

Studies in Vibrational Relaxation and Non-Linear Mixing
Using Excimer Lasers

by

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Abstract

This work describes the use of excimer lasers in two experiments.

Firstly, a discharge pumped KrF laser was used to probe an electron-beam excited KrF laser medium in order to measure the recovery time of the gain and deduce the vibrational relaxation time of the KrF* molecule. This information, not previously well defined, is relevant to the amplification of short (~ 1 ns) pulses in electron beam pumped KrF amplifiers. It was concluded that vibrational relaxation occurs on a sub-nanosecond timescale under typical laser conditions and the gain recovery time is approximately equal to the calculated fluorescence decay time.

Secondly, an excimer laser pumped dye laser system producing two independently tunable beams of ~ 1 GHz linewidth was constructed. Radiation of wavelength 248 to 250 nm was produced by frequency doubling the output of one dye laser and amplifying in a discharge pumped KrF amplifier. Resonantly enhanced four wave mixing was observed in Xenon by tuning this UV radiation to a two photon resonance at 249.6 nm and mixing with a second dye laser ($\lambda = 610\text{--}650$ nm) generating VUV radiation at $\lambda = 154.5\text{--}157$ nm with an output power of ~ 100 Watts. Alternative dyes will extend the wavelength range to 145–195 nm, a region of the spectrum where such a coherent, spectrally bright, tunable source of radiation has not previously been available.

The dependence of the VUV output power of the mixing process on the experimental parameters was investigated and the results are discussed and compared with theoretical work. Applications of the work are outlined.

To my mother and late father

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Chapter 1

Introduction

1.1 Excimer Lasers

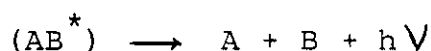
1.1.1 Rare Gas Halide Excimers

The term "excimer" was first introduced in 1960⁽¹⁾ and is an abbreviation of "excited dimer", which is a homopolar molecule with a dissociative electronic ground state, but which is associative in an excited electronic state. Examples of such molecules are Ar_2^* , Kr_2^* , Xe_2^* . Heteropolar molecules with this same characteristic, e.g. KrF^* , ArF^* , XeCl^* and XeF^* , which should strictly be termed "exciplexes" (an abbreviation for "excited complexes") have also commonly come to be known as excimers.

Fig. 1.1 shows a generalized potential energy against internuclear separation curve for an excimer molecule. The excimer is formed by interactions between the two atoms A and B, one of which is electronically excited.



This bound molecule $(\text{AB})^*$ can then dissociate by a radiative decay to the ground state



Because of the rapid dissociation of the ground state which occurs in $\sim 10^{-12}$ seconds, compared to a radiative lifetime for the upper level of $10^{-6} - 10^{-9}$ seconds population inversion is easily produced and maintained. This has allowed the development of powerful ultra-violet and blue lasers with diverse applications. Table 1.1 shows the wavelengths at which laser

Table 1.1

Emission wavelengths (nm) of rare gas halide excimer lasers (Ref. 2)

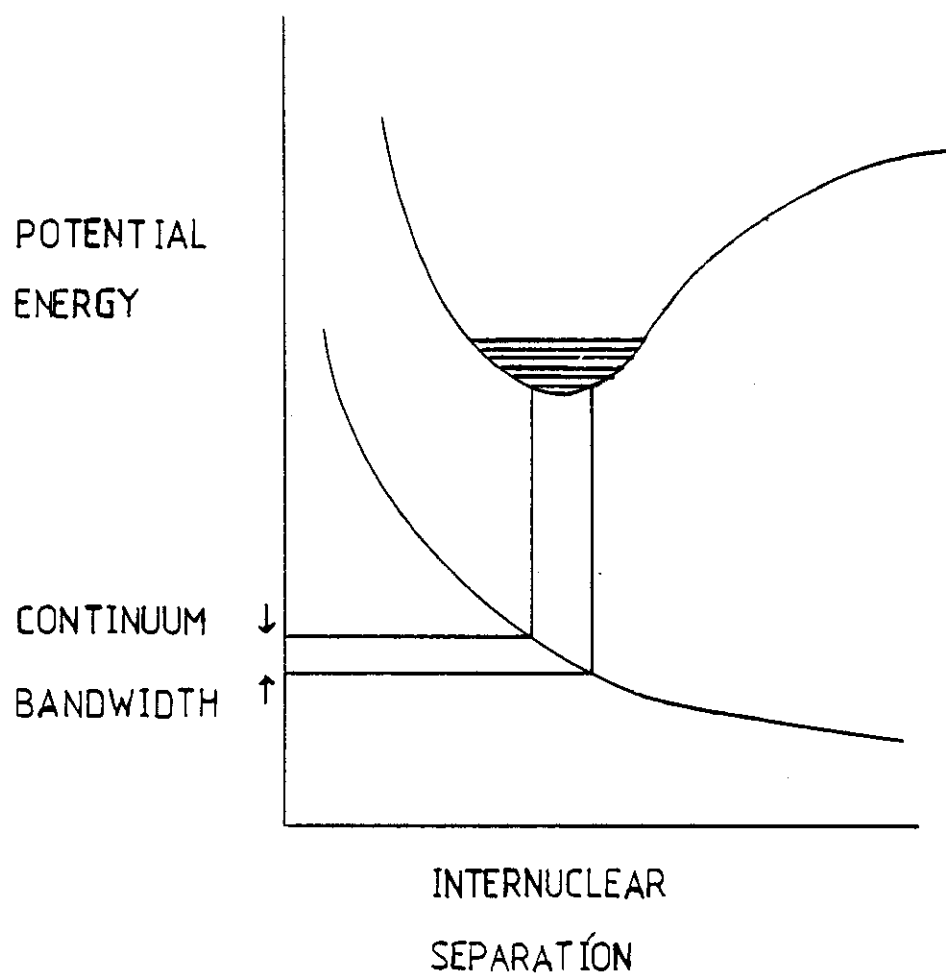
	F	Cl	Br
Xe	351	308	282
Kr	249	222	—
Ar	193	175	—

action has been observed from rare gas halide molecules⁽²⁾. As can be seen from Fig. 1.1, excimer lasers have a large homogeneously broadened linewidth, which means that they have potential for producing narrowband radiation tunable over the bandwidth of the transition which is typically a few nanometres⁽³⁾. However, the broad bandwidth gives rise to a low stimulated emission cross section, typically between 10^{-17} and $5 \times 10^{-16} \text{ cm}^2$, compared to 10^{-15} to 10^{-12} cm^2 for atomic and molecular transitions with comparable oscillator strengths in the visible. Laser action can only be achieved, therefore, by vigorous pumping by either electron beams or high voltage discharges.

Fig. 1.2 shows the potential energy curves for Krypton Fluoride (KrF) calculated by Dunning and Hay⁽⁴⁾. The energy states are labelled X, A, B, C and D in order of increasing energy. The covalently bonded ground state is formed from a Krypton atom in a 1S state and a Fluorine atom with a single electron in its outer 2p orbital. The two possible combinations of this p orbital with respect to the internuclear axis gives rise to the two molecular states $1^2 \Sigma^+$ and $1^2 \Pi$, where Σ and Π denote that the projection of the total electron orbital momentum along the internuclear axis is 0 and $\hbar$ respectively. The $1^2 \Sigma^+$ state is lower in energy than the $1^2 \Pi$ state, and is labelled X($\frac{1}{2}$). The $1^2 \Pi$ state is labelled A and consists of components A($\frac{1}{2}$) and A($\frac{3}{2}$), separated by the spin orbit effect, which is small enough, except in the more massive halogens, for the two states to be considered degenerate.

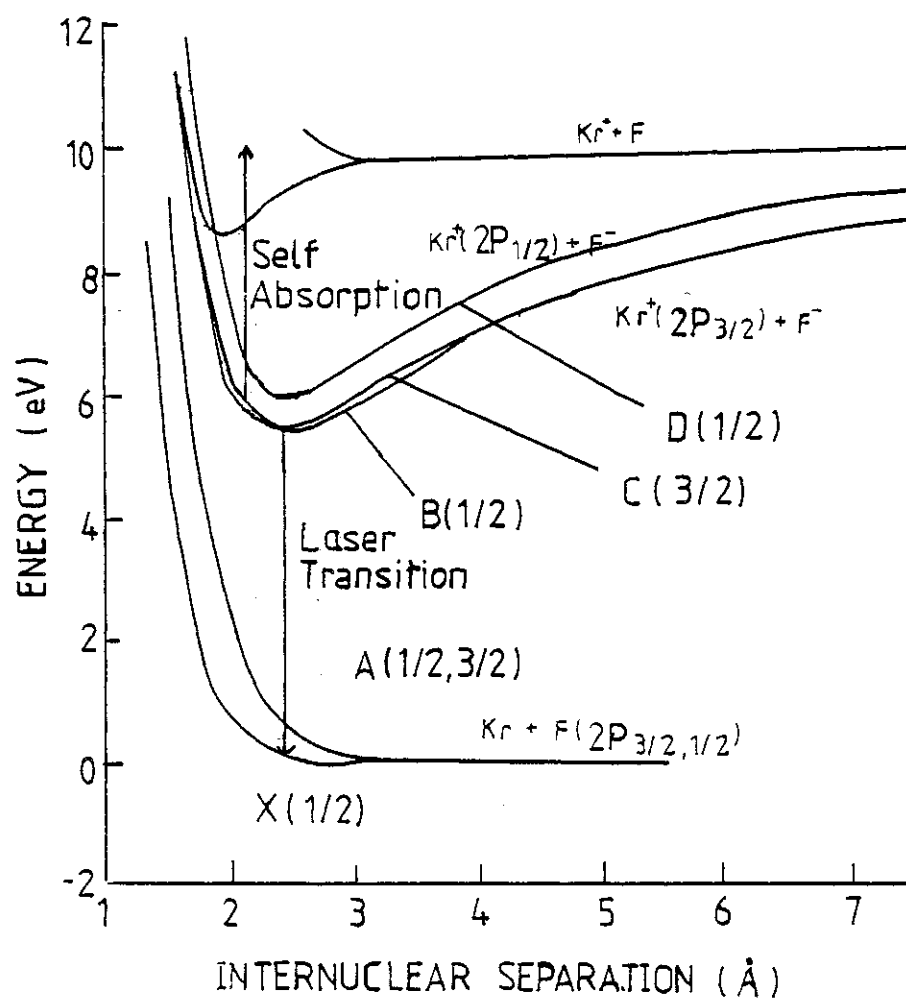
Similarly, the ionic states in the upper manifold are

FIG. 1.1



Generalised excimer potential energy curve showing the laser transition bandwidth.

FIG. 1.2

Potential Energy curves of KrF

denoted by $2^2\Sigma^+$ and $2^2\Pi$.

The

$2^2\Sigma^+$ state, being the lower in energy, is labelled $B(\frac{1}{2})$, while the $2^2\Pi$ state is split into two components with total electron angular momentum quantum number $\Omega = \frac{1}{2}$ and $3/2$ which are labelled $D(\frac{1}{2})$ and $C(3/2)$, the former being higher in energy. The $C(3/2)$ and $B(\frac{1}{2})$ states are nearly degenerate.

The allowed transitions are $D(\frac{1}{2})$ to $X(\frac{1}{2})$, $B(\frac{1}{2})$ to $X(\frac{1}{2})$ and $C(3/2)$ to $A(3/2)$. Lasing occurs almost exclusively on the B-X transition, which corresponds to an electron being transferred from the halide ion to the rare gas ion, yielding the rare-gas and halogen ground state atoms. There is evidence⁽⁵⁾ that the D state is strongly quenched and due to the highly repulsive nature of the A state the bandwidth of the C-A transition is large, as can be seen from Fig. 1.1. Hence the stimulated emission cross section determined from the equation⁽⁶⁾

$$\sigma = \frac{\lambda^4}{8\pi\tau\Delta\lambda c} \quad (1.1)$$

where τ is the lifetime of the upper state, λ is the wavelength of the transition, and $\Delta\lambda$ is the bandwidth, can be seen to be reduced. The only case of lasing on the C-A transition in such an excimer has been observed in XeF^(7,8) at 483 nm, where the C state is unusual in lying at a lower energy than the B state. Collisional relaxation can occur from the B state to the C state, and hence lasing can occur on both the B-X and C-A transitions.

The XeF (B-X) and XeCl lasers are untypical in that the ground $X(\frac{1}{2})$ states are bound by 1065 cm^{-1} ⁽⁹⁾ and 255 cm^{-1} ⁽¹⁰⁾ respectively. Their dissociation therefore relies on the energy available in random thermal collisions being greater

than the depth of the potential well and XeF laser efficiency has been observed to improve at increased temperature⁽¹¹⁾. The KrF laser is the most efficient excimer laser observed, the potential energy curves of the KrF molecule being shown in Fig. 1.2. The ground $X(\frac{1}{2})$ state is completely unbound and the covalent and ionic bonding potential curves cross at high internuclear separations, reducing the possibility of pre-dissociation. Pulse energies of up to 200 Joules⁽¹²⁾ have been obtained from KrF lasers pumped by relativistic electron beams, and discharge pumped KrF lasers with pulse energies of up to several Joules have been reported.

1.1.2 Pumping schemes for excimer lasers

The gain coefficient k for a lossless regime may be expressed

$$k = \sigma(\lambda) N \quad (1.2)$$

where N is the excimer number density and $\sigma(\lambda)$ is given by equation (1.1). So the pumping power (P) per unit volume required to produce a gain coefficient k per unit length is

$$P = \frac{hcN}{\lambda \tau \eta \Phi} = \frac{8\pi h k c^2 \Delta\lambda}{\lambda^5 \eta \Phi} \quad (1.3)$$

where Φ is the quantum efficiency, η is the efficiency of population of the upper laser level and h is Planck's constant. The λ^{-5} dependence indicates the difficulty of producing adequate pump power for short wavelength lasers.

The first excimers to be successfully used as laser media were the homopolar rare gas molecules Xe_2 , Kr_2 and Ar_2 , which lase at 172, 146 and 126 nm respectively in the vacuum ultra-

violet and due to the short wavelengths these required pumping by high power relativistic electron beams. Hence the rare gas halides were first investigated in electron beam pumped systems although their longer wavelengths and consequently larger stimulated emission cross sections (see equation 1.1) allows pumping by electrical discharges. The three pumping schemes generally used for this class of laser are described below.

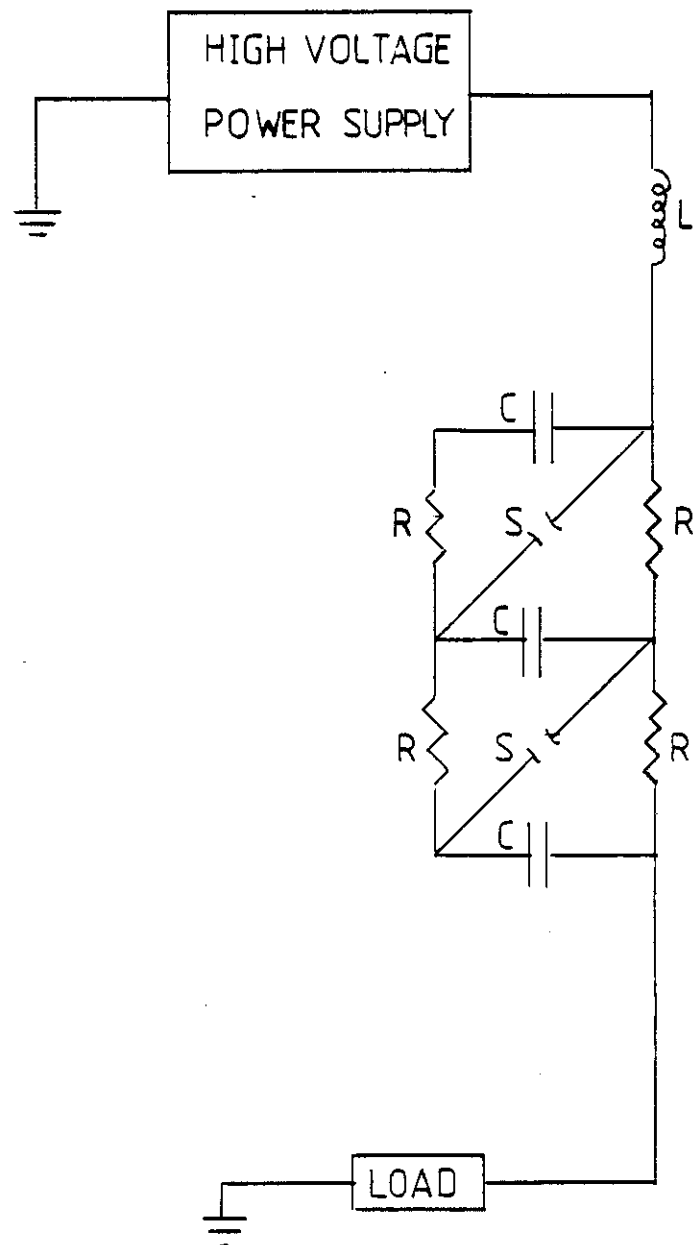
Electron-beam Pumping

An electron-beam (e-beam) pumped excimer laser system consists of a high voltage power supply capable of pulse charging a diode, to form a broad area electron beam which can then be injected into the laser medium through a metal foil. The most common form of high voltage generator is the Marx bank. A typical Marx bank circuit is shown in Fig. 1.3. The capacitors C are charged in parallel to a few tens of kilovolts. The spark gaps S are then triggered, erecting the capacitors into a series configuration, producing a voltage approximately equal to the product of the individual charging voltage and the number of stages of the Marx. The number of stages can be much greater than the three shown in Fig. 1.3.

A Febetron 705 pulse generator was used for some of the work presented in this thesis. This comprises an 80 stage Marx bank capable of generating output voltages up to 2.3 MV. As an alternative to Marx generators, Pulse Transformers are also used. The step up ratio is not as high as the ratio of the number of turns as in a low voltage transformer, since the turns cannot be closely coupled and still be insulated at the high voltage used.

If the high voltage pulse generator is coupled directly to a load the voltage pulse will have a rise time of L/R_{LOAD} , where L is the effective inductance of the circuit and the pulse will

FIG.1.3



Typical Marx bank circuit with 3 stages

L - Inductance, C - Capacitor, S - Spark gap, R - Resistor

decay in a time $R_{\text{LOAD}} C_M$ where C_M is the capacitance of the pulse generator. If the load is an e-beam diode, low energy electrons will be produced during the decay of the voltage pulse and the foil separating the diode from the laser cavity can be damaged due to its higher stopping power for these electrons. Methods for obviating this problem include firing a secondary spark gap to divert the energy in the tail of the pulse and using an additional unstressed metal foil to absorb the low energy electrons. It is also possible to use a Blumlein pulse forming line to produce a shortened, more square voltage pulse.

The main problem in the design of an e-beam diode is that the beam must be formed by field emission from a cold cathode, normally a sharp structure to enhance the local electric field⁽¹³⁾, at high vacuum ($\sim 10^{-5}$ Torr), but is required to excite a gas at a pressure of several atmospheres. The solution is to separate the diode cathode from the laser medium by a metal foil which becomes the anode. The foil must be supported to withstand the pressure differential. This introduces some loss of the e-beam energy, but this can be kept as low as 30%⁽⁶⁾.

The disadvantage of the cold-cathode field emission is that the plasma produced which provides the electrons to be accelerated to the anode also gives rise to diode closure, i.e. the effective separation of the cathode and anode is reduced as the plasma expands across the cathode-anode gap. The current density J (A cm^{-2}) is given by the Child-Langmuir Law⁽¹⁴⁾

$$J = 2.3 \times 10^3 V^{3/2} / d^2 \quad (1.4)$$

where V is the diode voltage (MV) and d is the vacuum gap (cm) and so the closure time $\tau_c = d/V_c$, where V_c is the closure

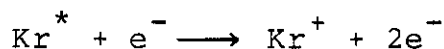
velocity, is a function of the voltage and current density. Pulse lengths are limited to $\sim 1 \mu\text{s}$.

A diode structure which decreases the problems of foil support, allows more uniform energy deposition in the laser medium, and is potentially scalable to high output powers is the co-axial diode configuration⁽¹⁵⁾ shown in Fig. 1.4. The lasing gas is contained in a thin walled metal tube acting as the anode, the cathode being mounted coaxially around the anode tube.

E-beam sustained discharges

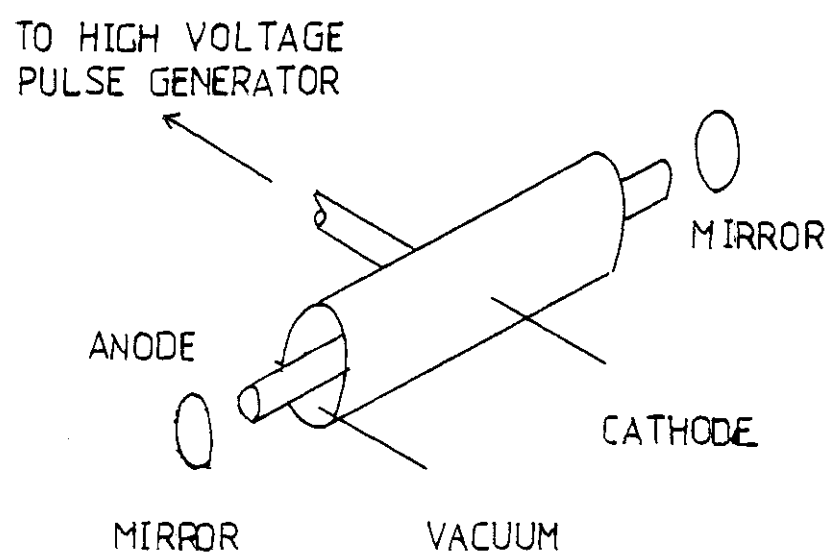
The stimulated emission cross sections of the rare gas halides are large enough to allow pumping by fast electrical discharges rather than electron beams. This has the advantage of a higher quantum efficiency as, in a discharge, metastable excited states of atoms are produced rather than ions. For example, in KrF the energy needed to form an ion-electron pair is $\sim 20 \text{ eV}$, while the energy of a laser photon is $\sim 5 \text{ eV}$. The energy required to form the metastable states is only $\sim 10 \text{ eV}$, so the quantum efficiency of the formation process is increased from 25% to 50%.

However, the ionization cross sections of the rare gases are $\sim 10^{-15} \text{ cm}^2$, which is a relatively large figure. Therefore the metastable states formed are likely to form ions by collision with electrons, e.g.



Daugherty et al⁽¹⁶⁾ calculated that for a discharge to remain stable the dissociative attachment rate, i.e. the rate at which ions and electrons recombine to form the metastables, must be greater than twice the rate of ionization. For this condition

FIG. 1.4



Schematic of coaxial diode e-beam pumping configuration

to be satisfied and hence the discharge to be maintained in a steady state, an external source of ionization must be provided, which can be done in an electron-beam sustained discharge⁽¹⁷⁾.

Usually the discharge and the electron beam use a common anode, normally a foil and mesh. The electron beam enters the discharge chamber through the anode and the uniformity of the ionization it produces is reflected in the high spatial quality of the laser output. These systems are suitable for long pulse operation and have higher efficiencies than pure electron beam pumped lasers. However, they are not as scalable to high power outputs.

Discharge Pumped Lasers

Simple unsustained discharges are inherently unstable since at a pressure of a few atmospheres the electric fields applied will cause rapid multiplication of electrons in avalanches. When the fields in these avalanches approach that applied across the discharge gap, electrons in weaker avalanches will be attracted towards them and a conducting filament will form on a timescale of ~ 10 ns, producing an arc which will effectively short circuit the discharge.

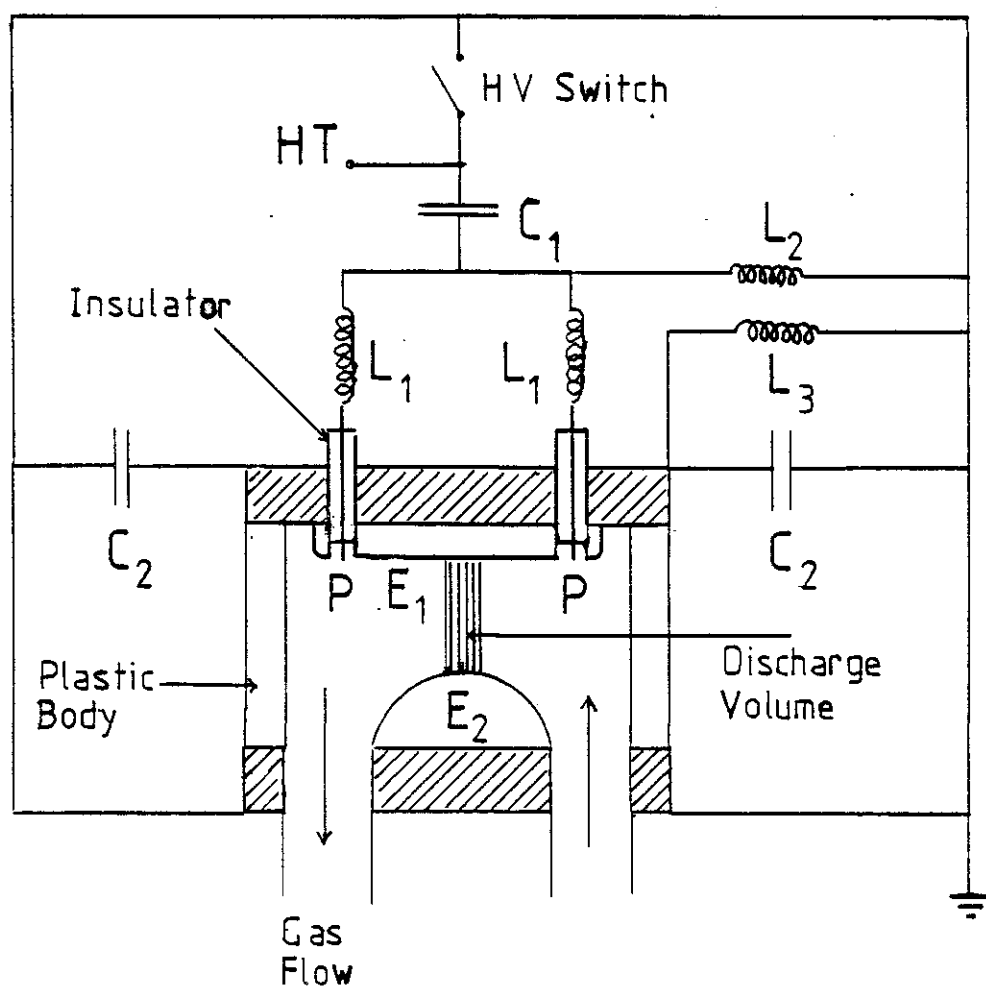
This problem has been overcome by preionizing the discharge gap, usually with ultraviolet light produced by spark gaps. If the preionization is sufficiently intense the initial electron density will be such that the avalanches will overlap and a uniform discharge will be produced. The mechanism for forming the excited excimer molecules is the collision between the electrons accelerated across the discharge gap and the atoms and molecules in the laser gas.

Once the avalanches have crossed the discharge gap, a homogeneous plasma is produced between the electrodes, the impedance of which rapidly decreases as further energy is fed

into it. It is therefore essential to use fast, transverse discharges⁽¹⁸⁾ to transfer energy to the discharge before the plasma impedance collapses.

Discharge excimer lasers have played a large part in the work described in this thesis. Both a Lambda Physik EMG 101 and a similar laser built at Imperial College were used and a schematic diagram of these lasers, showing a transverse section through the discharge channel, is given in Fig. 1.5. Along the length of the laser body there would be approximately twenty pairs of the feedthroughs P, each having its own inductor L_1 . The firing of the high voltage switch causes the energy stored in the capacitor C_1 to transfer into the capacitors C_2 via sparks between the preionizing pins P and the electrode E1. (The pins P protrude from the end of ceramic feedthroughs so that the sparks can only occur near the electrode surface). The sparks produce UV light which preionizes the discharge gap, ready for when the voltage across the gap reaches its maximum and energy begins to be transferred into the discharge.

For efficient operation of a discharge laser it is desirable to use a HV switch with a low inductance and hence a fast rise time, otherwise much of the stored energy in the capacitor C_1 will be dissipated in the switch itself as its conduction builds up. A spark gap satisfies this condition but has the disadvantage of jitter in the time delay between being triggered and firing. It also has a limited repetition rate. The alternative, when good synchronization is required, is the thyatron switch, which, instead of a single conducting filamentary spark as in a spark gap, builds up a broad area glow discharge between its electrodes. However, the inductance and consequent rise time of the conduction of a thyatron are



Schematic of a discharge excited rare gas halide laser

higher than those of a spark gap, and this limits laser performance. A solution that has recently become available and is used in the Lambda Physik EMG 101 is the grounded grid thyatron⁽¹⁹⁾. This is a modified version of the hydrogen thyatron, in which the main current pulse is carried by a metal vapor arc, which has a peak current capability of several tens of thousands of amps and an inductance of ~ 15 nH. Jitter of the order of ~ 2 ns can be achieved, the disadvantage being that the lifetime is less than that of conventional thyatrons, but is still up to $\sim 10^8$ shots.

