of the three-photon ionisation channel studied is not possible.

Clearly the laser system used in this work offers great flexibility and could be used for the investigation of a large

number of non-linear processes or as a source of coherent radiation generated by non-linear mixing. However, the particular capability for the production of high intensity narrow bandwidth radiation at 249.63nm makes the system especially suitable for the study of other two-photon-resonant processes in Xenon.

These include up-conversion, including the use of capillaries to increase interaction length and hence enhance the conversion efficiency of VUV generation in the spectral region around 105nm [Hutchinson and Zhou, 1986], and switched collision processes. In the latter, proposed by White, 1980, disociation is induced in a molecular species by forming that species in an excited state by laser-assisted collisional transfer with another excited atom or molecule. Laser-assisted collisions have been observed by, for example, Lukasik and Wallace, 1981.

One proposed scheme for laser-assisted collisional disociation involves the 6p, $J = 0$, excited state of Xenon in collision with ground state Carbon Dioxide molecules: disociation of the collisionally excited CO₂ molecules should lead to the production of excited state singlet Oxygen, with the possibility of a population inversion and associated laser action. The advantage of such a scheme is the rapid switching of energy by the laser-assisted collision. In comparison, the energy can initially be stored in the 6p state, by two-photon pumping, on a relatively slow timescale. Hence there are opportunities for the rapid production of population inversions in the disociation product species and an efficient method of laser pumping.

7.6 References

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ACKNOWLEDGEMENTS

I thank my supervisor, Dr Henry Hutchinson, for giving me the opportunity to work in experimental non-linear optics, for fostering my relationship with excimer and dye lasers and Xenon atoms, and for support and encouragement throughout the course of my time as a postgraduate student. I am also very grateful to Dr Peter Knight for many useful discussions on the theory of laser-induced continuum structure and for his interest and encouragement.

Many of the members of the Optics and Laser Groups at Imperial College have offered advice, comment, support and encouragement over the years and I am grateful to them all, past and present, as colleagues and friends: in particular, Drs Mike Osborne and Mike Damzen deserve thanks. I also thank Mr Roy Morrison and his colleagues in the Optics Workshop for technical support.

I am grateful to my colleagues and friends at work, for both their support and practical assistance, while I have been completing this thesis: in particular, thanks to Pam Weston for typing most of it, to others who have contributed to putting it into print, and to Dr Craig Sawyers for proof-reading.

I gratefully acknowledge the contribution of Martin Wooler who loaned me a computer and helped with much word-processing. Thanks also to Eddie Butterfield for producing many of the diagrams and to the SERC and Imperial College for financial support.

Last, but certainly not least, I thank my parents for never giving up hope.