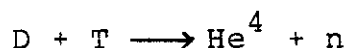
Discharge lasers with pulse energies greater than 1 Joule are available. Their main disadvantage is that they produce beams of poor spatial quality unless devices such as unstable resonators are used. Repetitive operation normally requires the gas mixture to be flowed, and rates of up to 1 kHz are possible.

1.2 Applications of excimer lasers

1.2.1 Inertial Confinement Fusion

A significant stimulus for the development of high power lasers, including the rare gas halide excimer lasers, has been research into the development of inertial confinement fusion. The method used for producing high density plasmas is to irradiate a spherical glass microballoon as uniformly as possible with several powerful laser beams. The microballoon consists of a glass envelope, inside which a mixture of Deuterium and Tritium is enclosed. The laser beams burn off the glass envelope and (by conservation of momentum) an implosion is caused, driving the remaining material progressively inwards, building up a plasma of increasing density until, if

the irradiation is sufficiently powerful, conditions are achieved where thermonuclear reactions can occur. Commercially the most important thermonuclear reaction is



which is exothermic, the excess energy being distributed as kinetic energy between the alpha particle and the neutron.

In this case, as for magnetic confinement fusion, the requirement for the total amount of energy generated to exceed the energy used in initiating the reaction is given by the Lawson criterion, i.e.

$$n \tau > 10^{14} \text{ nuclei cm}^{-3} \cdot \text{s} \quad (1.5)$$

where n is the number density of the reacting material and τ is the time for which it is contained at that density. In inertial confinement the parameter τ is determined by the time it takes a rarefaction wave to move into the centre of the sphere of hot fuel, lowering the density and stopping the reaction. This leads to a criterion for efficient operation in terms of density and radius given by⁽²⁰⁾

$$\rho R > 1 \text{ gm cm}^{-2} \quad (1.6)$$

Once this criterion has been achieved the alpha particles produced in the reaction, which will have an energy of 3 MeV and whose range is comparable to the fuel dimensions, will provide the energy to maintain the reaction, while the 14 MeV neutrons will escape and in a working fusion reactor will be used to generate power.

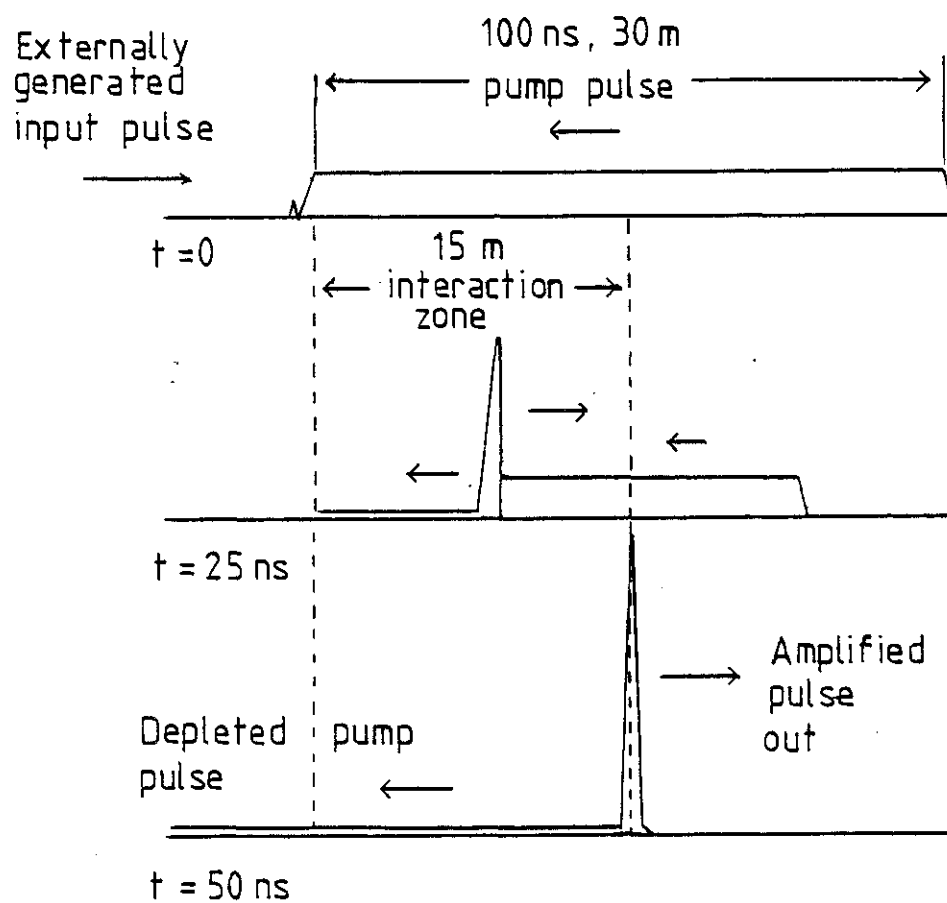
Experiments into laser plasma interactions at conditions below the threshold for efficient laser fusion have been going on at several laboratories, including the Lawrence Livermore

National Laboratory in the U.S.A. and at the Rutherford Appleton Laboratory in this country. All the experiments to date have used solid state lasers (Nd : YAG and Ruby) or their second and third harmonics. From these experiments it has been learnt that one problem in producing high density plasmas is the production of suprathermal electrons⁽²¹⁾ by laser plasma interaction. This is detrimental in that these high energy electrons can cause preheating of the core of the microballoon, reducing the maximum density that can be achieved. The production of suprathermal electrons increases with increasing laser intensity, and it has been found⁽²¹⁾ that there is a correlation between the suprathermal temperature produced and the parameter $I_L \lambda^2$, where I_L is the laser intensity and λ its wavelength. Therefore the use of shorter wavelength radiation is advantageous as it allows a higher laser intensity to be achieved before preheating of the target core becomes a problem. For this reason the KrF excimer laser, with a wavelength of 248 nm, has become a candidate for use in fusion experiments.

Electron-beam pumped KrF lasers appear to be capable of scaling to the energies required for inertial confinement fusion, but to be efficient fusion drivers their pulse duration would have to be shortened from 20-100 ns to ~ 1 ns, as this is the time in which the implosion of a microballoon takes place. Schemes for achieving this pulse shortening are outlined below.

The technique known as Raman pulse compression was originally proposed by Murray et al⁽²²⁾, and the principle of operation is shown in Fig. 1.6. A long pump pulse propagates from right to left in a cell filled with a Raman active medium, producing gain at the first Stokes frequency $\nu_s = \nu_p - \nu_r$

FIG. 1 · 6



Schematic representation of backward wave Raman pulse compression (Ref. 22)

where ν_p is the pump frequency and ν_r the frequency of the Raman mode excited. A short pulse at frequency ν_s is injected into the cell just as the pump pulse reaches the exit window. As the two pulses propagate through one another the Stokes pulse is amplified at the expense of the pump pulse, so the overall effect is to compress the energy in the long pulse at frequency ν_p into the small pulse at frequency ν_s . Murray et al⁽²²⁾ calculated that, using CH_4 as the Raman medium and a laser intensity of 1 J cm^{-2} , a conversion efficiency of 50% could be achieved from 248 to 268 nm.

A similar technique to backward wave Raman scattering is pulse compression using Brillouin scattering, which has recently been demonstrated in a tapered waveguide using a Ruby laser⁽²³⁾. The difference between the two processes is that instead of a photon of frequency ν_r being used in the scattering process, Brillouin scattering uses an acoustic phonon. Because of the much lower frequency of the phonon, the frequency shift between the pump and amplified pulses is negligible. Therefore, after pulse compression by Brillouin scattering, a KrF laser pulse could still be amplified in another KrF amplifier. Pulse compression has been demonstrated⁽²³⁾ by this method without the use of an externally generated Stokes pulse as in Fig. 1.6 by allowing the frequency shifted back scattered pulse to build up from noise at the end of a tapered waveguide. It is necessary in this case to use a narrowband input pulse, but this is a relatively minor complication compared with the large chain of amplifiers that would be required for a working fusion reactor.

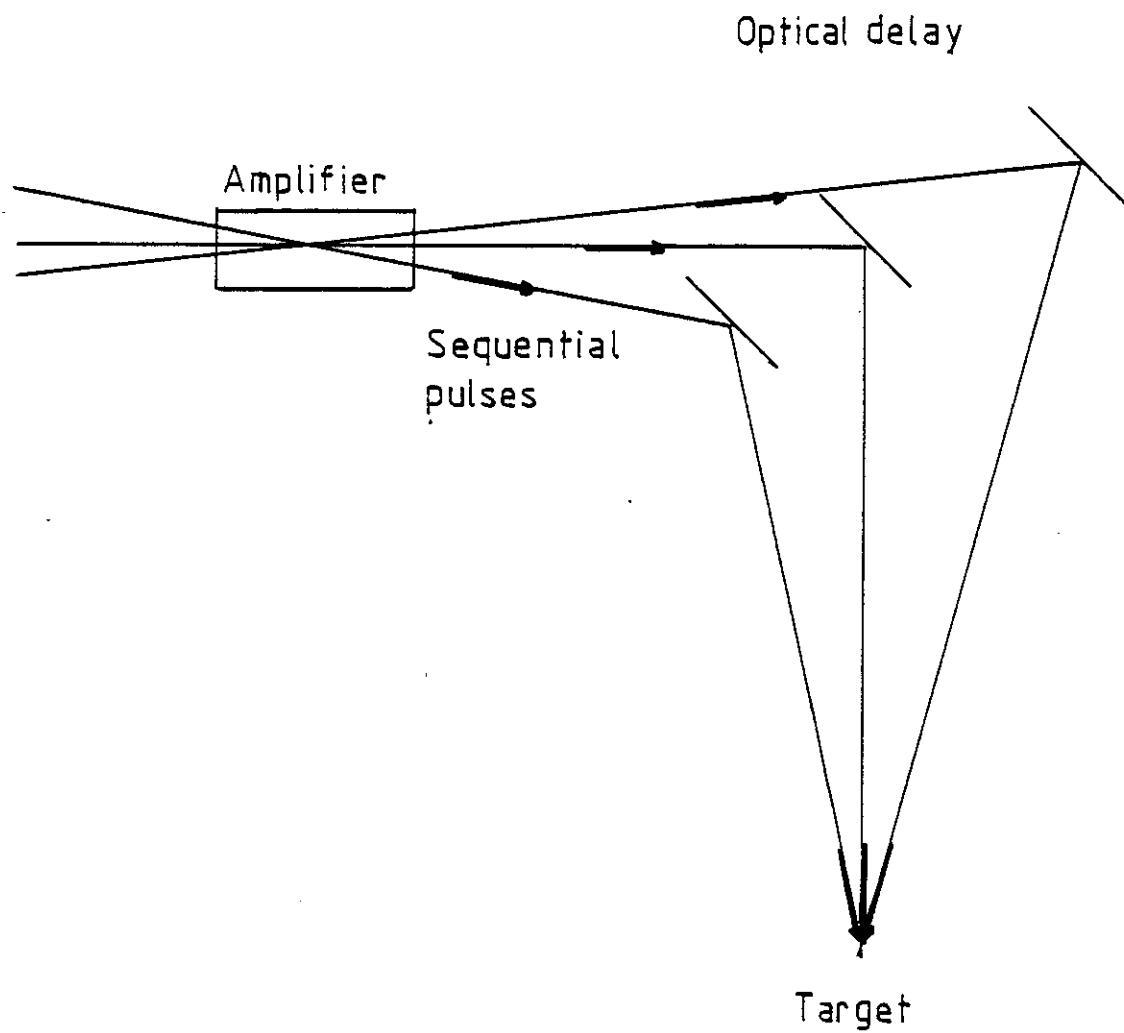
Once compressed KrF laser pulses have been obtained, for example by the method described above, they can subsequently be amplified in KrF amplifiers. One method for obtaining high power irradiation of a target is pulse stacking. Energy is

extracted from a KrF amplifier by a sequenced train of pulses which are time coded in some manner, e.g. by angle, as shown in Fig. 1.7. Pulses in the train are separated after amplification and by subjecting the pulses to the required time delays are simultaneously stacked on the target. One part of this thesis is devoted to a study of e-beam pumped KrF lasers with a view to finding the parameters determining their optimum performance as amplifiers of short pulses for use in such systems.

1.2.2 Spectroscopy and Photochemistry

Excimer lasers have been useful in extending the techniques of laser spectroscopy into the ultraviolet and vacuum ultraviolet. The advantage of lasers over conventional light sources at these wavelengths, apart from their higher brightness, is their monochromatic nature. This allows selective excitation of atomic and molecular transitions, facilitating the extraction of data. For example, an ArF laser at 193 nm has been used to produce emissions from single vibronic states in NO and O₂ molecules⁽²⁴⁾. The short pulses available from excimer lasers also allow time resolved studies of fluorescence, giving information on excited state lifetimes and extinction coefficients. Other more complex experimental techniques of laser spectroscopy are Coherent Anti-Raman Spectroscopy and multiphoton excitation⁽²⁵⁾.

The extension of the range of wavelengths available for laser spectroscopy provides a stimulus for the discovery of new laser lines and the development of coherent radiation sources in new regions of the spectrum. The number of laser lines available from excimer lasers can be increased by the technique of Stimulated Raman Scattering^(26,27). Broadly tunable ultraviolet laser radiation can be produced by pumping suitable dyes with excimer lasers, e.g. p-terphenyl with a KrF laser⁽²⁸⁾.



An angle coded pulse stacking arrangement

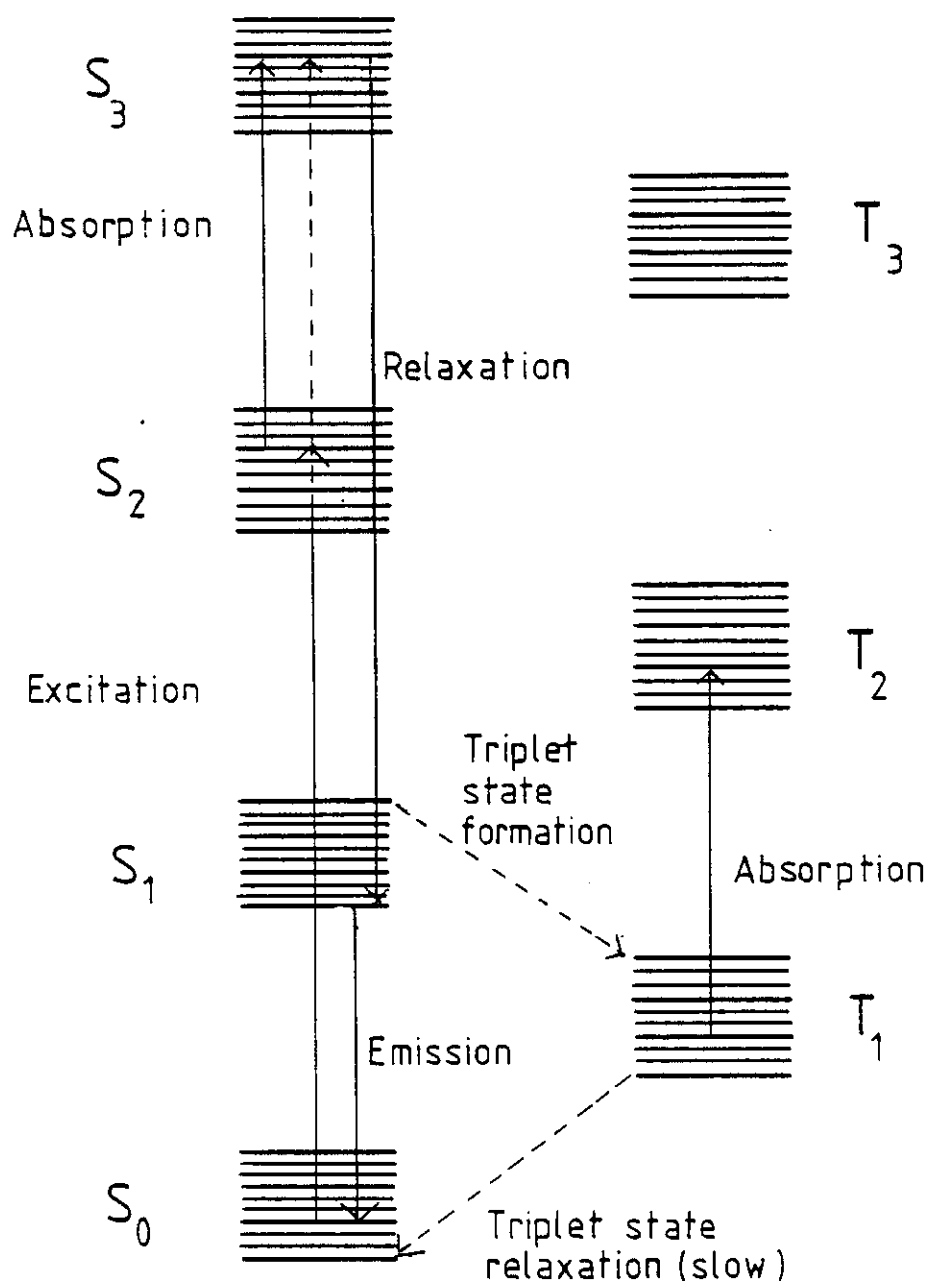
Excimer lasers have also been found useful in pumping visible dye lasers, as will be discussed in the next section. Part of this thesis will detail the development of a tunable narrow-band coherent vacuum ultra-violet (VUV) radiation source with applications in laser spectroscopy at previously unavailable wavelengths.

1.2.3 Dye Laser Pumping

Excimer lasers have in recent years been increasingly used in the pumping of dye lasers. Their short wavelengths have meant that dye lasers covering the entire visible region of the spectrum can be pumped with a single wavelength laser. Dye lasers have even been operated in the UV⁽²⁸⁾. This contrasts with the Nd:YAG laser (1060 nm), which requires frequency doubling or tripling to achieve the same wavelength coverage. The excimer lasers have the advantage of much higher pulse energies over the N₂ laser (337 nm), which has also been used as a dye laser pumping source. The most commonly used excimer laser for dye laser pumping is XeCl, since most visible emitting dyes have a strong absorption band at 308 nm, and XeCl has the longest gas fill "lifetime" of the excimer lasers (> 10⁶ shots with some commercial lasers). Most dyes emit in a spectral region typically ~ 30 nm broad, so a number of dyes are required to cover the entire visible spectral range.

Fig. 1.8 shows a schematic energy level diagram of a dye molecule. State S₀ is the ground state, S₁, S₂ and S₃ are excited singlet states, and T₁, T₂ and T₃ are excited triplet states. In a singlet (S) state the magnetic spin of the excited electron is antiparallel to the spin of the remaining molecule, whereas in a triplet (T) state they are parallel. Singlet-triplet and triplet-singlet transitions involve a spin flip and hence are far less likely than transitions between

FIG. 1·8



Schematic energy level diagram of a dye molecule

two singlet or two triplet states. Transitions between two singlet and two triplet states give rise to intense absorption and fluorescence. The characteristic colour of an organic dye is due to the range of wavelengths in its S_0 - S_1 absorption. This is the range over which the dye can be made to lase.

For optimum efficiency the frequency of the exciting laser would also lie within the $S_0 - S_1$ band. However, the excimer lasers have such a high efficiency that this offsets the disadvantage they suffer in only being able to excite the dyes into higher singlet states (see Fig. 1.8). Fast relaxation processes then lead to formation of the S_1 state with a high efficiency, so that a single UV laser can be used to pump a broad range of dyes. One problem, however, is that with successive absorption of UV photons the dye molecules can absorb enough energy to dissociate, so that the dye must be replaced more frequently than with longer wavelength pump lasers. There is a small probability that an excited molecule will decay to the triplet state T_1 , the rate being small, as this is a spin-forbidden transition. Similarly, the rate of relaxation to the ground state is low, so the triplet state T_1 acts as a trap for molecules. If the emission wavelength then coincides with the $T_1 - T_2$ transition, this increases the laser losses and can lead to quenching of the laser oscillation.

Efficient narrowband dye lasers can be built using diffraction gratings as dispersive elements since a dye is a homogeneously broadened four level system. Linewidths down to ~ 300 MHz are possible⁽²⁹⁾ and the design of such narrowband lasers will be discussed more fully in Chapter 4.

The narrowband radiation generated in such dye laser oscillators, which is tunable over the range of the $S_1 - S_0$

transition, can be amplified in the same dye to obtain high power narrowband pulses. The efficiency of conversion of pump light to dye laser energy can be improved by special attention to the solvents used as shown by Cassard et al⁽³⁰⁾.

The availability of such widely tunable, high power, monochromatic sources of coherent radiation is of great importance in laser spectroscopy and photoselective chemistry. The available wavelength range is also increased by frequency doubling, extending down to 217 nm and even further by higher order nonlinear processes.

1.2.4 Nonlinear Optics

Because of the homogeneous nature of their transitions, the excimers have the potential of providing high spectral brightness ultra violet laser radiation, which will be useful for frequency up-conversion to even shorter wavelengths and hence increasing the range of wavelengths available for spectroscopic studies. The potential of excimer lasers for nonlinear frequency conversion has been demonstrated by Hutchinson et al⁽³¹⁾ who generated coherent radiation at 57 nm by frequency tripling a Xenon laser and by Egger et al⁽³²⁾ who generated the third harmonic of a KrF laser at 83 nm.

The use of excimer lasers in nonlinear optical processes requires that their linewidth be narrowed to improve the spectral brightness of the radiation. The limited number of cavity round trips allowed by the pulse duration of a typical excimer laser means that the narrowness of the bandwidth that can be achieved by intracavity tuning elements is limited, and the low power outputs that result from narrowing the bandwidth mean that subsequent amplification is essential to reach power levels where efficient nonlinear mixing can take place. An alternative is to use the excimer laser as an amplifier for high quality

narrowband coherent radiation generated by other means. This approach has been demonstrated by Pummer et al⁽³³⁾ in generating radiation at around 64 nm by frequency tripling 193 nm radiation amplified in a series of ArF amplifiers.

The efficiency of four wave mixing processes can be enhanced by selecting laser frequencies which coincide with resonances in the atoms of the non-linear medium. This has been used in the frequency up-conversion of dye lasers in metal vapours where the generated frequencies lie below the ionization continuum. The shorter wavelengths of rare gas halide lasers allow similar experiments to be conducted in media with higher ionization potentials. For example, rare gases such as Xenon and Krypton can be used, which avoid the complication of a heat pipe necessary to produce a high pressure metal vapour. The limited tunability of excimer lasers results in there being fewer suitable resonances available; however, there is a two photon resonance at 249.6 nm within the gain bandwidth of the KrF laser which, as will be described in later chapters, promises the development of highly efficient sources of VUV radiation by four wave mixing.

1.2.5 Some Other Applications

As well as uses as research tools in photochemistry, excimer lasers have possible applications in the selective control of chemical reactions⁽³⁴⁾. An example of laser induced chemistry is the removal of PH_3 , AsH_3 and B_2H_6 impurities from silane (SiH_4) by selective photolysis with an ArF laser⁽³⁵⁾ inducing reactions only in the impurities. Sander et al⁽³⁶⁾ have demonstrated the enrichment of oxygen isotopes also with an ArF laser and this holds out the possibility of more efficient uranium isotope enrichment than by conventional techniques.

In conclusion, excimer lasers appear to be versatile tools

that will find a wide diversity of applications such as semiconductor processing⁽³⁷⁾, photolithography, remote sensing and combustion diagnostics as well as those already mentioned.

1.3 Objectives of this Work

This work describes the use of excimer lasers in two experiments whose objectives are outlined below.

1.3.1 Vibrational Relaxation Studies in E-beam Excited KrF^{*}

In section 1.2.2 it was mentioned that in laser plasma interactions coupling of laser energy to the plasma is expected as the laser wavelength is decreased. This is supported by both theoretical⁽³⁸⁾ and experimental studies^(21,39). Therefore it is envisaged that there will be a need for a short pulse (~ 1 ns) high power (~ 1 TW) laser for compression studies utilizing KrF^{*} as the active medium ($\lambda = 249$ nm). An e-beam pumped KrF laser is relatively efficient and energetically scalable⁽⁴⁰⁾, but its pulse length is generally longer than that believed useful for fusion studies. This problem can be overcome, by extracting the energy from the amplifier in a sequence of short (~ 1 ns) pulses which are then made to strike a target simultaneously (see Fig. 1.7). Following saturated amplification of one such pulse, sufficient time must be allowed for the gain in the medium to recover so that the following pulse may be amplified. Furthermore, the vibrational relaxation time in the electronically excited KrF^{*} molecule must be shorter than the duration of the pulse to be amplified if efficient extraction of energy from high lying vibrational levels is to be achieved. It is important therefore to have information about both the gain recovery time and the vibrational relaxation time for the design of high power laser amplifiers. Since significant disagreement exists in the published values of the vibrational relaxation time of KrF^{*}

(41,42,43,44) a new study of both this parameter and the gain recovery time under typical conditions in an electron beam pumped amplifier was undertaken and will be described in the next chapter.

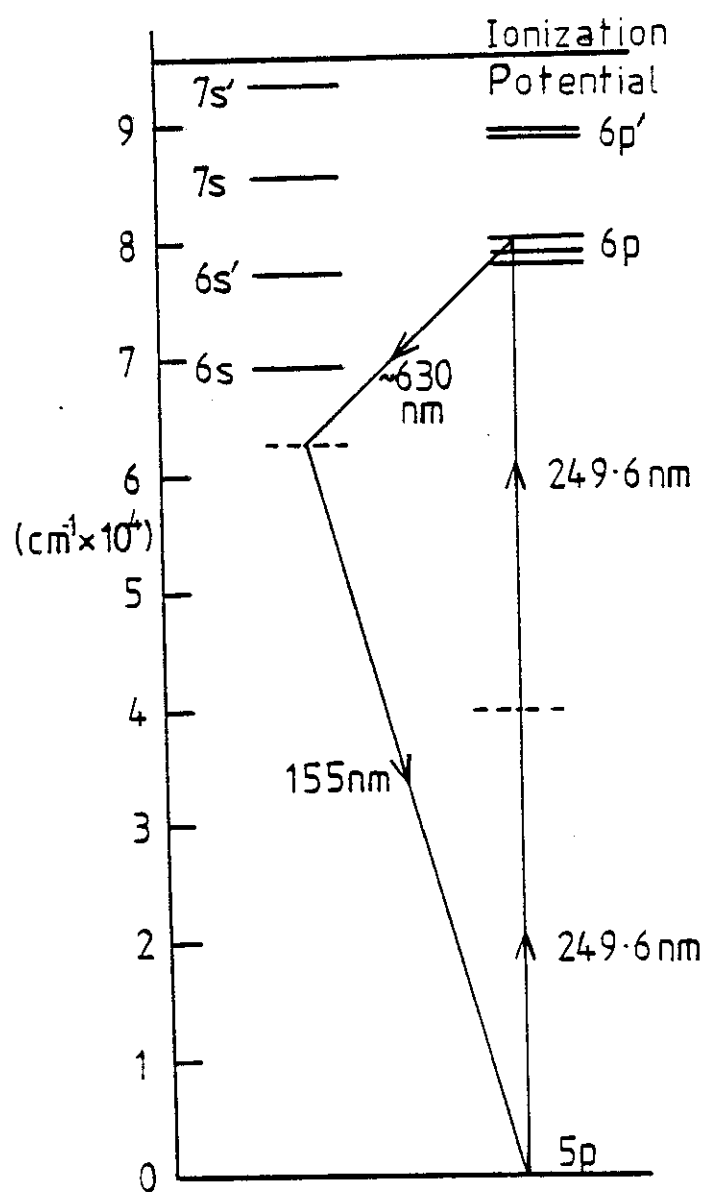
The method used to determine these parameters was to probe an electron beam excited KrF^* medium with a saturating pulse from a synchronized discharge pumped KrF laser. The population changes of the upper laser level due to the probe laser pulse were determined by monitoring the sidelight fluorescence from the medium. The magnitude and temporal profile of the observed depletion allowed the parameters of interest to be deduced.

1.3.2 Two-photon resonantly enhanced four wave mixing in Xenon

There is a two photon resonance in the Xenon atom between the $5p\ ^1S$ and the $6p\ [0\frac{1}{2}]$ states at a wavelength of 249.6 nm, as shown in Fig. 1.9. This lies within the spectral profile of the gain of a KrF laser so that a high spectral brightness source of coherent radiation at this wavelength can be generated. Therefore resonantly enhanced nonlinear mixing processes can take place, using the two photon resonance, which can provide an efficient means of generating short wavelength radiation. This work concentrates on the four wave difference frequency mixing process shown in Fig. 1.9, where if the two photon resonant radiation has a frequency ω_1 , then another laser of frequency ω_3 can be mixed with this radiation to generate a frequency ω_4 given by

$$\omega_4 = \omega_1 + \omega_1 - \omega_3 = 2\omega_1 - \omega_3 \quad (1.6)$$

If ω_1 is fixed at the two-photon resonance, tuning of the



Energy level diagram of the Xenon atom showing the photons taking part in the four-wave difference frequency mixing process

frequency ω_3 results in tuning of the output frequency ω_4 . The bandwidth of the radiation at ω_4 is determined by that of the fundamental beams at ω_1 and ω_3 . Hence, by the use of spectrally narrow sources of ultraviolet and tunable visible light at ω_1 and ω_3 narrow bandwidth, high spectral brightness tunable radiation at ω_4 in the vacuum ultraviolet can be produced.

This work describes the construction of such a VUV source using an XeCl excimer laser pumped dye laser system capable of generating two independently tunable, narrowband sources of visible laser light. One of these sources at a wavelength of ~ 500 nm was frequency doubled in a potassium pentaborate (KB5) crystal to generate radiation tunable around the two photon resonance in Xenon. The output of the crystal was amplified in a discharge pumped KrF amplifier to produce a high power, narrowband source of coherent UV light at the wavelength of the KrF laser. This was then used, together with the other tunable dye laser source, to generate the tunable narrowband vacuum ultraviolet radiation by resonantly enhanced four wave difference frequency mixing.

The purpose of this was both to produce a novel source of high quality tunable VUV radiation with applications in spectroscopy and photochemistry and to investigate the physics of the nonlinear process by comparison with the theory that will be developed in Chapter 3.

Chapter 2

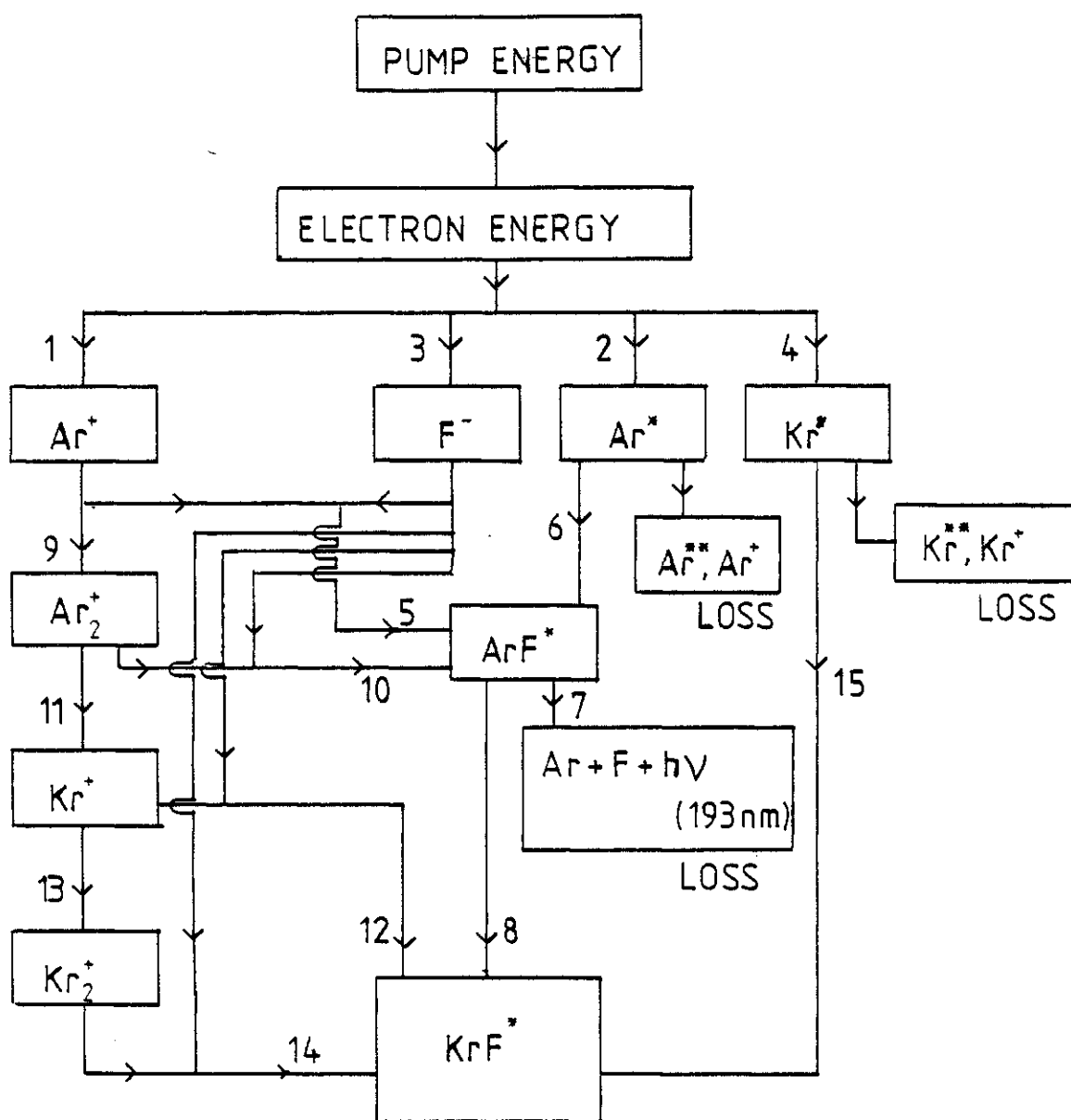
Vibrational Relaxation Studies on Electron-Beam Excited KrF^*

2.1 Kinetics of E-beam Excited KrF^* Lasers

The electronic states of KrF , as calculated by Dunning and Hay⁽⁴⁾ are shown in Fig. 1.2. It can be seen there that one reason for the high efficiency of KrF lasers is that the covalent and ionic excited state potentials cross at a high internuclear separation, preventing predissociation of the ionic states. This is useful in discharge pumped KrF lasers since the ionic states that form the upper laser level can be efficiently populated via the metastable covalent channel. The rate constants for rare gas halide quenching processes are also lower in KrF .

The formation kinetics of the rare gas halides are complex and depend both on the type of pumping used and the pressures of the constituent gases which include a buffer gas which is responsible for the initial absorption of most of the pump energy. In e-beam pumped KrF lasers the buffer gas would normally be Argon, and the formation processes in this case will be discussed here. Discharge pumped KrF lasers would use Helium as the buffer, but the formation processes would still be similar to those that will be described. For a KrF laser medium consisting of F_2 and Ar, the reactions that can occur during laser excitation are summarized in Table 2.1. The symbols e_p and e_s refer to primary electrons from the electron beam (or other pump source) and secondary electrons caused by ionization respectively. Reactions [1] to [15] occur in the formation of KrF^* , while [16] to [20] are quenching processes. Fig. 2.1 is a flow diagram of the formation channels

FIG. 2.1



KrF^* formation channels

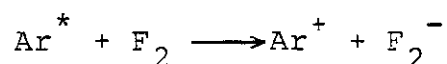
Table 2.1
Reactions Occurring in KrF* Formation

REACTION	RATE COEFFICIENT	REFERENCE
1 $\text{Ar} + \text{e}_p^- \rightarrow \text{Ar}^+ \text{e}_s^- + \text{e}_p^-$		
2 $\text{Ar} + \text{e}_p^- \rightarrow \text{Ar}^* + \text{e}_p^-$		
3 $\text{F}_2 + \text{e}_s^- \rightarrow \text{F} + \text{F}^-$	$\sim 2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$	45
4 $\text{Kr} + \text{e}_p^- \rightarrow \text{Kr}^* + \text{e}_p^-$		
5 $\text{Ar}^+ + \text{F}^- (+\text{Ar}) \rightarrow \text{ArF}^* (+\text{Ar})$	$\sim 2-3 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$	46
6 $\text{Ar}^* + \text{F}_2 \rightarrow \text{ArF}^* + \text{F}$	$7.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	47
7 $\text{ArF}^* \rightarrow \text{Ar} + \text{F} + h\nu @ 193 \text{ nm}$	$\tau = 4 \text{ ns}$	48
8 $\text{ArF}^* + \text{Kr} \rightarrow \text{KrF}^* + \text{Ar}$	$1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$	49
9 $\text{Ar}_2^+ + \text{Ar} (+\text{Ar}) \rightarrow \text{Ar}_2^+ (+\text{Ar})$	$1.9-3 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$	50-54
10 $\text{Ar}_2^+ + \text{F}^- (+\text{Ar}) \rightarrow \text{ArF}^* + \text{Ar} (+\text{Ar})$	$\sim 10^{-6} \text{ cm}^3 \text{ s}^{-1}$	46
11 $\text{Ar}_2^+ + \text{Kr} \rightarrow \text{Kr}^+ + 2\text{Ar}$	$7.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	55
12 $\text{Kr}^+ + \text{F}^- (+\text{Ar}) \rightarrow \text{KrF}^* (+\text{Ar})$	$1-2 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$	46
13 $\text{Kr}^+ + \text{Kr} + \text{Ar} \rightarrow \text{Kr}_2^+ + \text{Ar}$	$2.4 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$	56
14 $\text{Kr}_2^+ + \text{F}^- (+\text{Ar}) \rightarrow \text{KrF}^* + \text{Kr} (+\text{Ar})$	$\sim 10^{-6} \text{ cm}^3 \text{ s}^{-1}$	55
15 $\text{Kr}^* + \text{F}_2 \rightarrow \text{KrF}^* + \text{F}$	$7.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	57
16 $\text{KrF}^* + 2\text{Ar} \rightarrow \text{ArKrF}^* + \text{Ar}$	$0.7-1.1 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$	58-60
17 $\text{Kr} + \text{ArKrF}^* \rightarrow \text{Kr}_2\text{F}^* + \text{Ar}$	NOT DIRECTLY OBSERVED	
18 $\text{KrF}^* + \text{Kr} + \text{Kr} \rightarrow \text{Kr}_2\text{F}^* + \text{Kr}$	$2.9-9.7 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$	58,59,61
19 $\text{KrF}^* + \text{Kr} + \text{Ar} \rightarrow \text{Kr}_2\text{F}^* + \text{Ar}$	$6.5 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$	62
20 $\text{KrF}^* + \text{Kr} \rightarrow \text{Kr}_2\text{F}^*$	$1.6-8.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	58,59

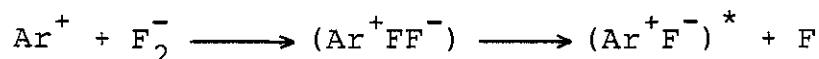
detailed in Table 2.1.

A typical composition of the gas fill of an e-beam pumped KrF laser for high output would be >90% Ar : <10% Kr : <0.5% F₂. About 50% of the e-beam energy will be channelled into the production of argon ion - electron pairs (Reaction [1] in Table 2.1) and 10% into argon metastables, Ar^{*}, ([2]). Secondary electrons will tend to form F⁻ ions by dissociative attachment with F₂ ([3]). Similar reactions occur when discharge pumping is used, but in that case KrF^{*} formation proceeds mainly via the metastable channels ([2] and [4]) and production of F⁻ ions ([3]).

In e-beam pumped lasers, although Ar⁺ and F⁻ ions can combine to form ArF^{*} ([5]) at total pressures greater than one atmosphere, the dominant process is the production of molecular ions, Ar₂⁺, by three body association ([9]). Recombination with an F⁻ ion can then take place to yield ArF^{*} ([10]). Alternatively the Ar₂⁺ can produce Kr⁺ by a charge exchange reaction with Kr ([11]). The formation of KrF^{*} then proceeds by either an exchange reaction between ArF^{*} and Kr ([8]) or by recombination of Kr⁺ and F⁻ ([12]). There is also a possibility of Kr₂⁺ being formed from Kr⁺ by three body association ([13]), especially with a high pressure of Krypton. KrF^{*} may then be created by the recombination of Kr₂⁺ and F⁻ ([14]). In an e-beam excited mixture only ~20% of the total energy would be absorbed via the metastable channels, so reactions [2], [4], [6] and [15] will not be of much importance in contrast to discharge pumped systems. In the metastable channel ArF^{*} is formed by a harpoon reaction between Ar^{*} and F₂ ([6]), so called because the Ar atom first loses an electron to the F₂ molecule



and then regains it in the second stage of the process



This reaction occurs with a branching ratio of 0.6 since Ar^* can form Ar^{**} and Ar^+ by collisions with electrons and these products are unusable in KrF^* formation. One loss process in KrF^* formation is excimer emission from the ArF^* ([7]), although at total pressures greater than 1 atmosphere the exchange reaction between ArF^* and Kr ([8]) will take place rapidly enough for this not to be a significant problem.

Krypton metastables (Kr^*) can also be produced ([4]) by excitation by electrons, especially in discharge pumped systems, which can combine with F_2 to form KrF^* ([15]) with branching ratio unity and low energy requirement. This would provide an efficient formation channel if it were not for the fact that the krypton pressure cannot be increased without rapidly quenching the KrF^* population.

Quenching can occur by two or three body collisions with F_2 , Ar and Kr, but the population of F_2 is so low that it does not play a significant part. The main quenching process involves the majority gas, Argon, in a three body collision ([16]) forming the triatomic excimer ArKrF^* which then produces Kr_2F^* by collision with Kr ([17]). The Kr_2F^* excimer can be formed directly by three body collision with Kr involving either another Kr ([18]) or an Ar ([19]) atom or by a two body collision [20].

The Kr_2F^* excimer has a lifetime of 132 ns⁽⁶³⁾, so large populations can build up. This is a disadvantage since it can absorb the laser emission at 249 nm. Photoabsorption can also occur in other species such as F_2 , F^- , Ar_2^+ , Kr_2^+ , Ar^* and Kr^* but Kr_2F^* is the dominant absorbing species⁽⁶⁴⁾, producing a loss of 0.44 m^{-1} at 1.7 atmospheres. An unavoidable loss in

any rare gas halide laser is that due to self absorption by the B state, as illustrated in Fig. 1.2, effectively reducing the stimulated emission cross section. The importance of this process depends on the detailed electronic structure of the excimer molecule. This is not a significant problem in KrF as only molecular states corresponding to the lowest ($\text{Kr}^* + \text{F}$) atomic state would give transitions in the required energy range.

2.2 Theory of the Rate Equations for Level Populations

2.2.1 The Rate Equations

In an ideal excimer laser or amplifier Franck-Condon transitions from the ground vibrational state of the upper laser level terminate high on the dissociative lower level. In this case reabsorption from the lower level is negligible and may be omitted from the laser rate equations. Hence, considering the amplification of a laser beam traversing the gain medium in the x direction, the rates of change of the two variables N_1 and F , namely the excimer density per unit volume (the upper laser level population) and the photon fluence (photons per unit area per unit time) respectively are given by the equations

$$\frac{dN_1}{dt} = P_1 - \frac{N_1}{\tau} - \sigma F N_1 \quad (2.1)$$

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + c \frac{\partial F}{\partial x} = c \sigma F N_1 \quad (2.2)$$

where P_1 is the pump rate into the upper laser level which has a lifetime τ . The term $\sigma F N_1$ is the rate of stimulated emission where σ is the stimulated emission cross section.

In the steady state, ($\frac{dN}{dt} = 0$), which corresponds to a laser pulse which is long compared to the upper state lifetime τ , the solution of equations (2.1) and (2.2) (in terms of the laser intensity $I = h\nu F$ where ν is the mean frequency of the laser transition) is

$$\frac{\partial I}{\partial x} = \frac{\alpha_0 I}{(1 + I / I_s)} \quad (2.3)$$

where $\alpha_0 = P_1 \sigma \tau$ is the small signal gain coefficient and

$$I_s = \frac{h\nu}{\sigma \tau} \quad (2.4)$$

is the saturation intensity. From (2.3) the performance of a laser amplifier of length l in terms of the input and output intensities I_{in} and I_{out} is shown in Fig. 2.2. In the small signal case where $I \ll I_s$

$$I_{out} = I_{in} \exp(\alpha_0 l) \quad (2.5)$$

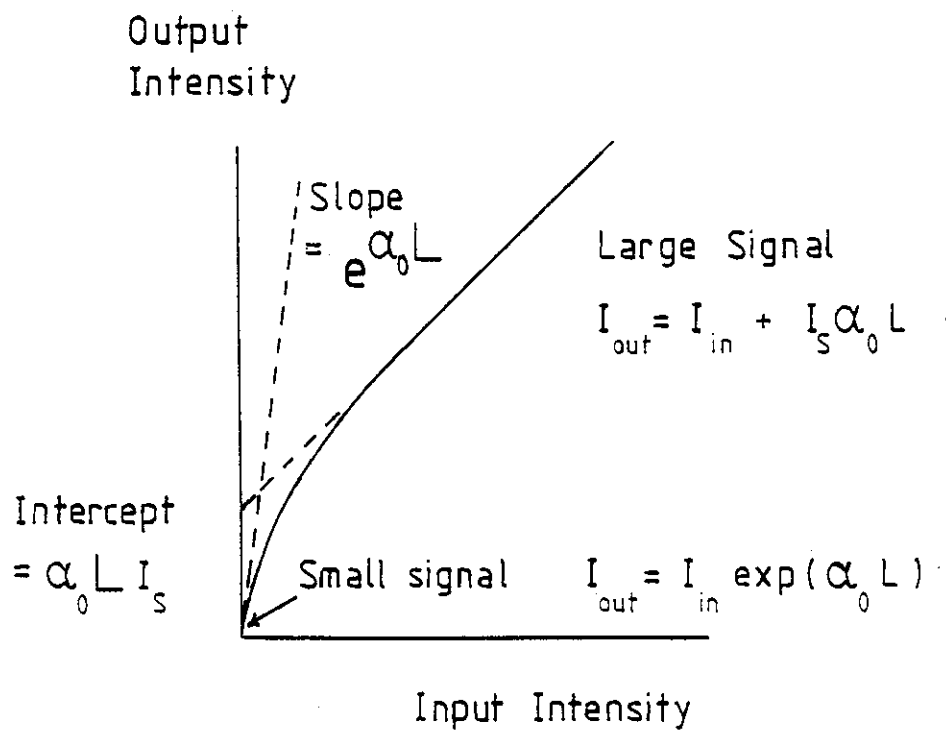
and in the large signal case, $I \gg I_s$

$$I_{out} = I_{in} + \alpha_0 I_s l \quad (2.6)$$

However, when the duration of the laser pulse to be amplified is shorter than the upper state lifetime τ , or it has a temporal variation which is significant in a timescale of that order, a steady state can no longer be assumed. In that case equations (2.1) and (2.2) must be solved numerically. Such a procedure was adopted to model the conditions applicable in the experiment to be described.

2.2.2 The Stimulated Emission Cross section

A knowledge of the stimulated emission cross section is



Output intensity I_{out} as a function of input intensity I_{in} for a laser amplifier given by the long pulse, steady state approximation (Ref. 6)

central to the approach outlined above. Semi-classical as opposed to quantum mechanical treatments have been used to obtain approximate values of this parameter, for example by Werner et al⁽⁶⁵⁾ and a simplified approach has been outlined by Shaw⁽⁶⁾.

Shaw applies the expression given by Mitchell and Zemansky⁽⁶⁶⁾ for the gain coefficient, $\alpha(V) = N_1 \sigma(V)$ to the case of zero ground state population, obtaining

$$\alpha(V) = \frac{c^2 A(V)}{8\pi V^2} \frac{\delta N_1}{\delta V} \quad (2.7)$$

where $A(V)$ is the Einstein Coefficient and $\frac{\delta N_1}{\delta V}$ is that fraction of the excimer concentration capable of emitting within the band δV at a frequency V . Shaw approximates the vibrational part of the wavefunction describing the nuclear motion to that for a linear harmonic oscillator⁽⁶⁷⁾ and assumes that the vibrational spacing in the upper bound state is $\gg kT$ so that only the ground vibrational state need be considered as contributing to laser action and also that the ground state potential is linear in the region of interest, so that it is sufficient to evaluate the derivative of the energy $\frac{dE(R)}{dR}$ at only one point, $R = R_e$, where R_e is the equilibrium internuclear separation.

Shaw⁽⁶⁾ obtains the result

$$\sigma(V) = \frac{\lambda_0^2}{8\pi \tau} \frac{h \sqrt{b/\pi} \exp(-br^2)}{(-dE/dR)}^{-1}_{R=R_e} \quad (2.8)$$

where $r = R - R_e$,

$$b = 4\pi \mu^2 V_e / h$$

λ_0 is the vacuum wavelength at the frequency ν , τ is the upper state lifetime, R_e is the equilibrium internuclear separation for the bound state, R is the internuclear separation, E is the energy, μ is the reduced mass and ν_e is the vibrational spacing. The gaussian distribution of the stimulated emission cross section results from the linear harmonic oscillator approximation. The full width at half maximum, $\Delta\nu$, is given by

$$\Delta\nu = -\left(\frac{dE(R)}{dR}\right)_{R=R_e} \sqrt{(\ln 2 / h\pi^2\mu\nu_e)} \quad (2.9)$$

and this allows the average stimulated emission cross section for the excimer band to be defined as

$$\sigma_{av} = \frac{\lambda^2}{8\pi\tau\Delta\nu} \quad (2.10)$$

Dunning and Hay⁽⁶⁸⁾ have calculated the molecular potentials of the KrF laser and find that the vibrational spacing in the upper level is 10^{13} Hz and $\frac{dE(R)}{dR}$ at $R = R_e$ is ~ 0.3 eV/A. This gives $\Delta\nu \sim 9.7 \times 10^{12}$ Hz and hence $\sigma\tau = 2.5 \times 10^{-24}$ cm²s, which compares with an experimentally determined value of $1.75 \pm 0.25 \times 10^{-24}$ cm²s⁽⁶⁴⁾. Taking these values and other experimental work⁽⁶⁹⁾ into account, a value of σ of 2×10^{-16} cm² was used in the calculations detailed below.

2.2.3 Numerical Solution of the Rate Equations

The upper laser level is composed of the lowest vibrational states of the $B(\frac{1}{2})$ ($^2\Sigma^+$) state and these are formed by collisionally induced vibrational relaxation from higher vibrational states formed by the excitation source which is an

electron beam in the experiment considered here. A computer program was developed to numerically solve the rate equations pertinent to the experiment.

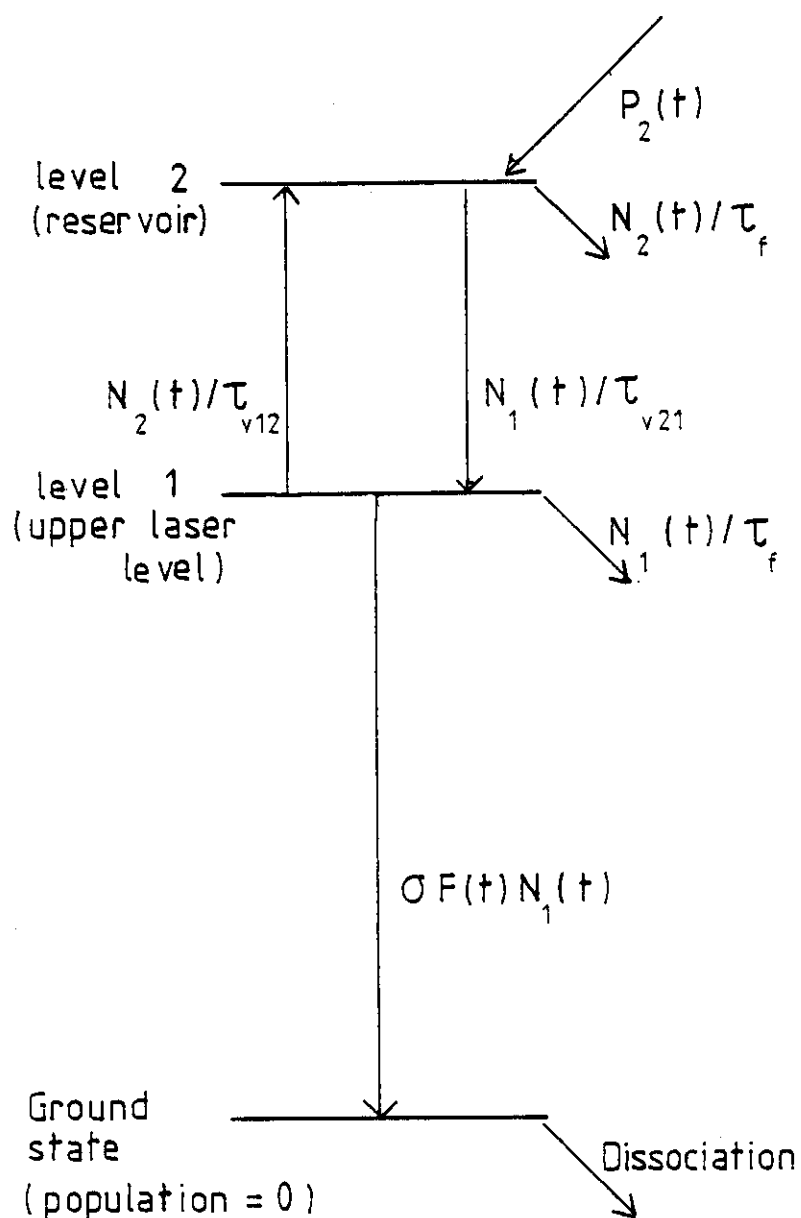
A single laser level (1) was considered in the system described by equation (2.1) being excited at a rate P_1 and having a population N_1 . In order to include the effects of vibrational relaxation in the model the excitation source was considered to populate level 1 via relaxation from another level (2) with population N_2 from which stimulated emission could not occur. Pumping occurs at a rate P_2 into level 2 and there is collisional mixing between this reservoir and the upper laser level (level 1).

A diagrammatic representation of the model is shown in Fig. 2.3. The rate of collisional mixing from the reservoir to the upper laser level (2-1) is $N_2 \tau_{V21}^{-1}$ and that in the opposite direction (1-2) is $N_1 \tau_{V12}^{-1}$. The parameter τ_{V21} is assumed to correspond to the vibrational relaxation time τ_V in the real KrF^* system, while the rate of collisional mixing from level 1 to level 2 is determined by τ_{V12} which is defined as

$$\tau_{V12} = K \tau_V \quad (2.11)$$

where K is an arbitrary constant to take into account the difference in the two rates.

The depopulation of the two levels by processes other than the collisional mixing is taken into account in the determination of the lifetimes of levels 1 and 2, which are both assumed to be equal to the fluorescence lifetime, τ_f , which is calculated from the natural lifetime τ_n and the two and three body rate constants for the quenching of KrF^*



Diagrammatic representation of computer model to solve the rate equations for a KrF laser

by the constituent gases of the laser medium according to the formula

$$\frac{1}{\tau_f} = \frac{1}{\tau_n} + \sum_c k_{2c} [Q_c] + k_{3c} [Q_c]^2 \quad (2.12)$$

The constants k_{2c} and k_{3c} are, respectively, the two and three body quenching rate constants for the constituent c and $[Q_c]$ is the concentration of that constituent. In the case under consideration the constituent c was Fluorine, Krypton or Argon. Table 2.2 shows the quenching rate constants for these gases, as determined by Eden et al⁽⁵⁹⁾. When stimulated emission due to a photon flux $F(t)$ is included, the rate equations governing the populations of levels 1 and 2 are

$$\frac{dN_1(t)}{dt} = \frac{N_2(t)}{\tau_{V21}} - \frac{N_1(t)}{\tau_{V12}} - \frac{N_1(t)}{\tau_f} - \sigma F(t) N_1(t) \quad (2.13)$$

$$\frac{dN_2(t)}{dt} = P_2(t) - \frac{N_2(t)}{\tau_f} - \frac{N_2(t)}{\tau_{V21}} + \frac{N_1(t)}{\tau_{V12}} \quad (2.14)$$

A possibly important process which has been neglected in these rate equations is quenching of the KrF^* population by electrons. However, the rate constant for this process is $2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ (70), which is sufficiently small for the effect to be negligible at the electron number densities that are to be expected in a typical electron beam pumped laser ($10^{12} - 10^{13} \text{ cm}^{-3}$).

The computer model uses an iterative procedure to determine

Table 2.2

The two and three body rate constants for quenching of KrF by Ar, Kr and F₂ (Ref. 59)

	k_2 (cm ³ s ⁻¹)	k_3 (cm ⁶ s ⁻¹)
Ar	1.8×10^{-12}	1.1×10^{-31}
Kr	8.6×10^{-12}	9.7×10^{-31}
F ₂	4.8×10^{-10}	-

the populations N_1 and N_2 according to the equations

$$N_1(t + \Delta t) = N_1(t) + \frac{dN_1(t)}{dt} \Delta t \quad (2.15)$$

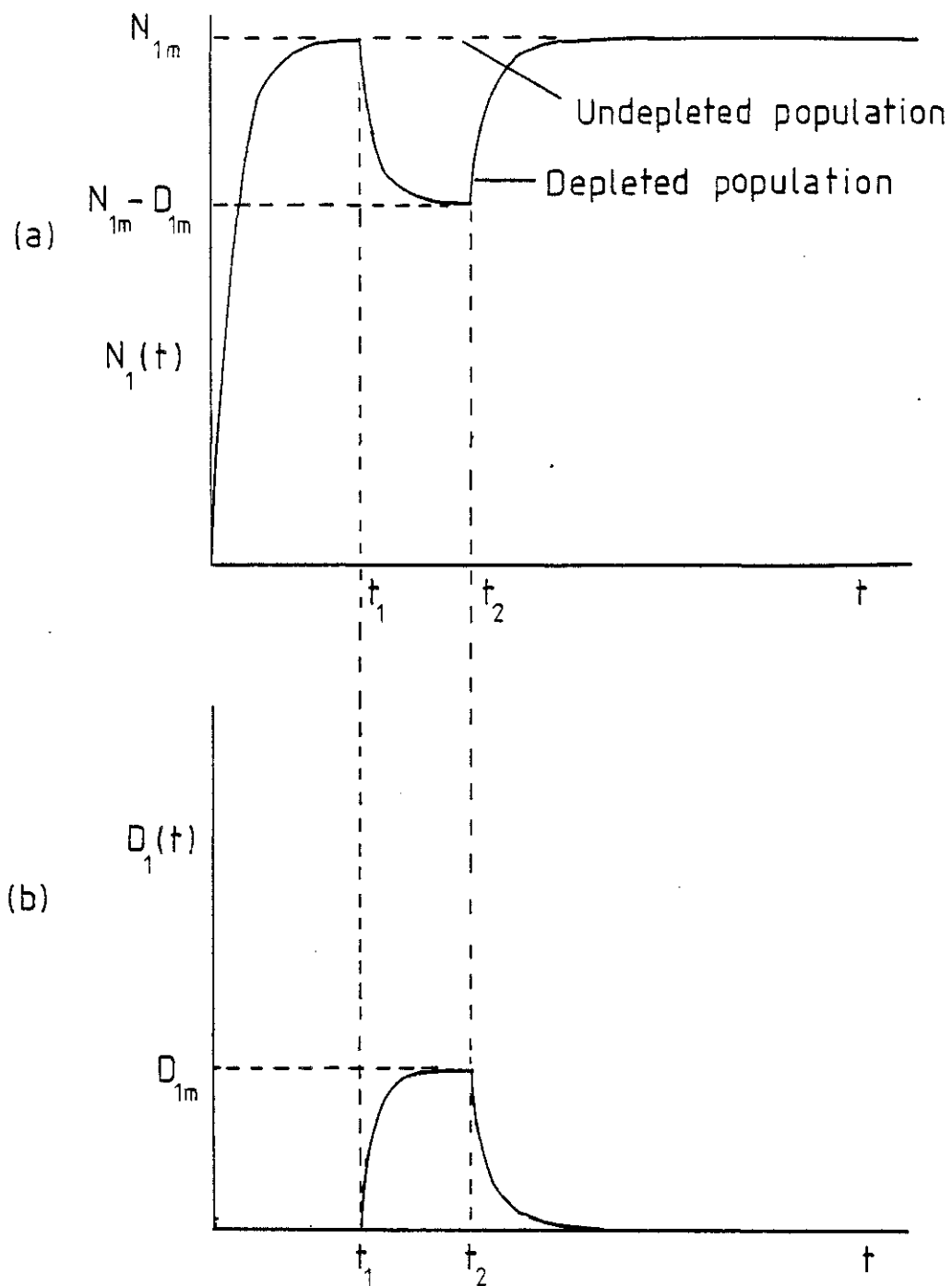
$$N_2(t + \Delta t) = N_2(t) + \frac{dN_2(t)}{dt} \Delta t \quad (2.16)$$

Hence, given the initial populations of levels 1 and 2 namely $N_1(0)$ and $N_2(0)$, the populations at a later time $t = n\Delta t$ can be calculated from equations (2.13) and (2.14). In the case being considered, the excited volume is limited by aperturing of the electron beam and so a probe laser pulse, represented by the photon fluence term $F(t)$, experiences negligible amplification due to the limited length of the gain region in which stimulated emission can occur. This greatly simplifies the calculation since the photon fluence $F(t)$ can be assumed constant during the traversal of the excited region. The pumping rate $P_2(t)$ and the probe laser photon fluence $F(t)$ could be given any desired temporal profile.

Fig. 2.4 is an example of the results of the numerical calculation applied to the idealized case, where the pumping rate $P_2(t)$ remains constant during the period of the calculation and the photon fluence is a step function such that

$$\begin{aligned} F(t) &= 0 ; 0 < t < t_1 \\ F(t) &= F ; t_1 < t < t_2 \\ F(t) &= 0 ; t > t_2 \end{aligned} \quad (2.17)$$

The populations N_1 and N_2 are set equal to zero at time $t = 0$ and the build up of population N_1 is seen in Fig. 2.4a to exponentially approach an equilibrium value denoted by N_{1m} . The photon fluence $F(t) = F$ starting at time $t = t_1$ causes a



Example of results of computer model for idealized functions $P_2(t)$ and $F(t)$.

(a) Population of upper laser level, $N_1(t)$

(b) Depletion of population, $D_1(t)$

depletion of the population N_1 which again exponentially approaches an equilibrium value.

Performing the calculation in the trivial case where

$$F(t) = 0 \text{ for all } t \quad (2.18)$$

provides a reference from which the depth of depletion $D_1(t)$ of the population $N_1(t)$ due to the photon flux $F(t)$ can be obtained as shown in Fig. 2.4b.

The depletion of the population in this idealized case is of interest since the build up and decay of the depletion after the laser of fluence F is abruptly switched on and off is independent of the effects that the temporal profile of a real laser pulse would have. It is desirable to define an "intrinsic gain depletion time", τ_D , and an "intrinsic gain recovery time", τ_R as the e-folding times of the depletion and recovery of the population respectively in this idealized case.

If the equilibrium value that the depletion would approach for an infinitely long probe laser pulse ($t_2 \rightarrow \infty$) is defined as D_{1m} , then τ_D and τ_R are given by

$$D_{1m} - D_1(t_1 + \tau_D) = D_{1m} / e \quad (2.19)$$

$$D_1(t_2 + \tau_R) = D_{1m} / e \quad (2.20)$$

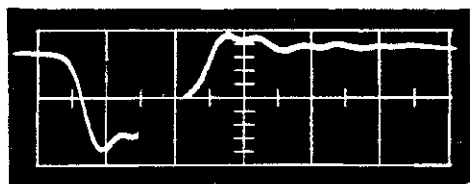
The functions $F(t)$ and $P_2(t)$ were given more realistic temporal variations to model experimental conditions. The results of the numerical calculations will be discussed later and comparisons made with the experimental results.

2.3 Apparatus

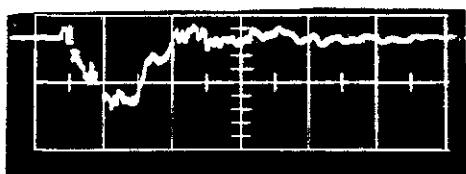
As can be seen from equations (2.1) and (2.2), both the gain experienced in the laser medium and the intensity of fluorescence from the upper laser level are proportional to the population N_1 of that level. Hence the fluorescence intensity transverse to the direction of the probe laser pulse, i.e. the sidelight fluorescence, provides a monitor of the upper laser level population and consequently of the gain of the medium. In this experiment the sidelight fluorescence from an electron beam excited KrF laser medium during the transit of a saturating probe laser pulse from a discharge pumped KrF laser.

The electron beam used to excite the KrF medium was generated by a Febetron 705 high voltage pulse generator which is a Marx bank, as described in Chapter 1 (section 1.1.2) (but with 80 stages instead of the 3 in Fig. 1.3) driving a 400 Ω electron beam diode. Fig. 2.5a shows the voltage waveform of the pulse generator and Fig. 2.5b is the electron-beam current as detected by a Faraday cup. The electron energy in the beam was ~ 1.5 MeV and the pulse duration was ~ 50 ns. The probe laser pulse was provided by a Lambda Physik EMG 101 discharge laser and its temporal variation is shown in the oscilloscope trace in Fig. 2.6. The pulse energy was ~ 200 mJ with a gas fill consisting of 120 mbar of 5% F_2 /95% He, 120 mbar of Kr and 2400 mbar He.

The experimental arrangement is illustrated in Fig. 2.7. The electron beam enters a cell containing the gas to be excited through a Kapton foil window. The laser beam, whose direction is perpendicular to the plane of the diagram in Fig. 2.7, passes axially along a metal cylinder within the gas cell and a limited region of electron beam pumping is

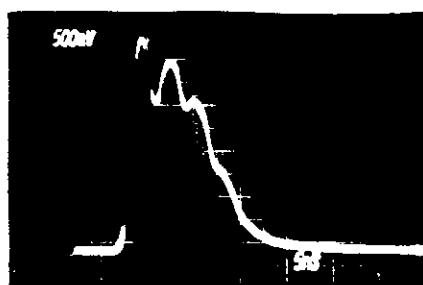


(a) Voltage waveform 50 ns/division



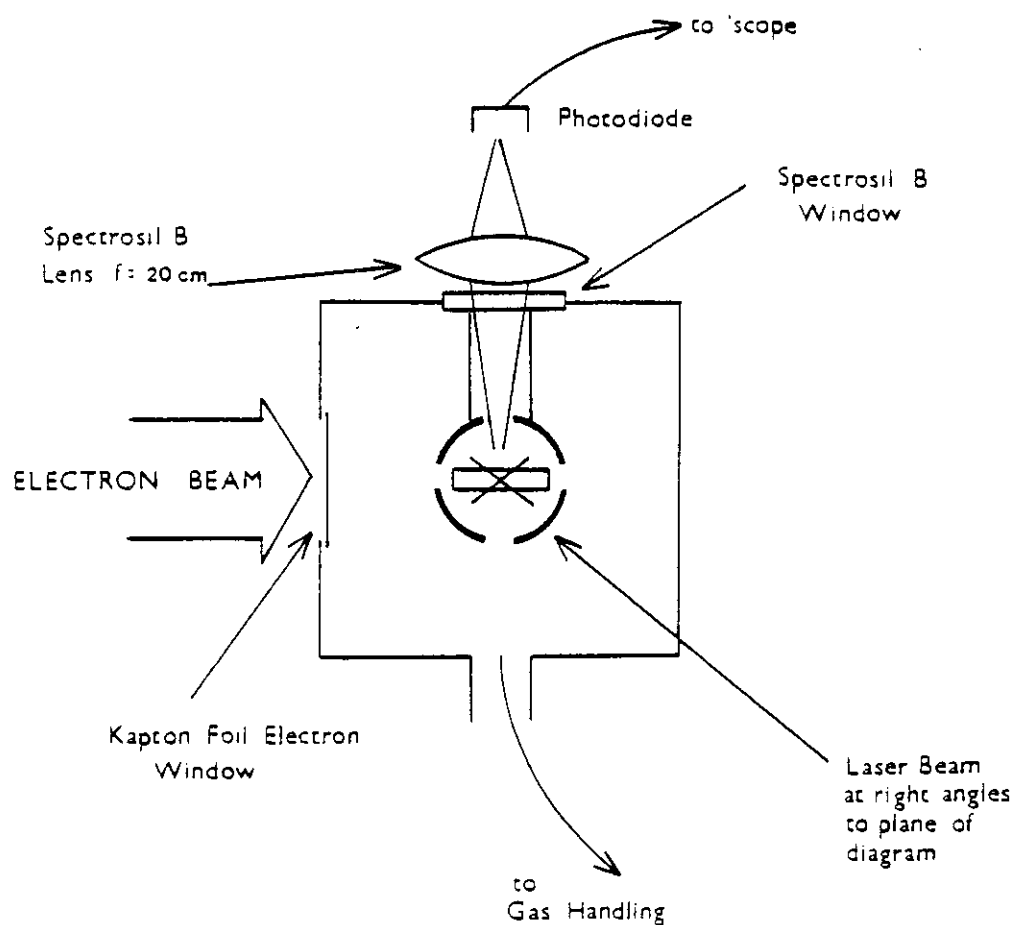
(b) E-beam current 50 ns/division

Voltage and E-beam current waveforms from
Febetron 705 pulse generator



5 ns / horizontal division

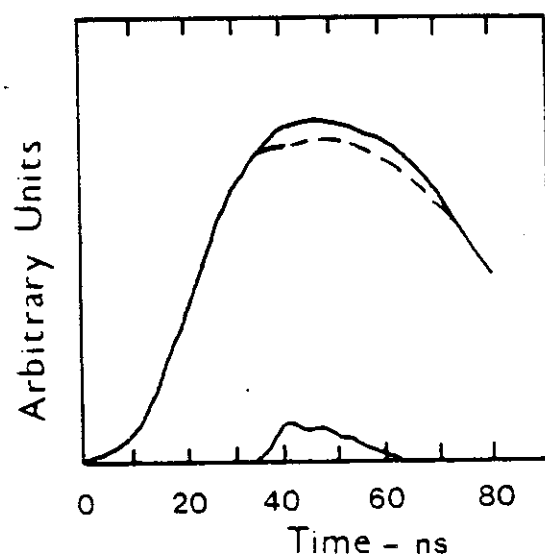
Oscilloscope trace of Lambda Physik EMG 101
laser pulse (249 nm)



Experimental arrangement for the vibrational relaxation time experiment

defined inside this cylinder by an aperture facing the incoming electron beam. This has the dual role of limiting the volume of excited gas from which fluorescence is detected to just that in which there is an overlap between the e-beam and the probe laser pulse as well as ensuring that the laser pulse can experience no significant gain while traversing the cell. The thyatron switches triggering the Febetron 705 and the Lambda Physik EMG 101 allowed the probe laser pulse to be synchronized to the centre of the ~ 50 ns electron beam pulse with an accuracy of $\sim \pm 5$ ns by the use of an electronic delay generator and also further cable delays. The laser beam was brought to a focus a few centimetres beyond the interaction region defined by the aperture in the cylinder in order to increase its intensity in this region while continuing to probe a large percentage of the e beam excited volume. The fluorescence from this interaction volume was collected by a lens and focused onto a fast response solar blind UV photodiode. A second metal cylinder leading from the interaction region to the quartz window through which the fluorescence was monitored prevented light from other regions in the gas cell also being collected.

The sidelight fluorescence, as detected by the photodiode, was displayed on a Tektronix 7834 Storage Oscilloscope. By triggering the oscilloscope from another photodiode aligned with a reflection of the incident laser beam the temporal position of the probe laser pulse with respect to a fluorescence trace and observed depletion could be precisely determined. Fig. 2.8 shows depleted and undepleted fluorescence traces superimposed, and also the temporal extent of the probe laser pulse.



Typical depleted (dashed curve) and undepleted (solid curve) fluorescence traces and the probe laser pulse (bottom curve)

2.4 Results and Discussion

Initially the cell was filled with a gas mixture comprising 6.5 mbar F_2 , 33 mbar Kr and 3.4 bar Ar, which is typical of electron beam pumped lasers. At these pressures the effective KrF^* fluorescence lifetime calculated according to equation (2.12) and using the quenching rate constants given in Table 2.2 (Ref. 59) is 0.6 ns. From a comparison of the depleted and undepleted fluorescence profiles, i.e. the fluorescence with and without the probe laser pulse traversing the e-beam excited region, the average observed maximum depth of depletion was $9 \pm 1\%$. From geometrical considerations the percentage of the excited volume whose fluorescence was being observed by the photodiode that was intersected by the probe laser pulse was $50 \pm 8\%$. Hence the maximum percentage depth of depletion in the interaction region is concluded to be $18 \pm 6\%$.

The computer model of the KrF laser medium described in Section 2.2.3 was used to estimate the vibrational relaxation time by comparison with this result. To do this the computer model was adjusted to model the experimental calculations as closely as possible. A good approximation of the calculated upper level population to the fluorescence profile was obtained by giving the pumping rate $P_2(t)$ the form

$$P_2(t) = P_{2max} \quad t / t_{rp} \quad : 0 < t < t_{rp}$$

$$P_2(t) = P_{2max} \quad (1 - (t - t_{rp}) / t_{fp}) \quad : t_{rp} < t < t_{rp} + t_{fp}$$

(2.21)

which is a triangular function which rises to a maximum value

$P_{2\max}$ in a time t_{rp} and falls back to zero in a time t_{fp} . A good fit was obtained for t_{rp} and t_{fp} both equal to 25 ns. The value of $P_{2\max}$ was found to have a negligible effect on the percentage depth of depletion, although it does affect the population $N_1(t)$ as increasing the pumping rate increases the number of excimers produced.

The parameter K in equation (2.11) which determines the ratio of the rates of collisional mixing from level 1 to 2 and from level 2 to 1 in the computer model was also found to have a negligible effect on the percentage depth of depletion for realistic values of the vibrational relaxation time τ_v . This is due to the fact that population lost from level 1 by excitation into the reservoir (level 2) is not lost to the system and can be rapidly transferred back to level 1 by collisional mixing in the opposite direction. The value of K was set at unity.

The function $F(t)$ representing the photon flux of the probe laser pulse was given the functional form

$$\begin{aligned}
 F(t) &= 0 & : 0 < t < t_1 \\
 F(t) &= F_{\max} \cdot (t - t_1) / t_{rl} & : t_1 < t < t_1 + t_{rl} \\
 F(t) &= F_{\max} \cdot (1 - (t - (t_1 + t_{rl})) / t_{fl}) & : t_1 + t_{rl} < t < t_1 + t_{rl} + t_{fl}
 \end{aligned}$$

(2.22)

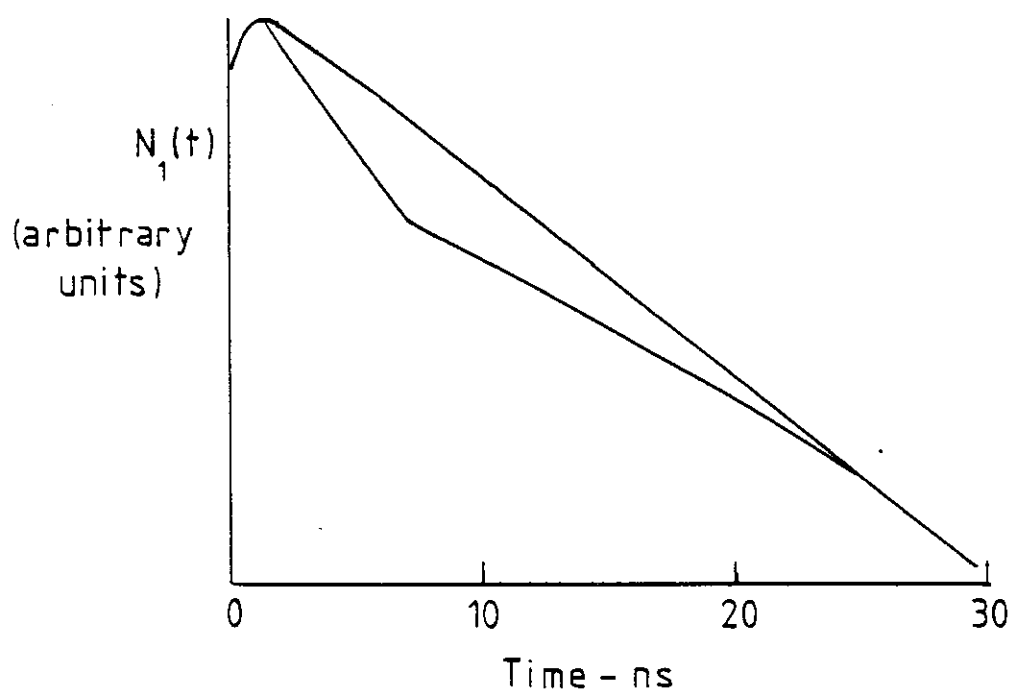
This is a function which has a linear rise in a time t_{rl} to a maximum value $F_{\max}$ and then a linear fall to zero in a time t_{fl} i.e. another triangular function. The values of t_{rl}

and t_{f1} that were measured to give a good representation of the actual laser pulse were 6 and 20 ns respectively. The time t_1 is the delay between the excitation of the gas mixture starting and the probe pulse reaching the interaction region and could be adjusted to match the experimental result under consideration. In this case the probe laser pulse was considered to begin at the centre of the pumping pulse, i.e. $t_1 = 25$ ns. The value of $F_{\max}$ was taken to be the peak photon flux of the probe laser pulse used in the experiment, measured to be $\sim 5 \times 10^{24} \text{ cm}^{-2} \text{ s}^{-1}$.

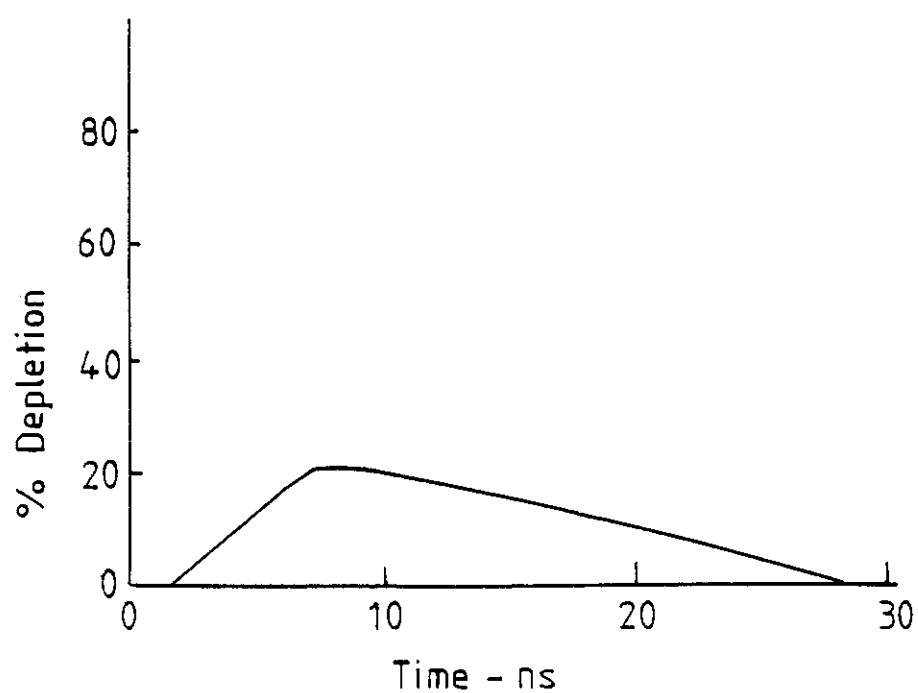
For a particular value of the vibrational relaxation time τ_v the numerical calculation was used to give the temporal profiles of the population $N_1(t)$ with and without the probe laser, as shown in Fig. 2.9a, and hence the percentage depth of depletion $D(t)$ in Fig. 2.9b. By compiling a series of these results for a range of values of τ_v the graph of maximum percentage depth of depletion against τ_v shown in Fig. 2.10 was determined.

When the experimentally measured maximum depletion of $18 \pm 6\%$ is compared with the graph in Fig. 2.10 it can be seen that the model predicts from this result an upper limit on the vibrational relaxation time of 450 ps.

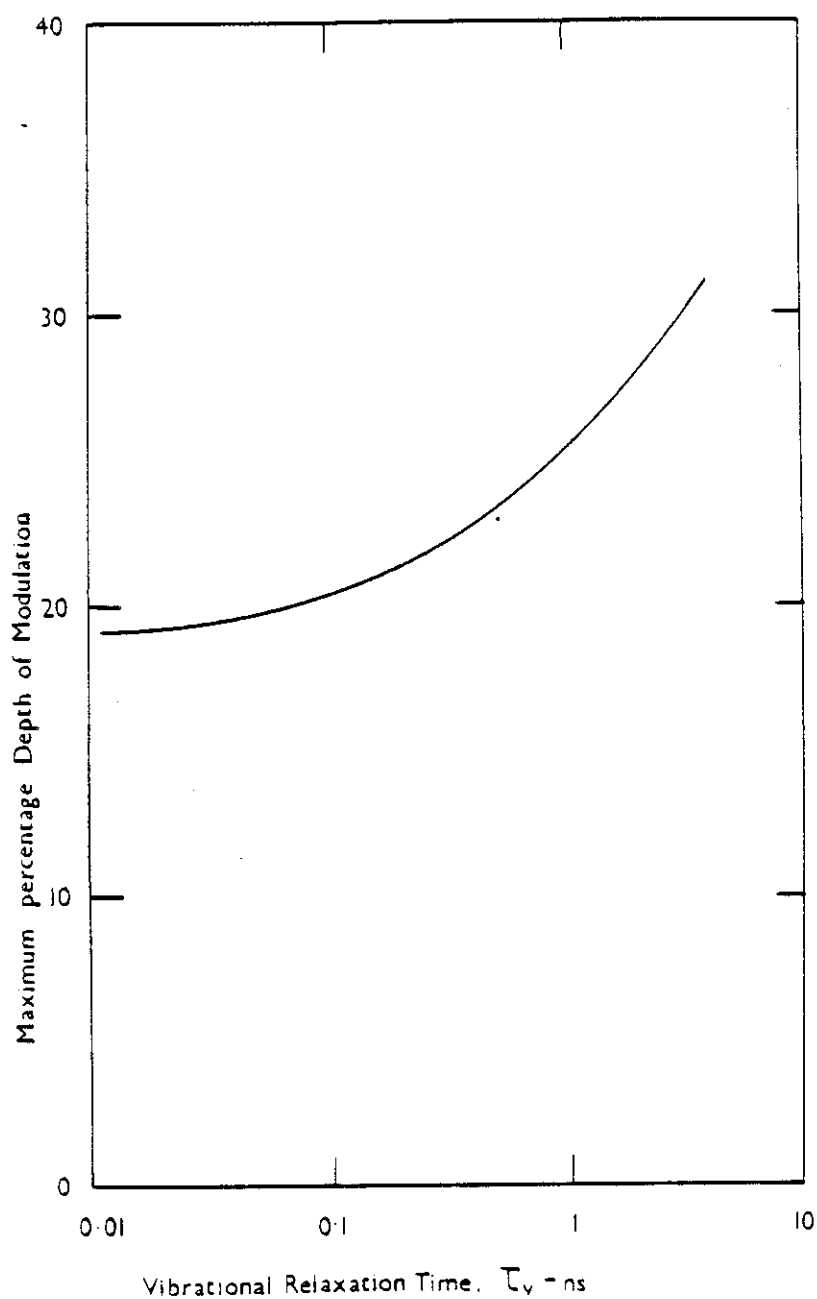
The low values of the maximum depletion of the sidelight fluorescence which are a consequence of the short vibrational relaxation time meant that it was difficult to determine accurately the temporal variation of the experimentally observed depletion. For this reason further results were taken with the interaction cell filled with a lower pressure gas mixture, namely 1 mbar F_2 , 20 mbar Kr and 1.3 bar Ar. At these lower pressures the coupling of the electron-beam energy



(a) Depleted and undepleted population $N_1(t)$ calculated by computer model



(b) Percentage depletion from (a)



Calculated dependence of maximum percentage depletion on vibrational relaxation time

to the gas is decreased with a consequent reduction in the intensity of the fluorescence and the kinetic processes are slowed, resulting in an increase of the fluorescence lifetime (calculated from equation (2.12) and Table 2.2) of KrF^* from 0.6 to 2.5 ns. The percentage depth of depletion is then increased for the same probe laser intensity.

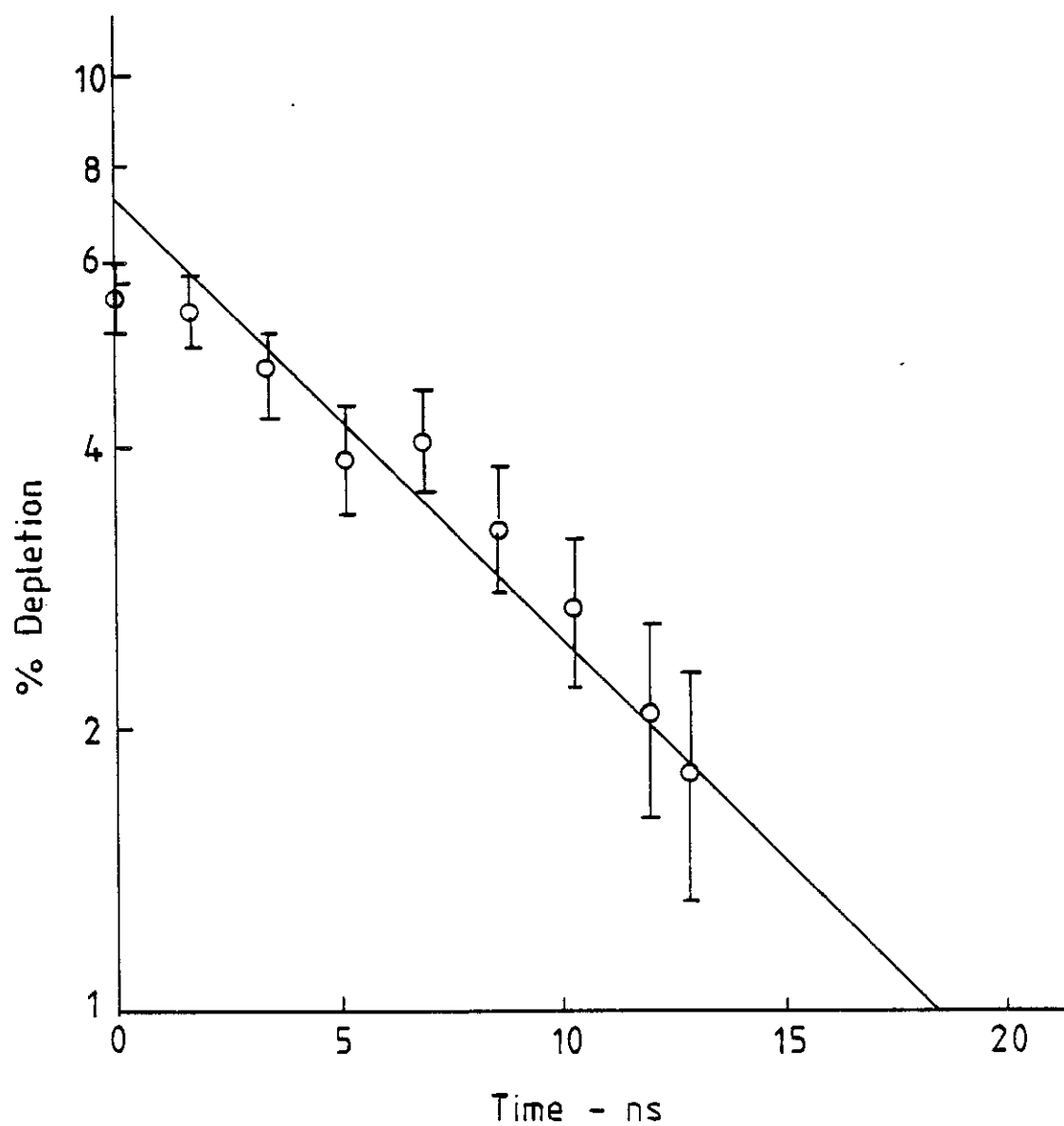
By measuring the percentage depletion from fluorescence traces such as the example in Fig. 2.8, graphs of the type shown in Fig. 2.11 could be obtained, showing the time dependence. By plotting the results on a logarithmic scale, the gradient of the best straight line fit gives the exponential recovery time of the sidelight fluorescence and hence of the upper laser level population and the gain. The graph in Fig. 2.11 gives the recovery time as 10.8 ± 3.0 ns. When the average of the results obtained was taken the exponential recovery time was concluded to be 11.5 ± 3.0 ns.

In order to simulate the conditions of this experiment with the computer model, the function $F(t)$ which had previously been given a linear fall as described in equation (2.22) was changed to the form

$$\begin{aligned}
 F(t) &= 0 & : 0 < t < t_1 \\
 F(t) &= F_{\max} \cdot (t - t_1) / t_{rl} & : t_1 < t < t_1 + t_{rl} \\
 F(t) &= F_{\max} \exp(-(t - (t_1 + t_{rl})) / \tau_{fl}) & : t > t_1 + t_{rl}
 \end{aligned}$$

(2.23)

i.e. it was given an exponential decay with e-folding time τ_{fl}

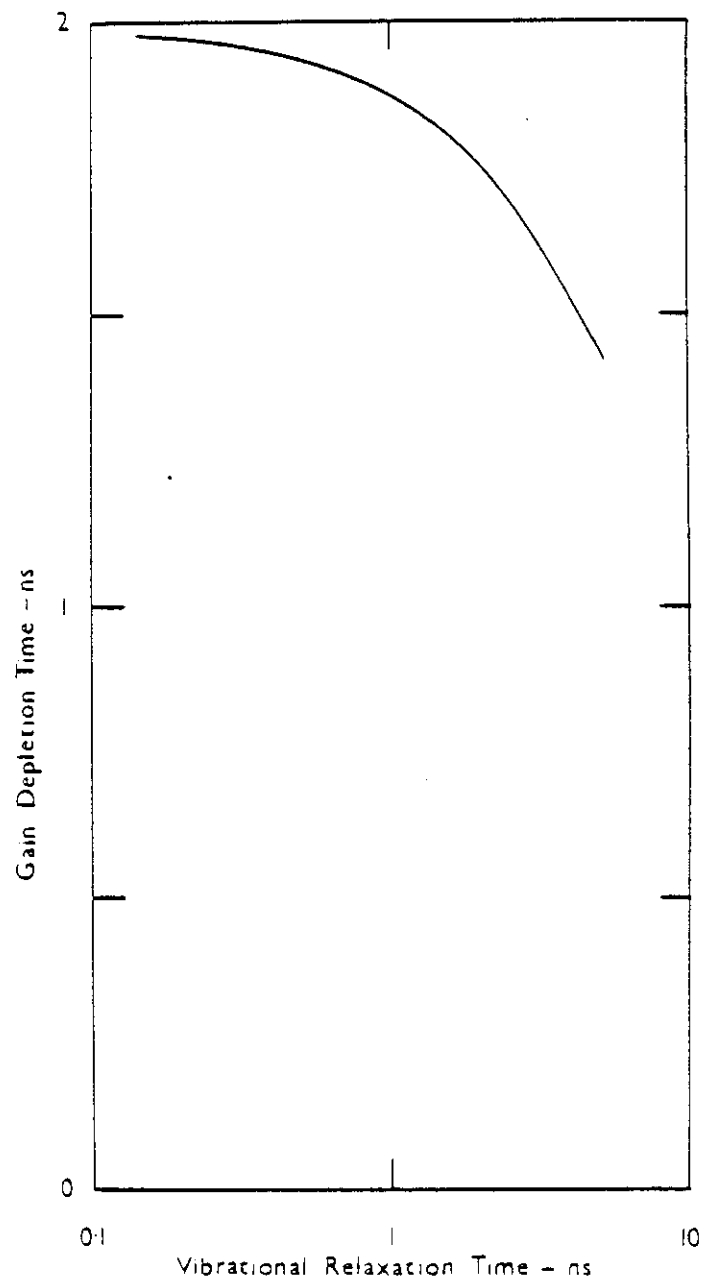


Percentage depletion of sidelight fluorescence
with time for a single fluorescence trace

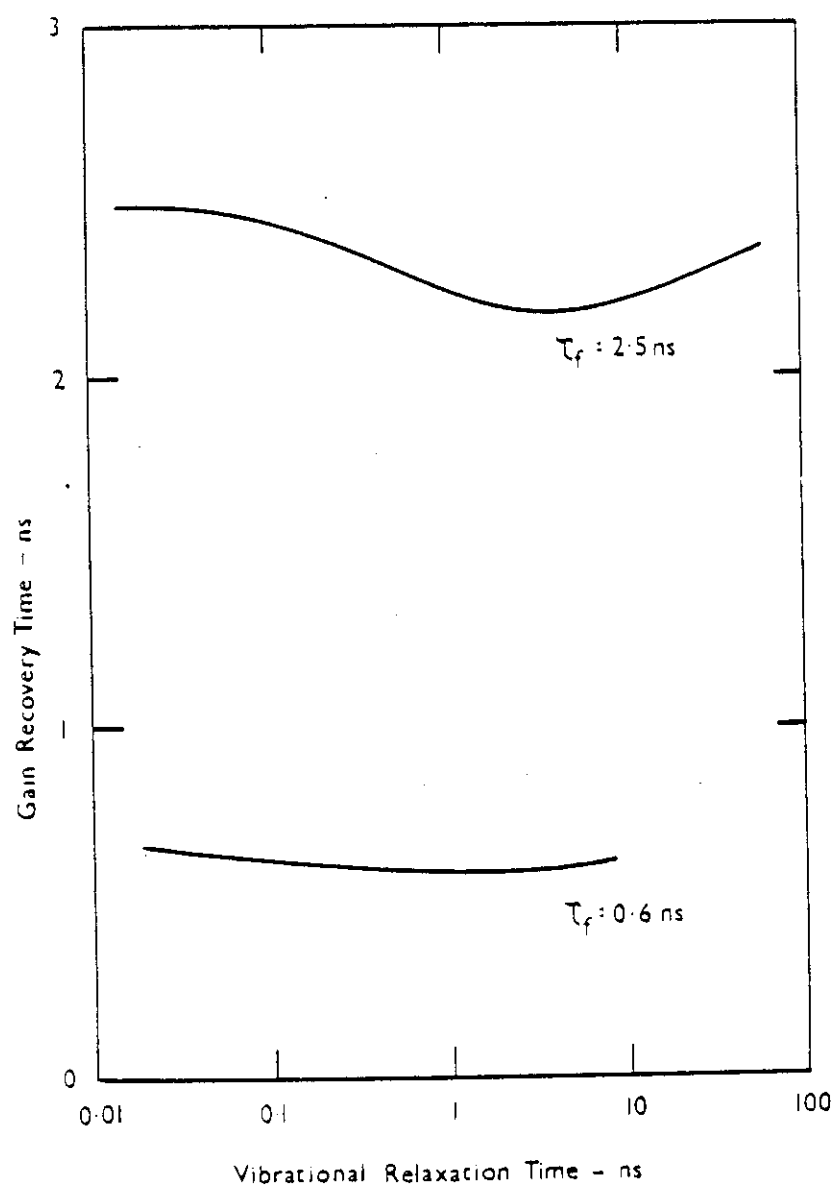
to reflect more accurately the shape of the actual laser pulse used in the experiment. From a measurement of the exponential decay of the laser pulse τ_{f1} was found to be 4.7 ± 0.3 ns, and this value was used in the model. It was assumed that the vibrational relaxation time τ_v scales inversely with gas pressure as in a two body process⁽⁴¹⁾ in order to calculate the expected vibrational relaxation time from the upper limit of 450 ps at the higher gas pressure of 3.5 bar.

The exponential recovery time predicted by the computer model under these conditions is 8.0 ± 1.0 ns, which agrees with the experimental result within the limits of measurement. The computer model can, then, provide an approximation to the behaviour of the real KrF^* system and hence make further predictions about it.

The model was used to predict the intrinsic gain depletion and recovery times, as defined in section 2.2.3, i.e. to remove the dependence on the temporal variation of the probe laser pulse. Fig. 2.12 shows the variation of the intrinsic gain depletion time with the vibrational relaxation time τ_v for a fluorescence lifetime τ_f of 2.5 ns. Fig. 2.13 shows the predicted variation of the intrinsic gain recovery time with τ_v for the fluorescence lifetimes of 2.5 and 0.6 ns calculated for the two gas pressures used in the experiment (the percentages of the constituents present remained the same for both). It can be seen that the intrinsic gain recovery time and, at low values of τ_v , the intrinsic gain depletion time, do not have a significant dependence on vibrational relaxation time, τ_v , and in fact, for the short vibrational relaxation times the experiment has suggested these parameters are approximately equal to the fluorescence lifetime of the upper laser level τ_f .



Calculated Intrinsic Gain Depletion Time against
 τ_v for $\tau_f = 2.5$ ns

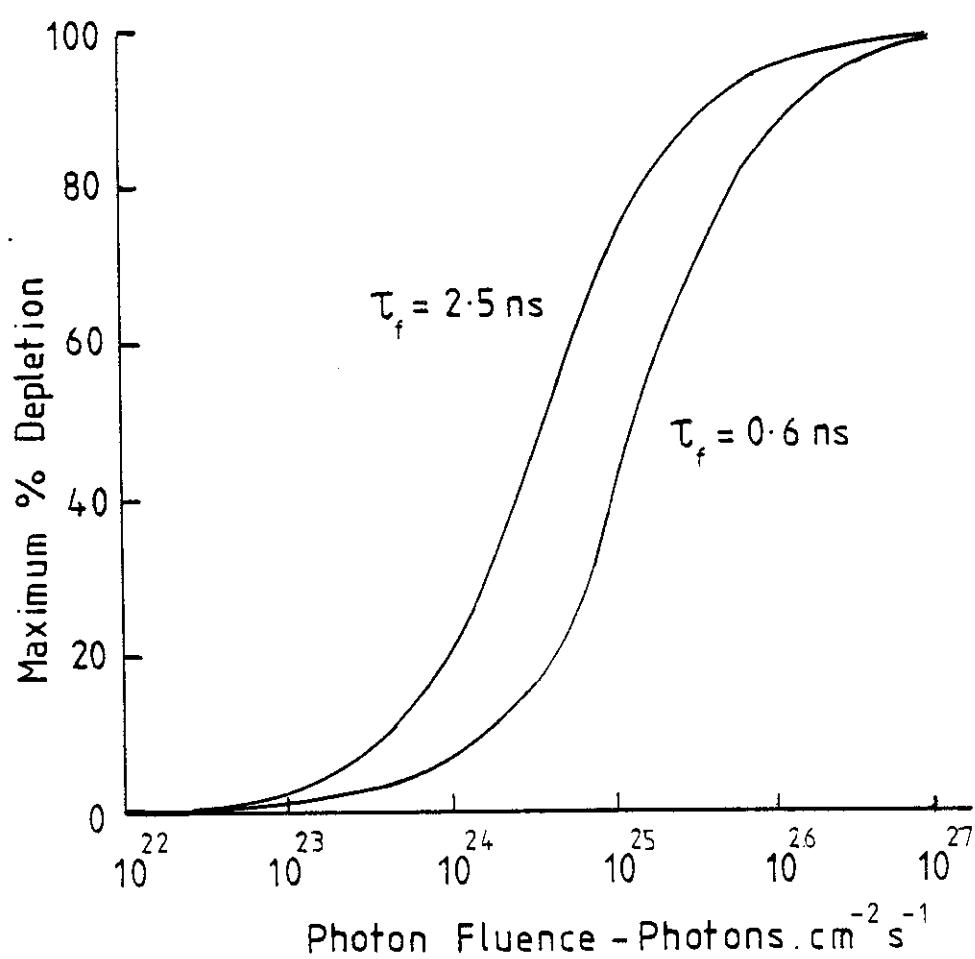


Calculated Intrinsic Gain Recovery Time against τ_v for $\tau_f = 2.5$ and 0.6 ns

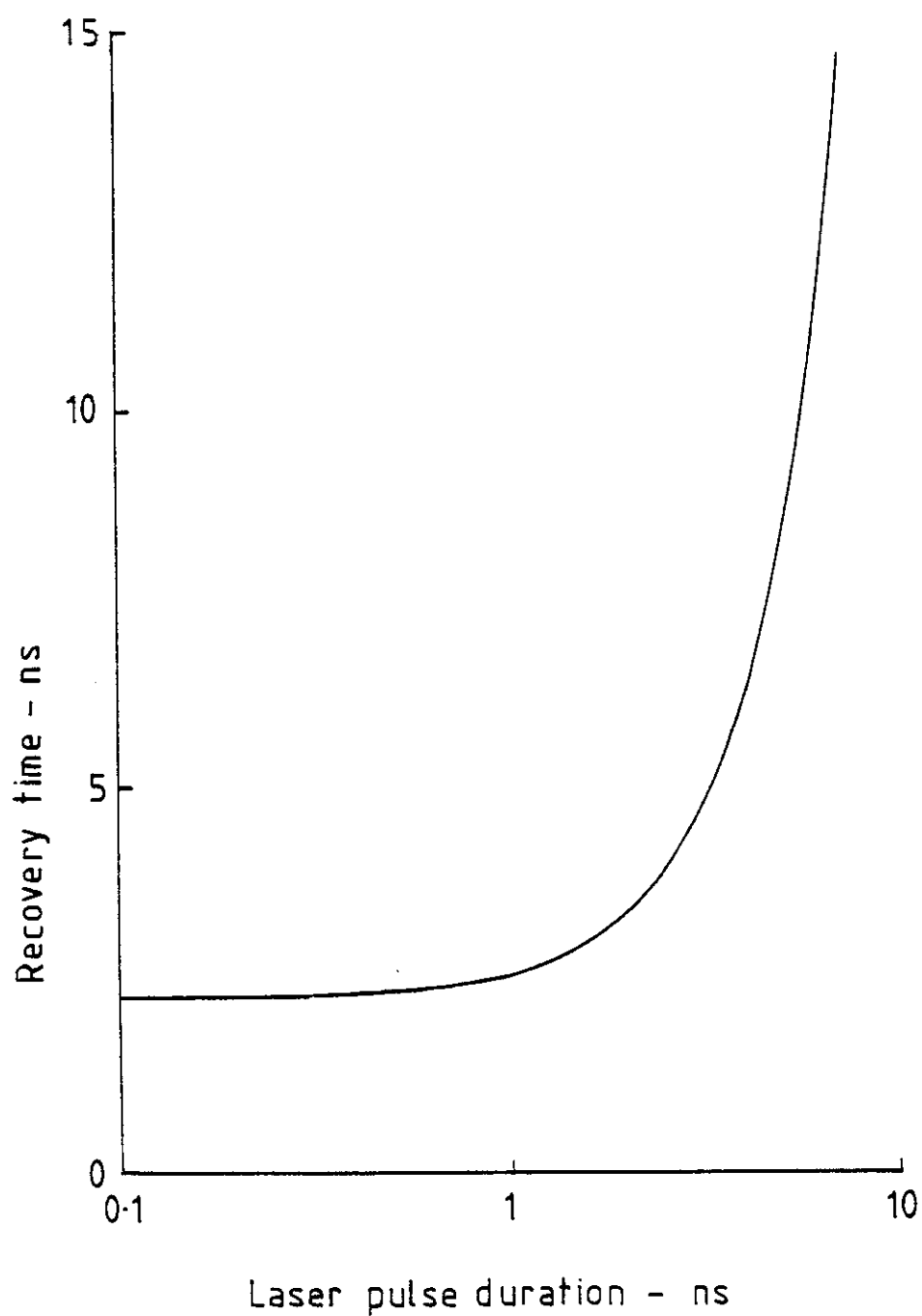
Fig. 2.14 shows how the maximum depth of depletion would be expected to vary with laser intensity (photons $\text{cm}^{-2} \text{s}^{-1}$) for the two values of τ_f (2.5 and 0.6 ns). The laser intensity would have to be increased by two orders of magnitude to approach 100% depletion. It is also possible to deduce how short a saturating laser pulse would have to be in order for the intrinsic gain recovery time to be directly observable. Fig. 2.15 shows how the observed gain recovery time would approach the intrinsic value with a reduction of the laser pulse duration. It can be seen that two become approximately equal for pulse lengths of the order of 1 ns.

The result obtained for τ_v (< 450 ps at 3.5 bar total pressure) is consistent with work by Jacob et al.⁽⁴¹⁾, where they quote a two body rate constant for vibrational relaxation of $5 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}$. This yields a value of 180 ps at 3.5 bar Ar which should be considered an upper limit as the relaxation time may be reduced by three body collisions. However, Pummer et al.⁽⁴²⁾ report a value for τ_v of 4 ± 2 ns determined from the decay of the observed depletion of the sidelight fluorescence in the tail of a saturating laser pulse. As shown in Fig. 2.13, the results of the computer model suggest that the recovery time has only a weak dependence on the vibrational relaxation time and so could not easily be used to determine its value. Furthermore, the computer model was able to reproduce a similar fluorescence profile to that given in Ref. 42 with a value of τ_v of 450 ps in contrast to the value of 4 ± 2 ns of Pummer et al. The two results are shown for comparison in Fig. 2.16 a and b. In Ref. 42 it is concluded that the limited depletion observed (35%) is due to incomplete vibrational relaxation within the $B(\frac{1}{2})$ state, whereas the results presented here suggest that this is in fact due to the vibrational relaxation

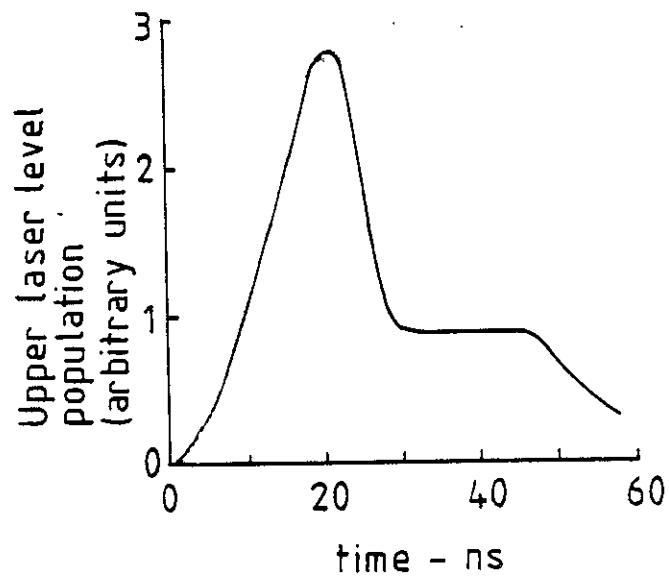
FIG. 2.14



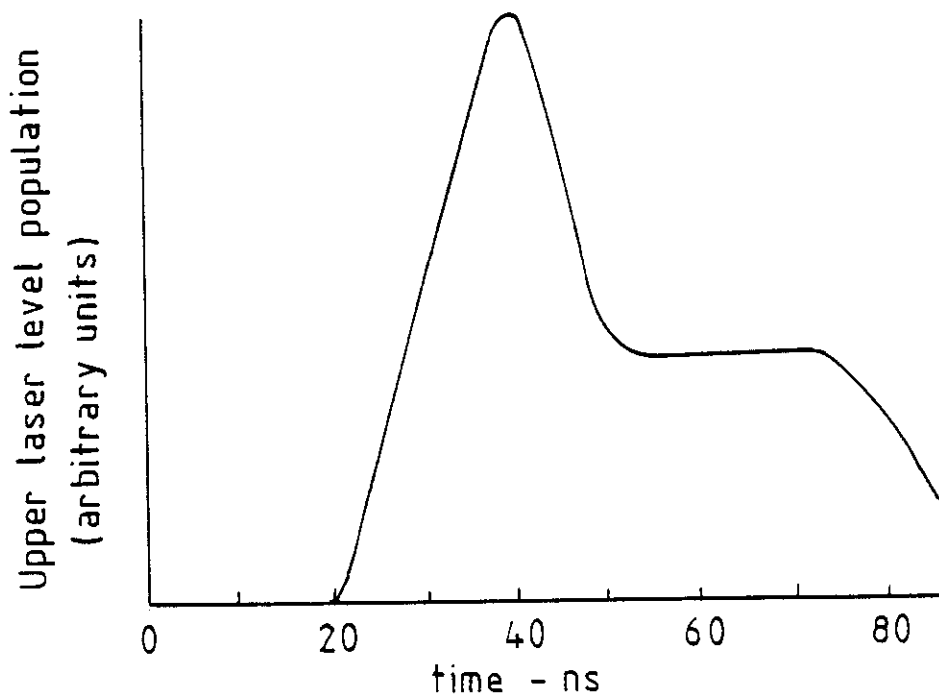
Calculated maximum percentage depletion against probe laser photon flux F for $\tau_f = 2.5$ and 0.6 ns



Calculated variation of gain recovery time with
laser pulse duration



(a) Experimental results from Ref. 42



(b) Results of computer simulation

Simulation of results given in Ref. 42 by computer model with $\tau_v = 450$ ps

being so fast that an equilibrium is reached between the stimulated emission and the pumping into the B state. The recovery time is then approximately equal to the fluorescence lifetime of the upper laser level, which is more consistent with the value of 4 ± 2 ns measured by Pummer et al⁽⁴²⁾.

Chapter 3

The Four Wave Mixing Experiment : Theory

3.1 Introduction

Since the advent of the laser in the early 1960s knowledge of atomic and molecular structure has been extended by techniques such as state selective spectroscopy. Such methods were for many years restricted to the visible and infra-red regions of the spectrum due to the lack of tunable light sources in the vacuum ultra-violet of sufficiently small linewidth. However, VUV sources, including the one described in this work, are becoming available and will open up the VUV region to high resolution spectroscopy.

There are in principle two different methods for the generation of coherent radiation in the VUV. First, stimulated emission can occur in systems such as the noble gas excimers. These are tunable, but, due to the poor quality of optical resonators in the VUV, they have linewidths of 10 cm^{-1} or larger, whereas high resolution spectroscopy requires a linewidth of 0.1 cm^{-1} or smaller. So far, systems of this kind are only possible by means of up conversion of high quality lasers operating in the visible part of the spectrum.

Frequency mixing and harmonic generation have been carried out for some time using nonlinear crystals and wavelengths as short as 217 nm can be generated⁽⁷¹⁾. However, in the VUV these crystals generally become opaque and can no longer be used.

Ward and New⁽⁷²⁾ were the first to demonstrate four wave mixing in gases, in their case the generation of the third harmonic of a ruby laser giving 231.4 nm radiation. The non-

linearities of gases are weak compared to those in crystalline solids due to the much lower densities. Therefore conversion efficiencies are low unless the nonlinearities can be enhanced by a resonance with an atomic transition.

At Stanford University researchers^(73,74,75) used metal vapours to provide practical sources of coherent VUV radiation by third harmonic generation. The first ionization potentials of these elements are lower than those in the rare gases, and so their various bound excited states lie in an energy range where resonant enhancement is possible due to coincidence of transitions with the energy of the visible input or VUV third harmonic output beams. Other groups^(76,77,78) utilized the further advantages to be gained by attaining an exact two photon resonance, namely the lack of linear absorption or dispersion⁽⁷⁹⁾ that occurs when a single or three photon resonance is used. In the experimental work mentioned above⁽⁷³⁻⁷⁸⁾ the input laser beams were of a fixed frequency. The use of tunable dye lasers pumped by nitrogen⁽⁸⁰⁾ or excimer lasers would enable the VUV radiation generated to be tuned.

Non resonant four wave mixing was reported in Xenon as early as 1974⁽⁸¹⁾. The high ionization potentials of the rare gases means that a two photon resonance will only occur for input beams with ultra violet wavelengths. There is a two photon resonance involving the $6p [0\frac{1}{2}]$ state in Xenon at

$\lambda = 249.6$ nm which was utilized by Egger et al⁽³²⁾ to enhance frequency tripling of the output of a KrF excimer laser and by workers at the University of Maryland⁽⁸²⁾ for two photon resonant upconversion with an Nd:YAG laser and a dye laser. Both these systems^(32,82) gave a fixed frequency output whereas the system built during the course of the work described here allows tuning of the VUV output by the use of a tunable dye

laser and a narrowband KrF source tuned to the 6p [0 $\frac{1}{2}$] two photon resonance. The laser system was outlined in Chapter 1 and will be described in detail in Chapter 4.

Third harmonic generation, which has been mentioned above, is a special case of the four wave mixing process

$$\omega_4 = \omega_1 + \omega_2 + \omega_3 \quad (3.1)$$

where $\omega_1 = \omega_2 = \omega_3$ (3.2)

Processes can also occur where

$$\omega_4 = \omega_1 + \omega_2 - \omega_3 \quad (3.3)$$

and $\omega_4 = \omega_1 - \omega_2 - \omega_3$ (3.4)

In the particular case of the experiment being considered

$$\omega_1 = \omega_2 \quad (3.5)$$

and is the frequency of the radiation at $\lambda = 249.6$ nm. The frequency ω_3 is that of the visible dye laser taking part in the mixing process. Two processes can occur, giving

$$\omega_4 = 2\omega_1 + \omega_3 \quad (3.6)$$

and $\omega_4 = 2\omega_1 - \omega_3$ (3.7)

These are known as sum and difference frequency mixing respectively.

The VUV frequencies generated by the sum frequency mixing process will lie close to the ionization continuum, a region with a dense population of states where the conditions of phase matching, which will be discussed later in this chapter,

will be hard to achieve. Also, the wavelengths generated are close to or beyond the cut off point for the transmission of VUV window materials. Therefore the difference frequency mixing process was used for the system's initial development and investigation, which is the subject of this work. The rest of this chapter describes the theory of the four wave difference frequency mixing process used in the experiment.

3.2 Theory

3.2.1 Nonlinear Processes

An electromagnetic wave propagating through a medium will induce a polarization in that medium. When the amplitude of the electromagnetic wave is small the polarization P is directly proportional to the electric field, i.e.

$$\underline{P} = \epsilon_0 \chi^{(1)} \underline{E}$$

where $\chi^{(1)}$ is the bulk linear susceptibility of the medium and ϵ_0 is the permittivity of free space. The refractive index n is related to $\chi^{(1)}$ by

$$\chi^{(1)} = n^2 - 1$$

However, this is only a special case valid for low electric fields. The induced polarization has, in general, contributions due to other non-linear terms whose influence only becomes apparent for large applied fields. The polarization is more correctly expressed as

$$\underline{P} = \epsilon \left(\overset{(1)}{\chi} \underline{E} + \overset{(2)}{\chi} \underline{E}^2 + \overset{(3)}{\chi} \underline{E}^3 + \dots \right)$$

Therefore, if a sinusoidal field

$$E = E_0 \cos \omega_1 t$$

is applied, part of the polarization induced will have a frequency $3 \omega_1$

$$P_3 \propto \chi^{(3)} \cos 3\omega_1 t$$

and hence gives rise to third harmonic generation.

For the case of interest here, where there are two input beams at frequencies ω_1 and ω_3 the electric field due to the fundamental beams will be

$$E = E_1 \cos \omega_1 t + E_2 \cos \omega_2 t$$

and a part of the polarization induced will oscillate at a frequency $2\omega_1 - \omega_3$. The calculation of the nonlinear susceptibility for this process will be discussed later.

From symmetry considerations it is apparent that four wave mixing processes can only occur in centrosymmetric media, i.e. those possessing a centre of symmetry, such as gases, whereas second harmonic generation can only occur in non centrosymmetric media. In symmetric media the term $\chi^{(2)}$ will be zero.

3.2.2 Four Wave Mixing with Tightly Focused Beams

To generate the high electric fields needed for nonlinear processes to occur it is usually necessary to focus the laser beams into the media being used. Four wave mixing processes under these conditions have been studied extensively, notably by Ward and New⁽⁷²⁾ and Miles and Harris⁽⁸³⁾, who treated the

special case of third harmonic generation. More recently Bjorkland⁽⁸⁴⁾ dealt with four wave mixing processes without making any such simplifying assumptions, and the analysis presented here closely follows his work, but applied specifically to difference frequency mixing with two of the input beams being degenerate, i.e.

$$\omega_4 = 2\omega_1 - \omega_3 \quad (3.7)$$

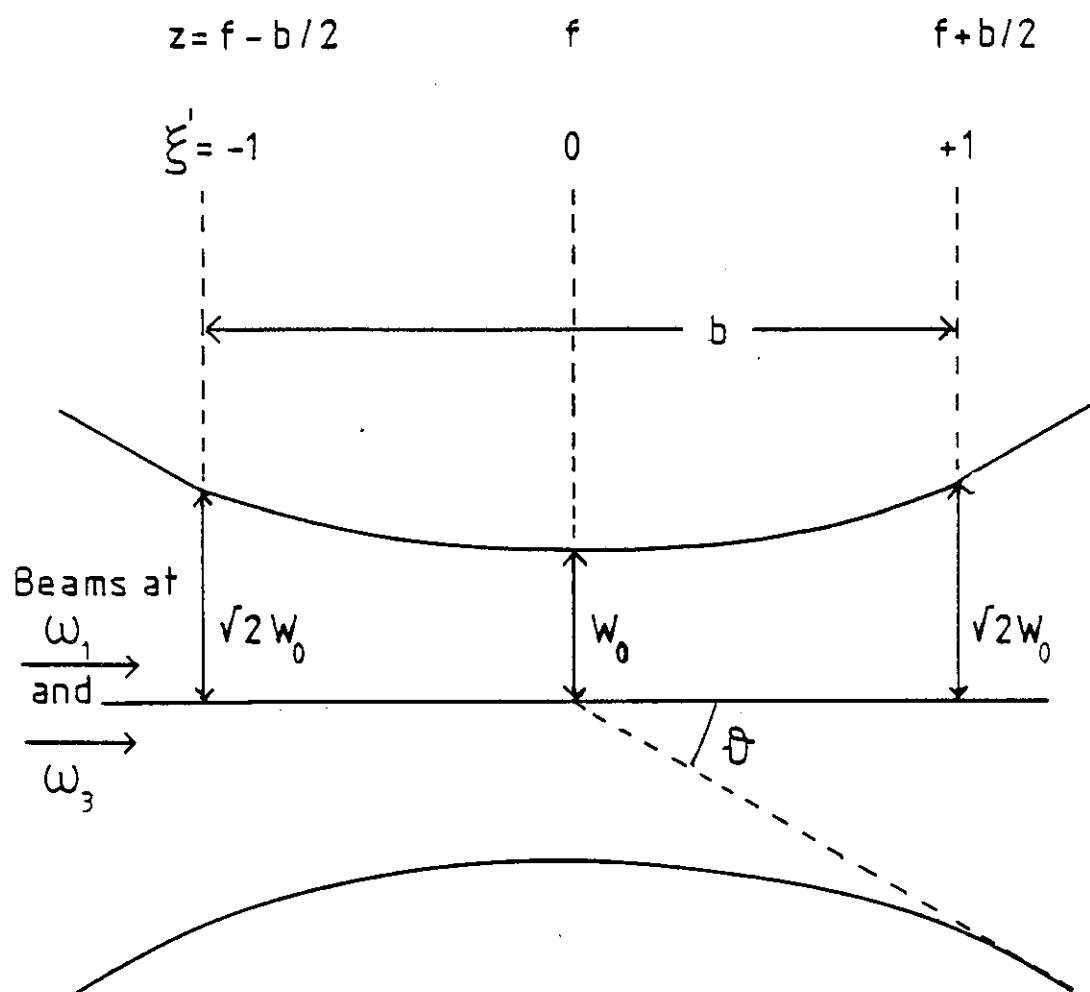
The fundamental beams at ω_1 and ω_3 are assumed to be lowest order Gaussian modes propagating concentrically along the z axis and are assumed to have identical waist locations and geometries. The geometry of the two focused Gaussian beams is depicted in Fig. 3.1. The confocal beam parameter b is defined such that $b/2$ is the distance from the centre of the beam waist in which the beam area doubles.

If the fundamental and generated beams are all assumed to be linearly polarized in the same direction, the vector nature of the electric fields as well as the tensor nature of the nonlinear susceptibility may be neglected. If the wavevectors of the fundamental beams at frequencies ω_1 and ω_3 in the nonlinear medium are taken as k_1 and k_3 respectively and the electric field amplitudes as E_{10} and E_{30} respectively, then the fundamental electric field is given by

$$E(r, t) = \text{Re}[E_1(r) \exp(-i\omega_1 t) + E_3(r) \exp(-i\omega_3 t)] \quad (3.8)$$

with E_n , where $n = 1$ and 3 , given by the theory of Boyd and Gordon⁽⁸⁵⁾ as

$$E_n(r) = E_{n0} \exp(ik_n z) (1 + i\xi)^{-1} \exp[-k_n(x^2 + y^2)/b(1 + i\xi)] \quad (3.9)$$



$$\xi' = 2(z - f)/b \quad w(\xi') = (1 + \xi'^2)^{1/2} w_0$$

$$b = 2\pi w_0^2 / \lambda \quad \theta = \lambda / \pi w_0$$

Geometry for focusing of gaussian beams

where b is the confocal parameter and

$$b = \frac{2\pi w_0^2}{\lambda} = \frac{2\pi w_0^2 n}{\lambda_0} = \frac{2\lambda_0}{n\theta^2} = kw_0^2 \quad (3.10)$$

where w_0 is the beam waist radius, n is the index of refraction, λ_0 is the vacuum wavelength, θ is the far field diffraction half-angle and ξ is a normalized co-ordinate along the z axis defined by

$$\xi = \frac{2(z-f)}{b} \quad (3.11)$$

where f is the position of the focus (beam waist) along the z axis, as shown in Fig. 3.1.

Equation (3.9) describes the phase difference between the Gaussian beam and an ideal plane wave, the reduction of the electric field amplitude away from the z axis and, due to the expansion of the beam, its reduction along the z axis.

Since all the beams involved have been assumed to be linearly polarized in the same direction, the tensor nature of the nonlinear susceptibility can be neglected and the driving polarization at frequency ω_4 is given by

$$P_4(r, t) = \text{Re} [P_4(r) \exp(-i(\omega_4 t))] \quad (3.12)$$

where

$$P_4(r) = \frac{3}{4} N \chi(-\omega_4; \omega_1, \omega_1, -\omega_3) E_1^2(r) E_3^*(r) \quad (3.13)$$

with χ being the nonlinear susceptibility for the difference frequency mixing process at the frequencies being used and N being the number density of the atoms of the nonlinear medium.

The nonlinear medium is considered to occupy the semi-infinite space $z > 0$ with the space $z < 0$ considered to be a vacuum. Then from (3.9) and (3.13) the driving polarization induced at frequency ω_4 is :-

$$\begin{aligned}
 P_4(r) = & \frac{3}{4} N X (-\omega_4; \omega_1, \omega_1, -\omega_3) E_{10}^2 E_{30} B(z) \\
 & \times \exp(ik'z) (1 + i\xi)^{-2} (1 - i\xi)^{-1} \\
 & \times \exp\left[\frac{(-k'' + i\xi k')(x^2 + y^2)}{b(1 + \xi^2)} \right]
 \end{aligned}
 \tag{3.14}$$

where

$$k' = 2k_1 - k_3 \tag{3.15}$$

and

$$k'' = 2k_1 + k_3 \tag{3.16}$$

Bjorkland⁽⁸⁴⁾ then performs a Fourier decomposition of $P_4(r)$ to give the amplitude of the plane-wave component $P_4(K)$ with wavevector K defined by

$$P_4(K) = (2\pi)^{-3} \int_{-\infty}^{\infty} dx'' \int_{-\infty}^{\infty} dy'' \int_{-\infty}^{\infty} dz'' P_4(r'') \exp(-i \underline{K} \cdot \underline{r}'') \tag{3.17}$$

If $E_{4(k)}(r)$ is defined as the generated radiation field arising

from the plane wave component of the driving polarization with wave vector $\underline{K}$ it can be shown to be related to $P_4(\underline{K})$, using Maxwell's Equations, by

$$\begin{aligned}\nabla \times \nabla \times \underline{E}_{4(\underline{K})}(\underline{r}) - k_4^2 \underline{E}_{4(\underline{K})}(\underline{r}) \\ = 4\pi k_0^2 P_4(\underline{K}) \exp(i\underline{K} \cdot \underline{r})\end{aligned}\quad (3.18)$$

where k_4 and k_0 are the wave vectors of the generated radiation in the nonlinear medium and in vacuum respectively. Equation (3.17) may be solved subject to the boundary condition that the tangential component of $\underline{E}_{4(\underline{K})}$ vanishes at the vacuum-medium interface. If $K_x, K_y \ll K_z$ and $|\underline{K}| - k_4 \ll |\underline{K}|$, k_4 where K_x, K_y and K_z are the components of $\underline{K}$ in the x, y and z direction respectively (3.17) has the solution⁽⁸⁶⁾

$$\underline{E}_{4(\underline{K})}(\underline{r}) = i[2\pi k_0^2 z/k_4] g(U_K) \exp(i\underline{K} \cdot \underline{r}) P_4(\underline{K}) \quad (3.19)$$

where

$$U_K = iz[K_z - k_4 + (K_x^2 + K_y^2)/2k_4] \quad (3.20)$$

and

$$g(x) = [1 - \exp(-x)]/x = \int_0^1 \exp(-xp) dp \quad (3.21)$$

We define the wavevector mismatch by

$$\Delta K = k_4 - k \quad (3.22)$$

This is determined by the refractive indices at the frequencies ω_1 , ω_3 and ω_4 . It should be noted that this has the opposite sign to the convention adopted by Ward and New⁽⁷²⁾.

Substituting $k_4 = k' + \Delta k$ and $p = \frac{-\frac{1}{2}b(\xi' - \xi)}{z}$ into (3.20) and (3.21) and assuming that $\Delta K \ll k_4$, k' it is found that

$$g(U_k) = (b/2z) \int_{-\zeta}^{\xi} d\xi' \exp\{ib[K_z - k' + (K_x^2 + K_y^2)/2k' - \Delta k] \\ \times (\xi' - \xi)/2\} \quad (3.23)$$

where $\xi = 2(z - f)/b$ and $\zeta = 2f/b$

The total generated field $E_4(r)$ is then found by combining all the $E_4(k)(r)$.

$$E_4(r) = \int_{-\infty}^{\infty} dK_x \int_{-\infty}^{\infty} dK_y \int_{-\infty}^{\infty} dK_z E_{4(k)}(r) \quad (3.24)$$

$E_{4(k)}(r)$ is defined by (3.19), (3.23) and (3.17).

By integrating over K_z , z'' , x'' , y'' , K_x and K_y in turn the solution is obtained

$$E_4(r) = i \frac{3N\pi k_0^2 b}{2k_4} (-\omega_4; \omega_1, \omega_1, -\omega_3) E_0^2 E_{30} \\ \times \exp(ik'z) \times \int_{-\zeta}^{\xi} d\xi'$$

$$\times \frac{\exp[-(ib/2) \Delta k (\xi' - \xi)] \exp[-(x^2 + y^2)/bH]}{(1 + i\xi') (k'' - ik'\xi') H} \quad (3.25)$$

where

$$H = H(\xi, \xi') = \frac{(1 + \xi'^2)}{(k'' - ik'\xi')} - \frac{i(\xi' - \xi)}{k'} \quad (3.26)$$

Assuming the non-linear medium to be contained in a cell of length L with the location of the focus being at $z = f$, then with

$\xi = 2(L-f)/b$, $\xi' = 2f/b$ and $z = L$, equation (3.25) completely describes the amplitude of the generated field at the plane of the output window.

It can be seen from (3.25) that for the difference frequency process $E_4(r)$ is not in general a single Gaussian mode except in the case when $k'' = k'$ in which case

$$H = \frac{(1 + \xi'^2)(1 + i\xi')}{k'} \quad (3.27)$$

The multimode output of the difference frequency mixing process may be explained as resulting from a mismatch between the size of the driving polarization beam waist and the size of the generated radiation beam waist which would correspond to the confocal parameter of the input beams.

$E_4(r)$ is circularly symmetric about the z axis and the total generated power at ω_4 is found by evaluating integrals of the form

$$\int_0^{\infty} 2\pi R |E_4(R)|^2 dR \quad (3.28)$$

where $R = (x^2 + y^2)^{\frac{1}{2}}$ and $z = L$.

If the dimensionless function $F(b\Delta k, b/L, f/L, k''/k')$ is defined as

$$F(b\Delta k, b/L, f/L, k''/k') = \frac{8 k_4^2 k'}{9 \pi^3 k_0^4} \frac{1}{b^3 |\chi|^2 |E_{10}^2 E_{30}|^2} \int_0^{\infty} 2\pi R |E_4(R)|^2 dR \quad (3.29)$$

then with wave vectors in units of cm^{-1} , b in centimetres, N in atoms/cubic centimetre and χ in ESU per atom the total generated power P_4 in Watts is given by

$$P_4 = 1.580 \times 10^{-4} \frac{k_0^4 k_1^2 k_3}{k_4^2 k} N^2 |\chi|^2 P_1^2 P_3 \times F(b\Delta k, b/L, f/L, k'', k') \quad (3.30)$$

where P_1 and P_3 are the total powers of each of the fundamental beams.

Thus the power of the output beam of the mixing process at frequency ω_4 is proportional to the power of the beam at ω_3 and the square of the power at ω_1 where

$$\omega_4 = 2\omega_1 - \omega_3 \quad (3.7)$$

It is also related to the function $F(b\Delta k, b/L, f/L, k''/k')$ which, substituting (3.25) into (3.29), is given by

$$F(b\Delta k, b/L, f/L, k''/k') = \frac{2k'}{\pi b} \int_0^\infty 2\pi R dR \times \left| \int_{-\zeta}^{\xi} d\xi' \frac{\exp[-(ib/2) \Delta k \xi']}{(1+i\xi')(k'' - k'\xi')H} \exp[-R^2/bH] \right|^2 \quad (3.31)$$

with H defined by (3.25) and k^1 and k^{11} defined by (3.15) and (3.16).

3.2.3 Phase Matching and Calculation of Δk

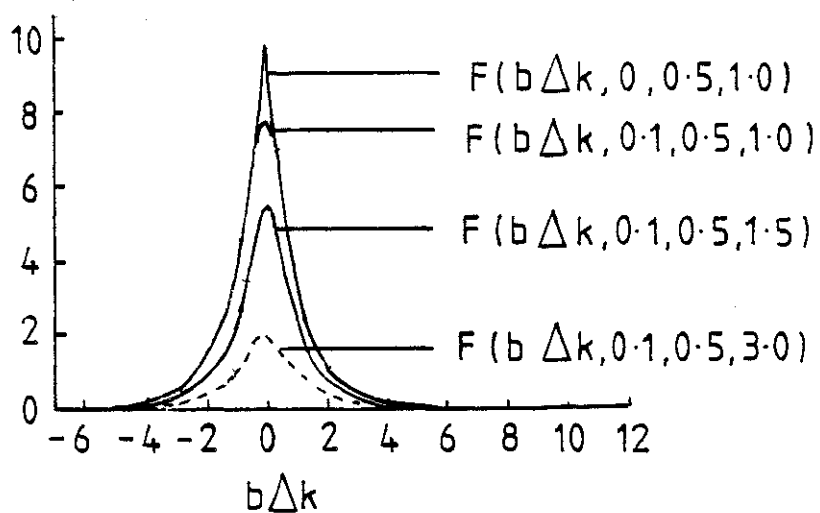
Equation (3.31) may be solved analytically in the tight focusing limit where b is short compared to the cell, the entire focal region is contained within the cell ($\xi, \zeta \rightarrow \infty$) and imposing the constraint that $k'' = k^1$ to give

$$F(b\Delta k, 0, 0.5, 1) = \pi^2 \exp[-b|\Delta k|] \quad (3.32)$$

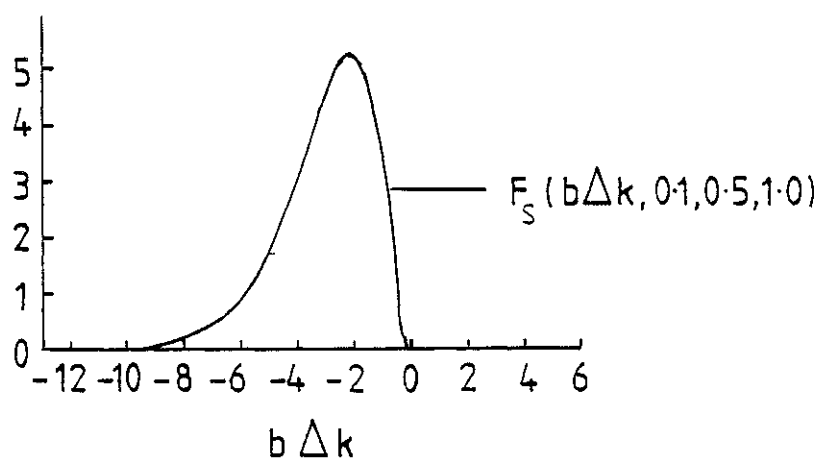
The calculation of the parameter Δk will be discussed presently.

Fig. 3.2a shows the shape of $F(b\Delta k, b/L, f/L, k''/k')$ for both the above case and when $b/L = 0.1$ with the function shown for values of $k^{11}/k^1 = 1.0, 1.5, 3.0$. For the experiment we are considering $k^{11}/k^1 = 1.5$, shown by the solid line.

(from Ref. 84)



(a) $F(b\Delta k, f/L, b/L, k''/k')$ for difference frequency mixing



(b) $F_S(b\Delta k, f/L, b/L, k''/k')$ for sum frequency mixing

Bjorkland⁽⁸⁴⁾ also derives a function $F_s(b \Delta k)$ for the sum frequency mixing process $2\omega_1 + \omega_3 \longrightarrow \omega_4$

$$F_s(b \Delta k, b/L, f/L, k''/k') = \left| \int_{\xi}^{\xi'} \frac{\exp[-(ib/2) \Delta k \xi']}{(1 + i \xi')^2} d\xi' \right|^2 \quad (3.33)$$

the total power generated still being given by (3.30) with F_s substituted for F . The curve $F_s(b \Delta k, 0, 0.5, 1.0)$ is shown in Fig. 3.2b. In this case

$$k' = 2k_1 + k_3 = k'' \quad (3.34)$$

Therefore it is always true that $k''/k' = 1$ so that the beam waist of the driving polarization matches the beam waist of the generated radiation with the same confocal parameter, allowing a lowest order Gaussian beam output to be obtained.

The parameter Δk is dependent on the refractive indices of the nonlinear medium at the frequencies of the input and output beams, and hence on the number density of the gas being used. The optimization of the output by varying the pressure of the gases is known as "phase matching".

If we examine equations (3.9) and (3.13) we find that the amplitude of the driving polarization strongly peaks in the region of the fundamental beam waists. If an arbitrary definition is made of a region of significant generation bounded by values of z for which the driving polarization falls to 10% of its peak value then, in the case of tight focusing when b is much less than L and the fundamental beam-waist region is located entirely within the cell, the

boundaries of the generating region may be regarded as

$$\xi = -2 \text{ and } \xi = +2 \text{ (} z = f-b \text{ and } z = f+b \text{ respectively).}$$

The term $(1 + i\xi)^{-1}$ in (3.9) may be re-expressed as

$$(1 + \xi^2)^{-1/2} \exp(-i \tan^{-1} \xi)$$

Thus, a focused lowest order Gaussian beam undergoes a shift in phase given by $\tan^{-1} \xi$ as it propagates through the waist region. The driving polarization for the process

$$2\omega_1 - \omega_3 \rightarrow \omega_4$$

can be seen from equation (3.13) to also experience a phase shift of $\tan^{-1} \xi$. Therefore there is no slip in phase between the driving polarization and the generated radiation.

This is not true, however, for the process

$$2\omega_1 + \omega_3 \rightarrow \omega_4 \quad \text{in which case the driving}$$

polarization experiences a phase shift of $3 \tan^{-1} \xi$, giving a slip in phase between the driving polarization and the generated radiation of $2 \tan^{-1} \xi$. This accounts for the difference between Figs. 3.2a and 3.2b. The wave vector mismatch Δk introduced by the dispersion of the nonlinear medium may be used to compensate for the slip in phase due to focusing. The optimum value of Δk , Δk_{opt} is that value which exactly cancels the total slip in phase that occurs in traversing the generating region.

In the tight focusing case this requires that

$$\Delta k_{\text{opt}} = -2.2 / b \quad (3.35)$$

for sum frequency mixing ($2\omega_1 + \omega_3 \rightarrow \omega_4$) and of course

$$\Delta k_{\text{opt}} = 0 \quad (3.36)$$

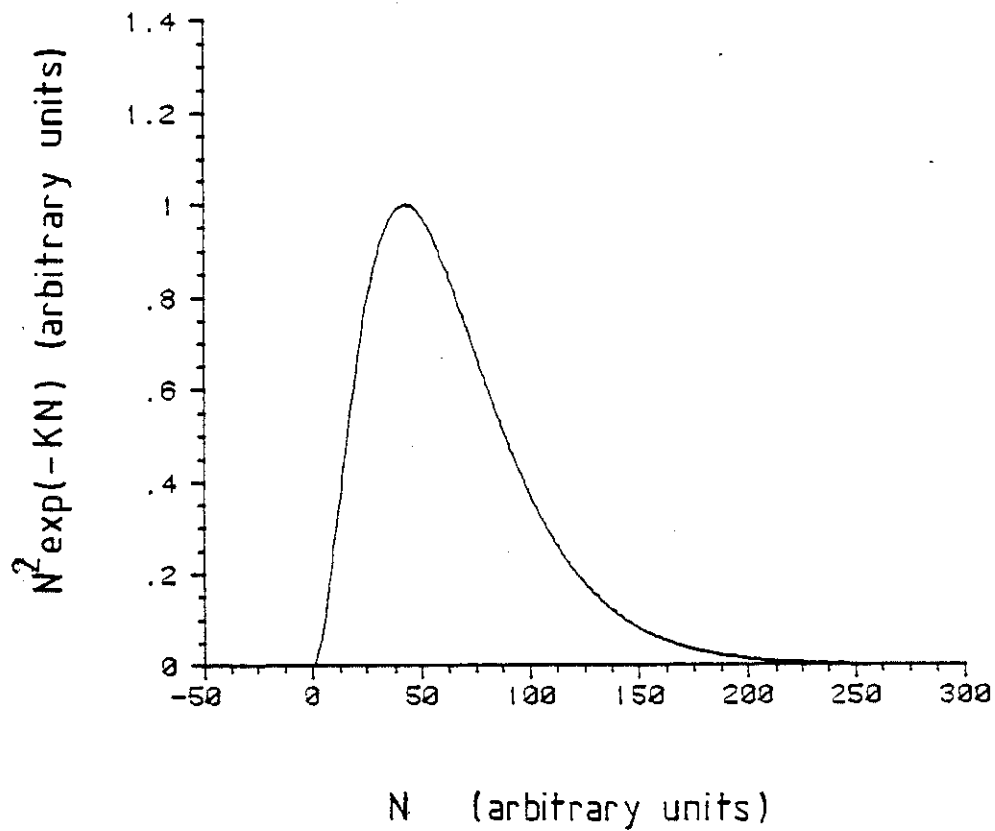
for difference frequency mixing ($2\omega_1 - \omega_3 \rightarrow \omega_4$). When generation is considered in the whole length of the cell in the tight focusing case for $2\omega_1 + \omega_3 \rightarrow \omega_4$ it is found that

$$\Delta k_{\text{opt}} = -2/b$$

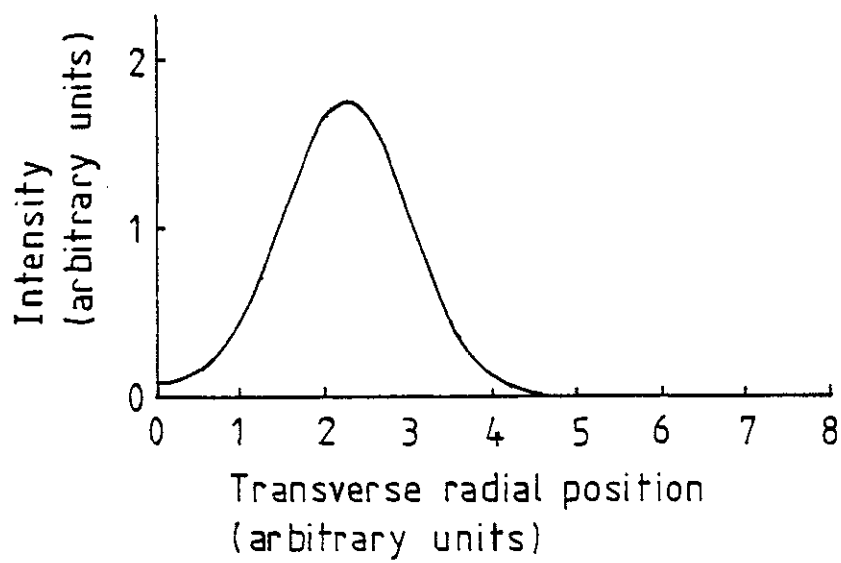
It can be seen from (3.36) and Fig. 3.2b that Δk must be negative for the sum frequency mixing process to occur, i.e. an anomalously dispersive medium is required. This imposes constraints on the range of wavelengths that can be generated, those having to be close to and on the short wavelength side of resonances in the atoms of the nonlinear medium. It is an advantage of the difference frequency mixing process that generation can occur for both positive and negative values of Δk , giving this process potentially a much wider wavelength range. However, unless an anomalously dispersive gas is added to the nonlinear medium it will not be possible to make Δk equal to zero as is required for optimization. In the experiment Xenon alone was used, and in this case Δk will be proportional to N (the number density of atoms). As can be seen from equations (3.30) and (3.32), the generated power at ω_4 will then have the functional form

$$P_4 = K_1 N^2 \exp[-K_2 N] \quad (3.37)$$

where K_1 and K_2 are constants which is a curve of the type shown in Fig. 3.3. Since N is proportional to the pressure of the gas, there will be an optimum gas pressure for the generation of the frequency ω_4 .



Theoretical dependence of the VUV power generated by difference frequency mixing on the Xenon atom number density N when $\Delta k \propto N$



Far field intensity distribution of output of difference frequency mixing for $b\Delta k = 2$, $b/L = 0.1$, $f/L = 0.5$ and $k''/k' = 3$ from Ref. 84.

Bjorkland⁽⁸⁴⁾ calculated the far field intensity distribution for the difference frequency mixing process, and it appears that the output radiation will have a ring pattern, as shown in Fig. 3.4 for $b\Delta k = 2$. This is in agreement with the far field intensity distribution which would arise from a lowest possible order Gaussian mode at the frequency ω_4 with the confocal parameter and waist location of the fundamental beams.

Calculation of Δk

The parameter Δk can be calculated from the refractive indices of the gas at the wavelengths present

$$\begin{aligned}\Delta k &= k_4 - 2k_1 + k_3 \\ &= 2\pi c \left(\frac{n_4}{\lambda_4} - 2\frac{n_1}{\lambda_1} + \frac{n_3}{\lambda_3} \right)\end{aligned}\tag{3.38}$$

where n_1 , n_3 and n_4 are the refractive indices of the nonlinear medium at the wavelengths λ_1 , λ_3 and λ_4 respectively. Equation (3.38) applies to the difference frequency mixing. For sum frequency mixing it should be noted that the n_3/λ_3 term will be of opposite sign. Given that

$$\omega_4 = 2\omega_1 - \omega_3\tag{3.7}$$

it can be seen that

$$\frac{1}{\lambda_4} = \frac{2}{\lambda_1} - \frac{1}{\lambda_3}\tag{3.39}$$

hence

$$\Delta k = \frac{2(n_4 - n_1)}{\lambda_1} + \frac{(n_3 - n_4)}{\lambda_3} \quad (3.40)$$

The refractive index $n(\lambda)$ can be calculated from the Sellmeier equation

$$n(\lambda) - 1 = \frac{N r_e}{2\pi} \sum_i \frac{f_i}{[1/\lambda_i^2 - 1/\lambda^2]} \quad (3.41)$$

where $r_e = 2.818 \times 10^{-13}$ cm

f_i is the oscillator strength of the i 'th transition

λ_i is the wavelength of the i 'th transition in centimetres

Values for f_i are given by Geiger⁽⁸⁷⁾, and those used in the calculation are shown in Table 3.1. Those values marked with an asterisk are theoretical predictions, whereas the majority are experimental results from high energy electron spectroscopy.

In order to prevent $n(\lambda) - 1$ approaching infinity as $\lambda \rightarrow \lambda_i$ a linewidth was introduced into the calculation, the complex frequency of the transition being

$$\Omega_i = \omega_i + i \Delta\omega_i \quad (3.42)$$

where $\omega_i = \frac{2\pi c}{\lambda_i}$

and $\Delta\omega$ is taken to be the Doppler width of the transition given by

$$\frac{\Delta\omega_i}{\omega_i} = \left(\frac{8kT \ln 2}{Mc^2} \right)^{1/2} \quad (3.43)$$

Table 3.1

Oscillator strengths of transitions from the 5p ground state in Xenon used in the calculation of $\Delta k/P$.

Level	Wavelength of transition from 5p level (nm)	Oscillator strength
6s	147.34	0.26
6s'	129.90	0.19
5d	125.35	0.0095
7s	117.35	0.0968
6d	113.23	0.0025
6 $\bar{d}$	111.36	0.0862
8s	110.26	0.0236
7d	108.82	0.0217
7 $\bar{d}$	108.14	0.004
9s	107.32	0.006
5d'	107.10	0.205
8d	106.40	0.0096
8 $\bar{d}$	105.89	0.123
10s	105.78	0.0204
9d	105.29	0.0042
9 $\bar{d}$	104.99	0.0625
11s	104.89	0.0025
7s'	104.66	0.029
10d	104.53	0.0035
10 $\bar{d}$	104.39	0.0386
12s	104.30	0.005
11d	104.09	0.0005*
11 $\bar{d}$	103.98	0.025
13s	103.92	0.0023*
12d	103.77	0.0005*
12 $\bar{d}$	103.69	0.016
14s	103.64	0.0014*
5 $\bar{f}$	119.52	0.395

Oscillator strengths marked * are theoretical predictions.
The others have been experimentally determined.

where M is the mass of the Xenon atom (kg)

k is Boltzmann's constant - $1.381 \times 10^{-23} \text{ JK}^{-1}$

T is the temperature, taken to be 300K

The result of this calculation of Δk is shown in Fig. 3.5a plotted against the generated wavelength λ_4 . The number density of Xenon atoms used in the calculation is that for a pressure of 1 Torr at 300K. The product of the value obtained from the graph and the pressure in Torr will give the value of Δk at that pressure.

The calculation can also be done for the sum frequency mixing process $2(\omega_1 + \omega_3) \rightarrow \omega_4$ and this is shown in Fig. 3.5b. Since the wavelengths generated lie at the limit of the transitions with known oscillator strengths, additional transitions have been included by assuming that the s , d , $\bar{d}$, s' and d' series continue as Rydberg series and assigning transitions extrapolated by this method oscillator strengths of 0.002. For this reason and due to the high density of states in this region, the value of Δk calculated for the sum frequency mixing process can only be regarded as approximate. However, Fig. 3.5b does show that there may be regions of anomalous dispersion available at these wavelengths allowing VUV radiation of wavelength approaching 100 nm to be produced by this method. Phase matching would be achieved by adding a positively dispersive gas such as Helium or Neon to the anomalously dispersive Xenon and adjusting the concentrations to give $\Delta k = -2/b$.

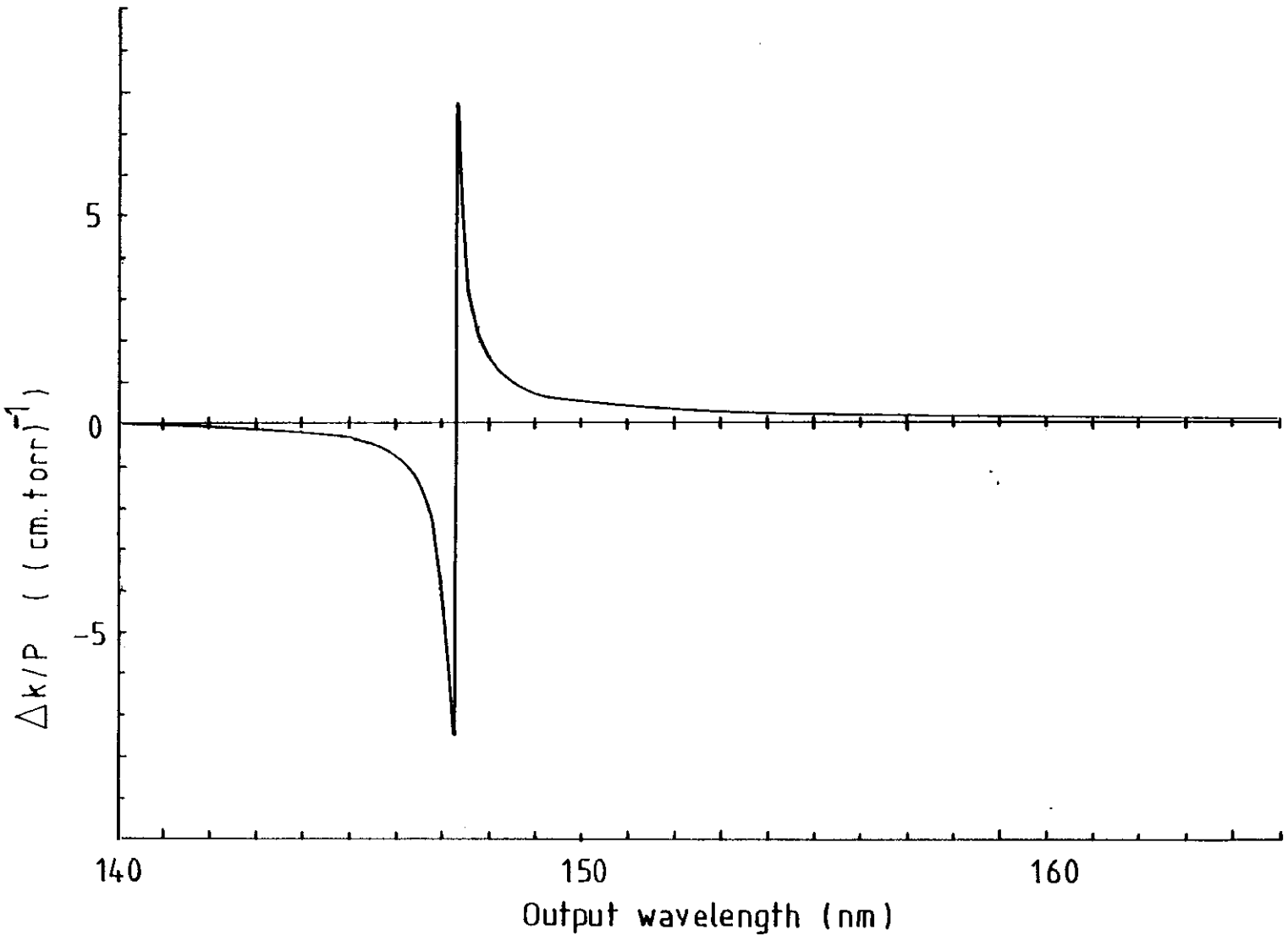
3.2.4 The Nonlinear Susceptibility

The electric-dipole interaction between matter and radiation is given by

$$V = - \mathbf{Q} \cdot \mathbf{E}(\mathbf{r}, t)$$

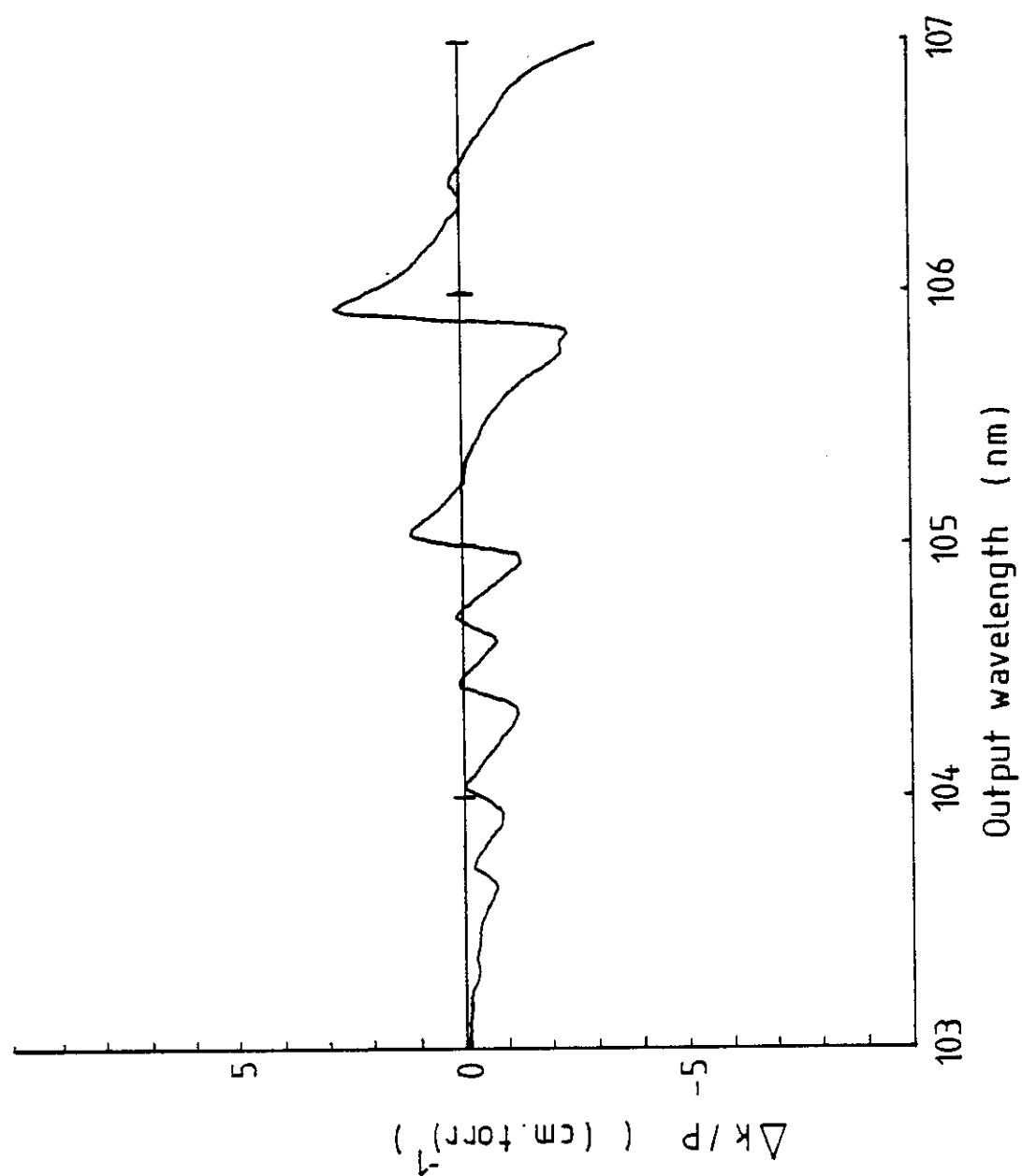
(3.44)

FIG. 3.5a



Calculation of $\Delta k/P$ against λ_c for difference frequency mixing

FIG. 3.5b



Calculation of $\Delta k/P$ against λ_4 for sum
frequency mixing

where $\underline{Q}$ is the electric-dipole-moment operator for the atom. If an atom in an unperturbed stationary state $|g\rangle$ evolves into the state $|g\rangle'$ then the induced dipole moment will be the expectation value

$$\underline{\mu}(t) = \langle g | \underline{Q} | g \rangle \quad (3.45)$$

which appears as a power series in V and thus of the applied field, the terms of which may be sorted according to the powers. The macroscopic polarization is given by

$$\underline{P}^{(n)}(\underline{r}, t) = N \overline{\underline{\mu}^{(n)}} \propto N \chi^{(n)} \underline{E} \quad (3.46)$$

where N is the number density of atoms and the bar denotes an orientation average. The result is

$$\begin{aligned} & \chi^{(n)}(-\omega_g, \omega_1, \dots, \omega_n) \\ &= \frac{q_T}{n! \hbar \epsilon_0} \sum_{gb1 \dots bn} \rho(g) \frac{\mu_{gb1} \mu_{b1b2} \dots \mu_{bng}}{(\Omega_{b1g} - \omega_1 - \dots - \omega_n)(\Omega_{b2g} - \omega_2 - \dots - \omega_n) \dots (\Omega_{bng} - \omega_n)} \end{aligned} \quad (3.47)$$

g refers to the ground state and b_n refers to the n th state. The transition frequencies Ω_{ij} are defined by

$$\Omega_{ij} = (E_i - E_j) / \hbar \quad (3.48)$$

where E_i and E_j are the atomic energy levels of the states $|i\rangle$ and $|j\rangle$. The μ_{ij} are matrix elements between stationary states of the unperturbed atoms

$$\mu_{ij} = e \langle i | \underline{x} | j \rangle \quad (3.49)$$

where the incident fields are assumed to be linearly polarized in the x-direction. The summations $\sum_{gb_1 \dots b_n}$ are performed over all the atomic states. The factor $\rho(g)$ is the probability of occupancy of the ground state.

G_T is the overall permutation operator requiring that the expression following it is summed over all permutations of $-\omega_\sigma, \omega_1, \dots, \omega_n$. This would give in the case of equation (3.47) $(n+1)!$ terms; however, this is reduced if some frequencies are equal.

This theory was first developed by Butcher⁽⁸⁸⁾, and the form of (3.47) is that quoted by Hanna, Yuratich and Cotter⁽⁸⁹⁾.

The terms in (3.47) are most easily understood by the use of the diagrammatic representation scheme given by Ward⁽⁹⁰⁾. The positive frequency $|\omega_i|$ is associated with the destruction of a photon, and the negative frequency $-|\omega_i|$ is, accordingly, associated with the creation of a photon. The denominator $\hbar(\Omega_{bna} - \omega_n)$ represents the net change in energy of the atom-field system as the atom undergoes the transition $a \rightarrow b_n$ and the field loses a photon of frequency ω_n through absorption; the associated matrix element is μ_{bna} . Energy conservation is not required for the individual steps in the process since the states are virtual, i.e. they are occupied

for a time less than that determined by the uncertainty relation

$$\Delta E \Delta t \gtrsim \hbar, \text{ although energy is, of course, conserved overall.}$$

Diagrammatically the RHS of (3.47) becomes

$$\frac{N}{n! \hbar^n \epsilon_0} \sum_g \rho(g) Q_T$$

(3.50)

where summation over the intermediate states $b_1 \dots b_n$ is implied.

A downward pointing arrow corresponds to absorption and a positive frequency, while an upward pointing arrow corresponds to emission and a negative frequency. Q_T generates the sum of all $(n+1)!$ diagrams that result from the different permutations of the arrows in the diagram.

In the experiment we are considering we are interested in $\chi^{(3)}(-\omega_4; \omega_1, \omega_1, -\omega_3)$ where $\omega_4 = 2\omega_1 - \omega_3$. The diagrammatic representation of this is shown in Fig. 3.6a, while Fig. 3.6b shows an energy level diagram with the transitions referred to by the first subdiagram in Fig. 3.6a.

Therefore the expression will read

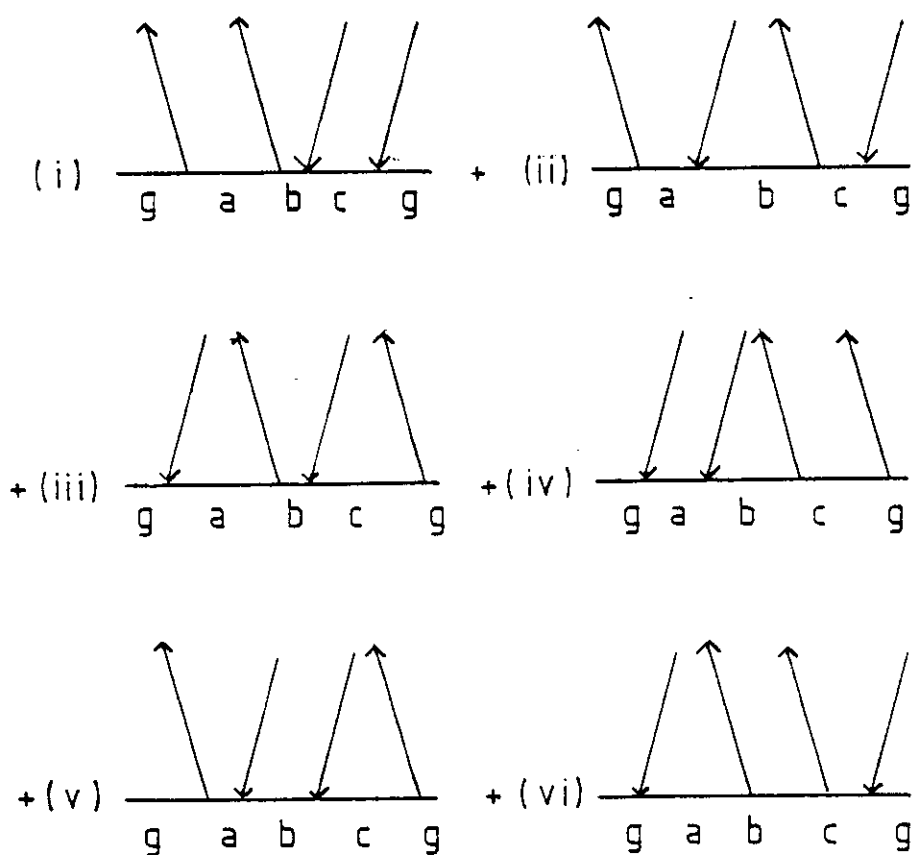
$$\chi^{(3)}_{\substack{4 \\ -\omega; \omega_1, \omega_1, -\omega_3}} = \frac{2N}{3! \hbar^3 \epsilon_0} \sum_{gabc} \rho(g) \mu_{ga} \mu_{ab} \mu_{bc} \mu_{cg} A_{abc}$$

(3.51)

FIG. 3.6a (part 1)

Diagrammatic representation of the nonlinear susceptibility calculation

The overall sum consists of



These six parts are made up as follows

$$(i) \quad \begin{array}{c} \omega_4 \quad \omega_3 \quad \omega_1 \quad \omega_1 \\ \nearrow \quad \nearrow \quad \searrow \quad \searrow \end{array} \times 2 \quad + \quad \begin{array}{c} \omega_3 \quad \omega_4 \quad \omega_1 \quad \omega_1 \\ \nearrow \quad \nearrow \quad \searrow \quad \searrow \end{array} \times 2$$

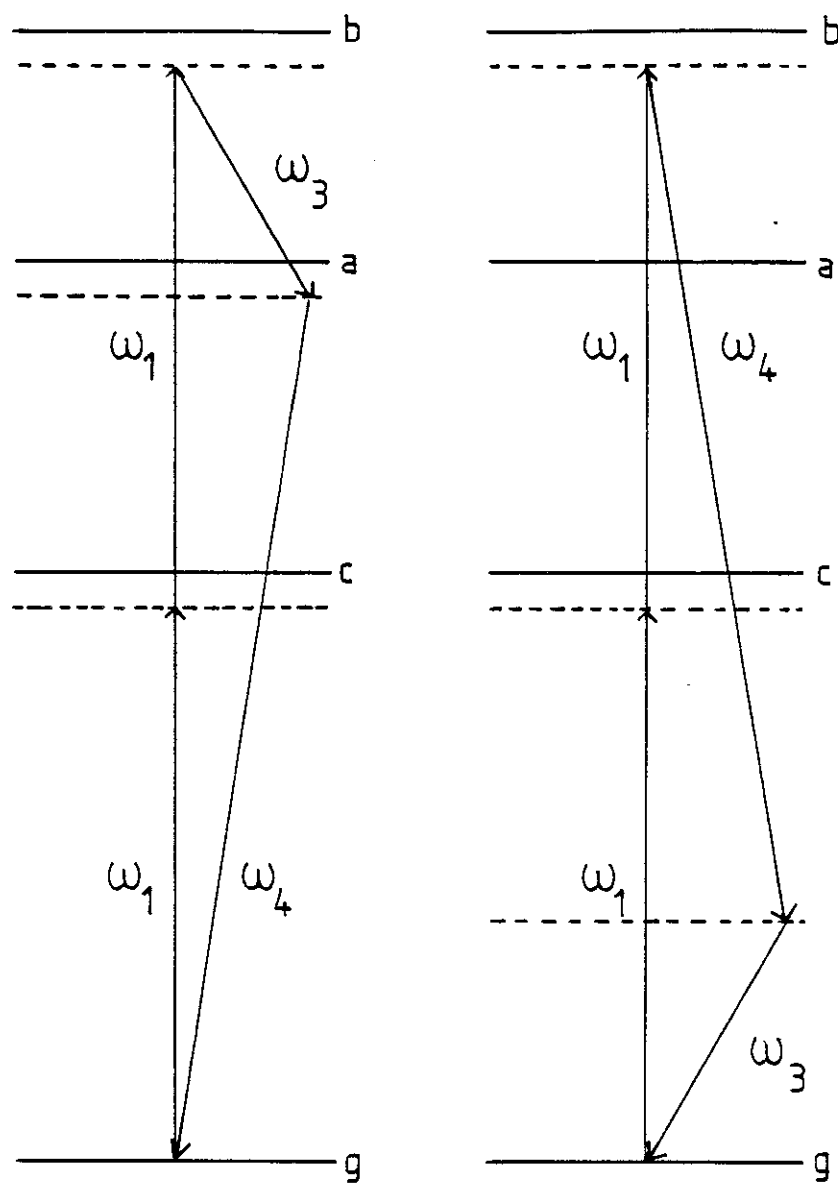
$$(ii) \quad \begin{array}{c} \omega_4 \quad \omega_1 \quad \omega_3 \quad \omega_1 \\ \nearrow \quad \searrow \quad \nearrow \quad \searrow \end{array} \times 2 \quad + \quad \begin{array}{c} \omega_3 \quad \omega_1 \quad \omega_4 \quad \omega_1 \\ \nearrow \quad \searrow \quad \nearrow \quad \searrow \end{array} \times 2$$

$$(iii) \quad \begin{array}{c} \omega_1 \quad \omega_4 \quad \omega_1 \quad \omega_3 \\ \nwarrow \quad \nwarrow \quad \nwarrow \quad \nwarrow \end{array} \times 2 \quad + \quad \begin{array}{c} \omega_1 \quad \omega_3 \quad \omega_1 \quad \omega_4 \\ \nwarrow \quad \nwarrow \quad \nwarrow \quad \nwarrow \end{array} \times 2$$

$$(iv) \quad \begin{array}{c} \omega_1 \quad \omega_1 \quad \omega_4 \quad \omega_3 \\ \nwarrow \quad \nwarrow \quad \nwarrow \quad \nwarrow \end{array} \times 2 \quad + \quad \begin{array}{c} \omega_1 \quad \omega_1 \quad \omega_3 \quad \omega_4 \\ \nwarrow \quad \nwarrow \quad \nwarrow \quad \nwarrow \end{array} \times 2$$

$$(v) \quad \begin{array}{c} \omega_4 \quad \omega_1 \quad \omega_1 \quad \omega_3 \\ \nwarrow \quad \nwarrow \quad \nwarrow \quad \nwarrow \end{array} \times 2 \quad + \quad \begin{array}{c} \omega_3 \quad \omega_1 \quad \omega_1 \quad \omega_4 \\ \nwarrow \quad \nwarrow \quad \nwarrow \quad \nwarrow \end{array} \times 2$$

$$(vi) \quad \begin{array}{c} \omega_1 \quad \omega_4 \quad \omega_3 \quad \omega_1 \\ \nwarrow \quad \nwarrow \quad \nwarrow \quad \nwarrow \end{array} \times 2 \quad + \quad \begin{array}{c} \omega_1 \quad \omega_3 \quad \omega_4 \quad \omega_1 \\ \nwarrow \quad \nwarrow \quad \nwarrow \quad \nwarrow \end{array} \times 2$$



Energy level diagram for (i) in Fig. 3-6 a

where, remembering that $2\omega_1 - \omega_3 = \omega_4$

$$\begin{aligned}
 A_{abc} = & \frac{1}{(\Omega - \omega)_{cg1}(\Omega - 2\omega)_{bg1}(\Omega - \omega)_{ag4}} + \frac{1}{(\Omega - \omega)_{cg1}(\Omega - 2\omega)_{bg1}(\Omega - \omega)_{ag3}} \\
 & + \frac{1}{(\Omega - \omega)_{cg1}(\Omega - (\omega - \omega))_{bg1}(\Omega - \omega)_{ag4}} + \frac{1}{(\Omega - \omega)_{cg1}(\Omega - \omega)_{bg4}(\Omega - \omega)_{ag3}} \\
 & + \frac{1}{(\Omega + \omega)_{cg3}(\Omega - (\omega - \omega))_{bg1}(\Omega + \omega)_{ag1}} + \frac{1}{(\Omega + \omega)_{cg4}(\Omega - (\omega - \omega))_{bg4}(\Omega + \omega)_{ag1}} \\
 & + \frac{1}{(\Omega + \omega)_{cg3}(\Omega + (\omega + \omega))_{bg3}(\Omega + \omega)_{ag1}} + \frac{1}{(\Omega + \omega)_{cg4}(\Omega + (\omega + \omega))_{bg3}(\Omega + \omega)_{ag1}} \\
 & + \frac{1}{(\Omega + \omega)_{cg3}(\Omega - (\omega - \omega))_{bg1}(\Omega - \omega)_{ag4}} + \frac{1}{(\Omega + \omega)_{cg4}(\Omega - (\omega - \omega))_{bg1}(\Omega - \omega)_{ag3}} \\
 & + \frac{1}{(\Omega - \omega)_{cg1}(\Omega - (\omega - \omega))_{bg1}(\Omega + \omega)_{ag1}} + \frac{1}{(\Omega - \omega)_{cg1}(\Omega - (\omega - \omega))_{bg1}(\Omega + \omega)_{ag4}}
 \end{aligned}$$

(3.52)

The μ_{ij} are non-zero only for states of opposite parity. Therefore the states $|b\rangle$ and $|g\rangle$ must have equal parity. The susceptibility may be enhanced by choosing wavelengths such that there is a two photon resonance for either $2\omega_1$ or $\omega_1 - \omega_3$ ($\omega_1 > \omega_3$). If $2\omega_1$ is close to a two photon resonance then

$$A_{abc} \approx \frac{1}{(\Omega_{cg} - \omega_1)(\Omega_{bg} - 2\omega_1)(\Omega_{ag} - \omega_1)} + \frac{1}{(\Omega_{cg} - \omega_1)(\Omega_{bg} - 2\omega_1)(\Omega_{ag} - \omega_3)}$$

(3.53)

A two photon resonance like that present in the Xenon atom for $\lambda_1 = 249.6 \text{ nm}$ ($5p^3S \rightarrow 6p [0\frac{1}{2}]\rangle$) has the advantage that there is not the strong single photon absorption that would occur for a single photon resonance, e.g. $\omega_1 \approx \Omega_{ag}$ or the absorption of the generated radiation that would occur for $2\omega_1 - \omega_3 \approx \Omega_{cg}$. Both of these cases could still be used to enhance the susceptibility.

Equation (3.51) includes a summation over all possible atomic states. For two electron atoms, such as Xenon, it is difficult to calculate the matrix elements and it is simpler to use tabulated values of the oscillator strengths. Unfortunately, only some of these are known^(87,91) and since the relation between matrix elements and oscillator strength⁽⁸⁹⁾

is

$$|\mu_{xy}|^2 = e^2 \frac{\hbar}{2 m_e \Omega_{xy}} f_{xy} \frac{3(l+1)}{2l+3} \quad (3.54)$$

where f_{xy} is the oscillator strength for the transition from state x with angular momentum quantum number l to state y with quantum number $(l+1)$, Ω_{xy} is the energy difference between these levels and m_e and e are the electronic mass and charge respectively, it can be seen that only the magnitude of μ_{xy} is known exactly and not its sign. This leads to ambiguity in the way the different terms in the summation in (3.51) should be added together, making a precise calculation of X impossible by this method.

However, an estimate of the off resonance susceptibility was made by assuming a random walk average of the terms in the summation. The summation was only performed over a and c since the ground state g is always the $5p$ level while the $6p$ state, being near a two photon resonance, provides the main contribution to the summation over b . Table 3.2 shows the transitions which were included in the calculation, those involving higher levels have been neglected. Oscillator strengths for transitions involving the $6p$ level were assumed to be 0.1, as experimental values were not available.

In a random walk of n steps of unit length the expected distance from the origin is $\sqrt{n}$. Therefore with 9 terms in the summation contributing to the susceptibility $|X|$ the overall result was assumed to be

$$|X| = \left| \overline{X} \right| \cdot \sqrt{9}$$

where $\left| \overline{X} \right|$ is the arithmetic mean of the susceptibilities

Table 3.2

Oscillator strengths and energies of transitions considered in the calculation of the off-resonance non-linear susceptibility (* denotes estimated oscillator strength).

Transition	Oscillator Strength	Energy Difference (eV)
5p-6s	0.183	8.44
5p-6s'	0.169	9.57
5p-5d	0.395	10.40
6s-6p	0.1*	1.49
6s'-6p	0.1*	0.36
5d-6p	0.1*	-0.47

Table 3.3

Contributions, $|\chi_c|$, to the nonlinear susceptibility
 ($\times 10^{-34}$ ESU) from the summation over transitions
 $g \rightarrow a \rightarrow b \rightarrow c \rightarrow g$, where g and b are the 5p and 6p levels
 and a and c are the levels shown.

c a	6s	6s'	5d
6s	0.99	0.70	0.62
6s'	1.81	0.98	0.86
5d	1.97	0.54	0.94

that would result from only considering each of the possible transition routes separately. The mean of the terms $|\bar{X}|_c$ was found to be 1.05×10^{-34} ESU/atom, and therefore the total susceptibility was taken to be 3.15×10^{-34} ESU/atom.

It should be stressed that this is only an approximate calculation, this method of obtaining the summation being purely arbitrary. It does, however, suggest that the susceptibility of Xenon for this nonlinear process is at least as high as that for comparable processes in the metal vapours previously used for nonlinear mixing⁽⁷³⁻⁷⁸⁾.

The divergence inherent in equation (3.51) due to resonance at $\Omega_{bg} = 2\omega_1$ is clearly unphysical and arises from the fact that the large changes in the atoms implied by the resonance introduce level shifts into the denominator, resulting in a finite polarization. It is common practice to insert a complex $i\Gamma$ into the denominator to account for the various damping processes. Thus $(\Omega_{bg} - 2\omega_1)$ becomes $(\Omega_{bg} - 2\omega_1 - i\Gamma)$

Therefore the power generated by the nonlinear process which is proportional to $|X|^2$ will change from being proportional to

$$\frac{1}{(\Omega_{bg} - 2\omega_1)^2}$$

off resonance to being proportional to

$$\frac{1}{\Gamma^2}$$

on resonance. Therefore the degree of resonant enhancement that can be achieved is limited by the broadness of the two photon transition. For example, from the power output that would be obtained for a detuning of 5×10^{13} rad s⁻¹ used in the calculation of $|X|$, if the linewidth Γ was equivalent

to the Doppler width, i.e. $\sim 10^{10} \text{ rad s}^{-1}$, then an enhancement of 2.5×10^7 could be expected. But, with an order of magnitude increase in the broadness of the two photon transition, due to other broadening processes, this enhancement would drop by two orders of magnitude.

Broadening mechanisms will be described in the next section, and in Chapter 5 the theories developed in this chapter will be compared with the experimental results.

3.3 Saturation and Broadening Processes

The theory described in section 3.2 made the assumption that there was no significant change in the nonlinear medium itself during the irradiation necessary to produce the four-wave mixing process. However, when this process is resonantly enhanced, as is the case in the experiment of interest here, this condition is not in general fulfilled. Interactions can occur which limit the output power which can be achieved. This has been observed in experiments on two photon resonantly enhanced third harmonic generation in Cesium^(92,93) and Thallium⁽⁹⁴⁾ vapour, and also, more recently, by Hager and Wallace⁽⁹⁵⁾ in four wave difference frequency mixing in Xenon. The main causes of such saturation are thought to be reduction of the ground state population of Xenon atoms due to two-photon absorption and photoionization and a reduction in the resonant enhancement due to broadening of the two photon transition by processes such as Stark broadening by photoelectrons. Stark shifting of the resonant 6p level could also be detrimental to the resonant enhancement, due to the effective detuning it produces. The dispersion of the nonlinear medium will be modified by the ground state depopulation and possibly also, at higher pressures, by the presence of Xe_2^* dimer molecules,

with a consequent alteration in the phase matching conditions. These processes are discussed in the following subsections.

3.3.1 Two Photon Absorption and Photoionization

The application of second order perturbation theory to the estimation of two photon absorption cross sections has been reviewed by Bischel et al⁽⁹⁶⁾, where it is shown that the two photon absorption cross section for two photons of frequency ν_1 is

$$\alpha(\nu_1) = \frac{(2\pi)^3}{h c^2} \nu_1 |M_{bg}|^2 g(\nu_1, \nu_1) \quad (3.55)$$

where $g(\nu_1, \nu_1)$ is the lineshape factor and M_{bg} is the two-quantum matrix element given by

$$M_{bg} = 2 \sum_a \frac{\langle b | \hat{\epsilon}_1 \cdot \bar{\mu}_{op} | a \rangle \langle a | \hat{\epsilon}_1 \cdot \bar{\mu}_{op} | g \rangle}{E_{ag} - h\nu_1} \quad (3.56)$$

In this expression $\hat{\epsilon}_1$ denotes the polarization of the optical wave, $\bar{\mu}_{op}$ represents the electric dipole operator and g , a and b denote the ground, intermediate and final states respectively.

The two photon absorption cross section for the 5p - 6p transition in Xenon can be estimated⁽⁹⁷⁾ by assuming line centre pumping of a Doppler broadened transition, in which case $g(\nu_1, \nu_1)$ becomes $0.939/\Delta\nu$ where $\Delta\nu$ is, as shown by Marx et al⁽⁹⁸⁾, given by

$$\Delta\nu = (2\Delta_L^2 + \Delta\nu_D^2)^{1/2} \quad (3.57)$$

where Δ_L is the laser linewidth, assuming that the laser's spectral intensity can be approximated to a Gaussian distribution and ΔV_D is the Doppler width of the two photon transition given by

$$\Delta V_D = V_{bg} \left(\frac{8 k T \ln 2}{M c^2} \right)^{1/2} \quad (3.58)$$

where $V_{bg} = 2 V_1$, k is Boltzmann's constant, T is the absolute temperature and M is the mass of the Xenon atom (2.2×10^{-25} kg). At a temperature of 300 K, ΔV_D is found to be 2.6 GHz. For a laser linewidth of 1.5 GHz at a wavelength of 249.6 nm the two photon absorption cross section is found to be $1.0 \times 10^{-28} \text{ cm}^4 \text{ W}^{-1}$.

Under irradiation by a laser beam of intensity I_1 at the two photon resonant frequency $V_1 = \omega_1 / 2\pi$ the rate of two photon absorption is given by

$$\frac{\alpha(V_1) I_1^2 N_g(t)}{\hbar \omega_1}$$

where $N_g(t)$ is the ground state population per unit volume.

Once an atom has been excited into the 6p state by two photon absorption the absorption of another photon at 249.6 nm will be sufficient to produce ionization. The rate for this process will be

$$\frac{\sigma_{pi} I_1 N_b(t)}{\hbar \omega_1}$$

The rate equations for the population $N_g(t)$ and $N_b(t)$ will be

$$\frac{dN_g(t)}{dt} = \frac{\alpha(V_1) I_1^2}{\hbar \omega_1} (N_b(t) - N_g(t)) \quad (3.59)$$

$$\frac{dN_b(t)}{dt} = -\frac{dN_g(t)}{dt} - \frac{N_b(t)}{\tau_{eff}} - \frac{\sigma_{pi} I_1 N_b(t)}{\hbar \omega} \quad (3.60)$$

$$\text{where} \quad \frac{1}{\tau_{eff}} = \frac{1}{\tau_{rad}} + k_g N_g(t) \quad (3.61)$$

τ_{rad} being the radiative lifetime of the two photon resonant state and k_g being the quenching rate by ground state atoms.

If $I_1 = 1 \text{ GW cm}^{-2}$, $\alpha(V_1) = 10^{-28} \text{ cm}^4 \text{ W}^{-1}$ as calculated and $\sigma_{pi} \sim 10^{-18} \text{ cm}^2$ (97), then

$$\frac{\alpha(V_1) I_1^2}{\hbar \omega_1} = 1.26 \times 10^8 \text{ s}^{-1} \quad (3.62)$$

and

$$\frac{\sigma_{pi} I_1}{\hbar \omega_1} = 1.26 \times 10^9 \text{ s}^{-1} \quad (3.63)$$

Since initially the excited state population $N_b(0) = 0$ then it is reasonable to assume that $-\frac{dN_g(t)}{dt} \geq 0$ and therefore

due to the relative magnitudes of the rate constants given by equations (3.62) and (3.63) the populations of the two states must obey the condition

$$N_g(t) \gg N_b(t) \quad (3.64)$$

Hence the first term in equation (3.59) is negligible and this equation has the solution

$$N_g(t) = N_g(0) \exp\left[-\frac{\alpha(V_1)}{\hbar \omega_1} I_1^2 t\right] \quad (3.65)$$

given the boundary condition $N_g(t) = N_g(0)$ at time $t = 0$. For $I_1 = 1 \text{ GW cm}^{-2}$ the ground state population will decay to $1/e$ (i.e. 37%) of its original value in 8 ns, and hence the ground state population can be expected to be depleted during the transit of intense laser pulses of a few nanoseconds duration at a wavelength of 249.6 nm.

Since the inverse of the rate constant for photionization of the excited state at $I_1 = 1 \text{ GW cm}^{-2}$ is 0.8 ns, excited atoms formed by two photon absorption will be rapidly ionized. Hence during the passage of a laser pulse the ground state population will decay and the ion population build up.

The absorption of two visible photons of wavelength $\lambda = 630 \text{ nm}$ from the other incident beam in the four wave mixing experiment will also be sufficient to cause ionization. Due to the large number of levels that would be involved in a calculation of the transition rate for this process, it is not possible to quantify the photoionization that would be expected. Being a two photon process the transition rate would have a quadratic dependence on the intensity of the 630 nm beam.

It is also possible for photoionization to occur directly from the 5p ground state. This would be a multiphoton process

involving two photons at 249.6 nm plus either another UV photon or two visible (630 nm) photons. These processes would experience resonant enhancement due to the two photon resonance as in the four wave mixing process. In Fig. 3.7 the most efficient photoionization channels in Xenon at these wavelengths are shown. Depopulation of the ground state would also occur due to these photoionization processes which have been neglected in equation (3.59). Other effects of photoionization are described in Section 3.3.3.

3.3.2 Stark Shifting

When atoms are subjected to an optical frequency field there is a repartitioning of the energy in the atom-field system which causes a level shift in the atom. This is known as the AC Stark effect. Consider the energy level scheme shown in Fig. 3.8. The relative optical Stark shift of levels 2 and 1, $\delta\Omega_s$ is given by⁽⁹⁹⁾

$$\delta\Omega_s = (\zeta_2 - \zeta_1) I_1 \quad (3.66)$$

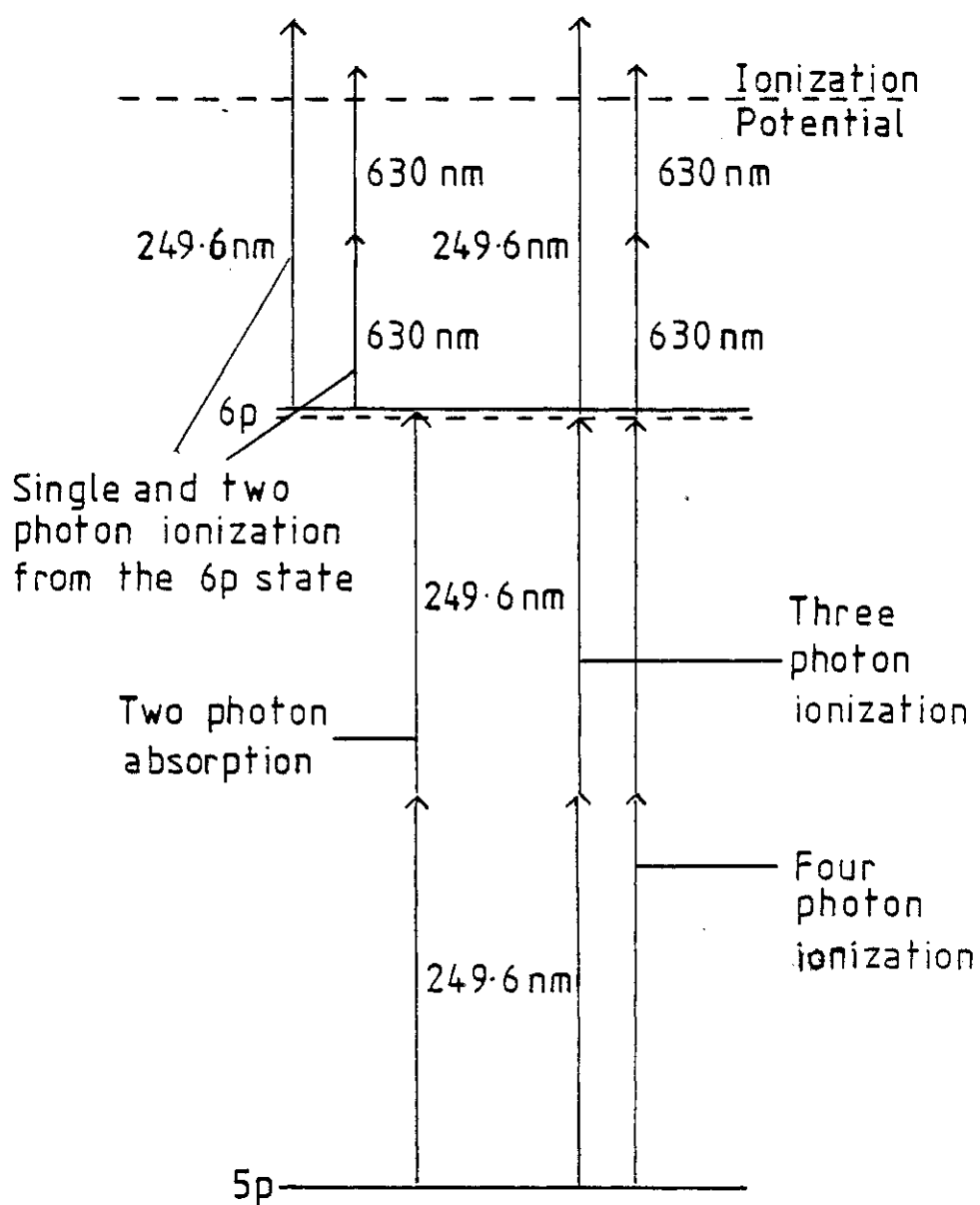
where

$$\zeta = (2 c \epsilon_0 \hbar^2)^{-1} \sum_k \frac{2\Omega_{ik} |\mu_{ki}|^2}{\Omega_{ik}^2 - \omega_1^2} \quad (3.67)$$

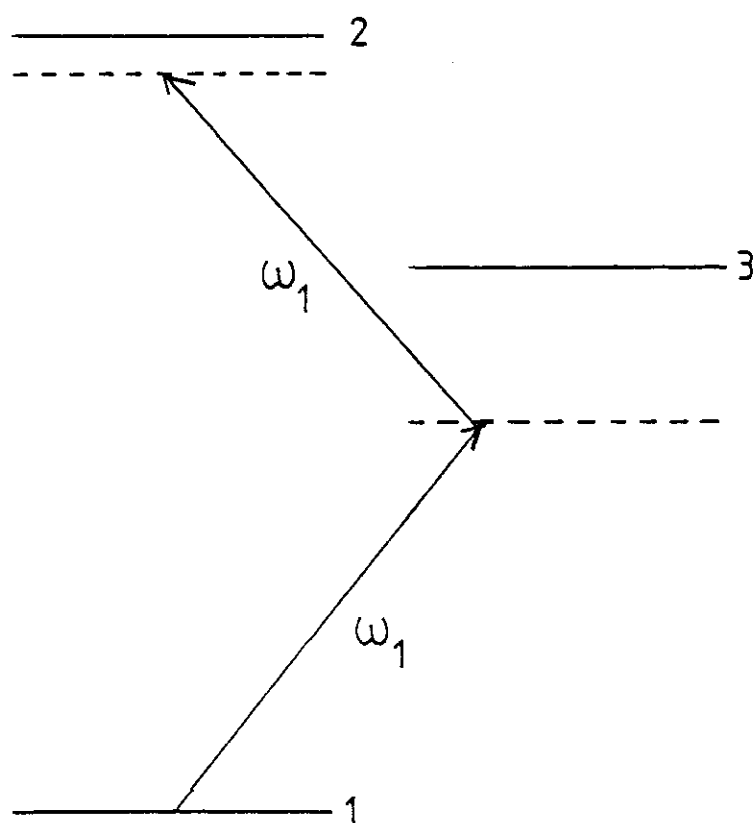
and the intensity of the fundamental wave is

$$I_1 = \frac{1}{2} c \epsilon_0 |E_1|^2 \quad (3.68)$$

This is important in resonantly enhanced nonlinear processes since the detuning from the resonant frequency is altered,



The main photoionization channels in Xenon



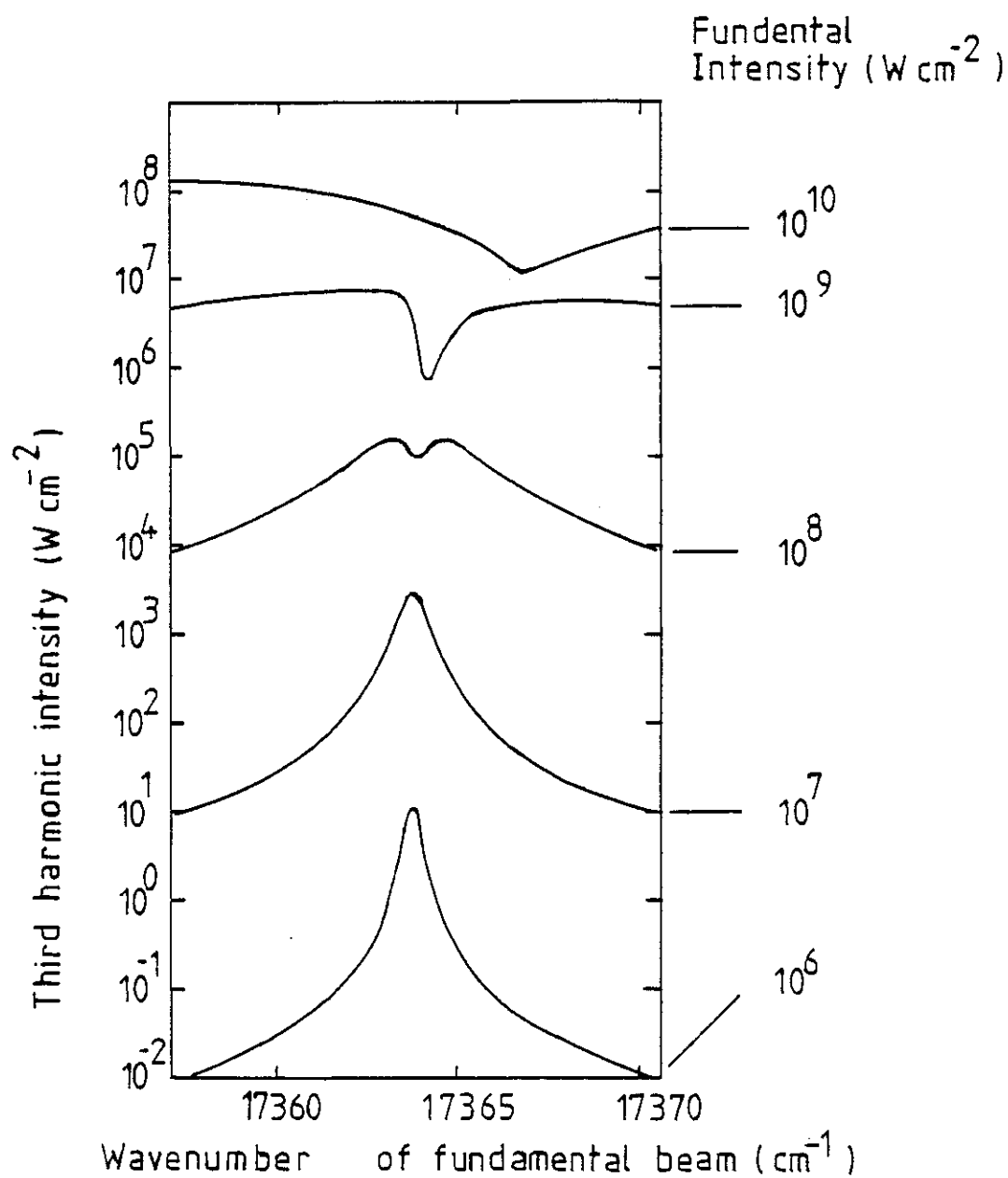
The energy level scheme for the calculation of Stark shifts

affecting the nonlinear susceptibility. In the calculation of the nonlinear susceptibility already described the intensity dependent term $\delta\Omega_s$ has to be added to the transition frequencies. For instance, for a two photon resonant transition of unperturbed frequency Ω_{bg} the actual frequency to be used in the calculation of the susceptibility (equations (3.51) and (3.53)) would be Ω'_{bg} where

$$\Omega'_{bg} = \Omega_{bg} + \delta\Omega_s - i\Gamma \quad (3.69)$$

where the damping term $i\Gamma$ allows for the finite resonant enhancement that can be achieved due to the linewidth of the transition as mentioned in Section 3.2.4. It can be seen that accurately modelling the four wave mixing process for focused, pulsed input laser beams would present great difficulties since the intensity dependence of the Stark shift would cause both a temporal and spatial variation of the nonlinear susceptibility.

Scheingraber and Vidal⁽¹⁰⁰⁾ included the effects of Stark shifting in numerical calculations of the intensity of two photon resonantly enhanced third harmonic generation in Strontium vapour as well as pump wave depletion, reabsorption of the third harmonic radiation and changes in the phase matching conditions due to variations in the population densities. The result of their calculations of the frequency dependence of the third harmonic intensity around the two photon resonance for increasing fundamental beam intensity is shown in Fig. 3.9. It can be seen that a minimum appears in the curve of third harmonic intensity at high input intensities. This is due to population of the two photon resonant level. The minimum



Calculated frequency dependence of third harmonic intensity (generated in Sr vapour) for increasing fundamental intensity from Ref. 100.

becomes shifted as the intensity increases, due to the Stark shift.

These results⁽¹⁰⁰⁾ are consistent with the work of Ward and Smith⁽⁹²⁾, who predicted that, for a saturated, homogeneously broadened two photon transition, the frequency lineshape of the third harmonic intensity would have a complicated dependence on the fundamental power, broadening for increasing I_1 and having an on-resonance dip. Since in the case of the four wave mixing experiment in Xenon the laser linewidth and the Doppler and pressure broadened transition linewidths⁽⁹⁶⁾ are all

~ 1 GHz, the two photon transition should be homogeneously broadened. However, if the population of the two photon resonant level is rapidly ionized, saturation is more likely to be caused by ground state depopulation, rather than the build-up of the two photon resonant state population, as considered by Ward and Smith⁽⁹²⁾.

3.3.3 Photoionization Effects

The depopulation of the 5p ground state caused by both multiphoton ionization and two photon absorption affects the efficiency of the four wave mixing process, both by the reduction of the bulk nonlinear susceptibility of the medium and by destruction of the phase matching. Photoionization can have other effects. By depopulating the two photon resonant level, the photoionization from that state can reduce its effective lifetime. This is a mechanism for linewidth broadening according to the uncertainty principle

$$\Delta\nu \Delta t \sim 1 \quad (3.70)$$

It should be noted that if a population inversion were produced between the 6p state and, for example, the 6s state

(see Fig. 1.9), stimulated emission could have a similar broadening effect.

The presence of large populations of ions and photoelectrons can produce broadening of the atomic transitions via the Stark effect, reducing the susceptibility of a nonlinear process. If the perturbing field that 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 by⁽⁸⁸⁾

$$\Delta E = \left(\frac{Ze}{4\pi\epsilon_0 R^2} \right)^2 \sum_a \frac{|\langle b | \mu_{ab} | a \rangle|^2}{E_b - E_a} \quad (3.71)$$

and Hindmarsh⁽¹⁰¹⁾ showed that, within the impact approximation, the Stark broadened linewidth γ (FWHM rad s^{-1}) is given by

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

where

$$C_4 = \left(\frac{Ze}{4\pi\epsilon_0} \right)^2 \sum_a \frac{|\langle b | \mu_{ab} | a \rangle|^2}{E_b - E_a} \quad (3.72)$$

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

$$\Delta E \ll (\hbar \bar{v})^{4/3} (C_4)^{-1/3} \quad (3.73)$$

The dominant broadening is therefore due to photoelectrons rather than ions because of their higher velocities. Line-

widths of tens of GHz are calculated⁽⁸⁸⁾ for a number density $N = 10^{22} \text{ m}^{-3}$ of Cesium atoms whose matrix elements are better known than those of Xenon.

Under extreme conditions the initial photoelectrons can gain energy by inverse bremsstrahlung absorption and then by an avalanche ionization process finally form an opaque plasma⁽⁸³⁾. However, phase matching conditions would almost certainly have been violated before the energy density required for this process would have been achieved.

3.3.4 Dimer Formation

It is possible for bound excited states of the Xe_2 molecule to be formed by absorption of two photons at 249 nm⁽⁹¹⁾ or a single VUV photon⁽¹⁰²⁾. This could affect the dispersion of the nonlinear medium with a consequent alteration in the phase matching conditions. For absorption to occur the molecules must already be present in their loosely bound ground state. It has been estimated⁽¹⁰²⁾ that the ratio of molecules to atoms at 1 bar and 300 K is 0.6%. Therefore the effect of this is likely to be negligible compared to saturation effects caused by two photon absorption and photoionization except at high Xenon pressures.

Chapter 4

The Four Wave Mixing Experiment : Apparatus

Introduction

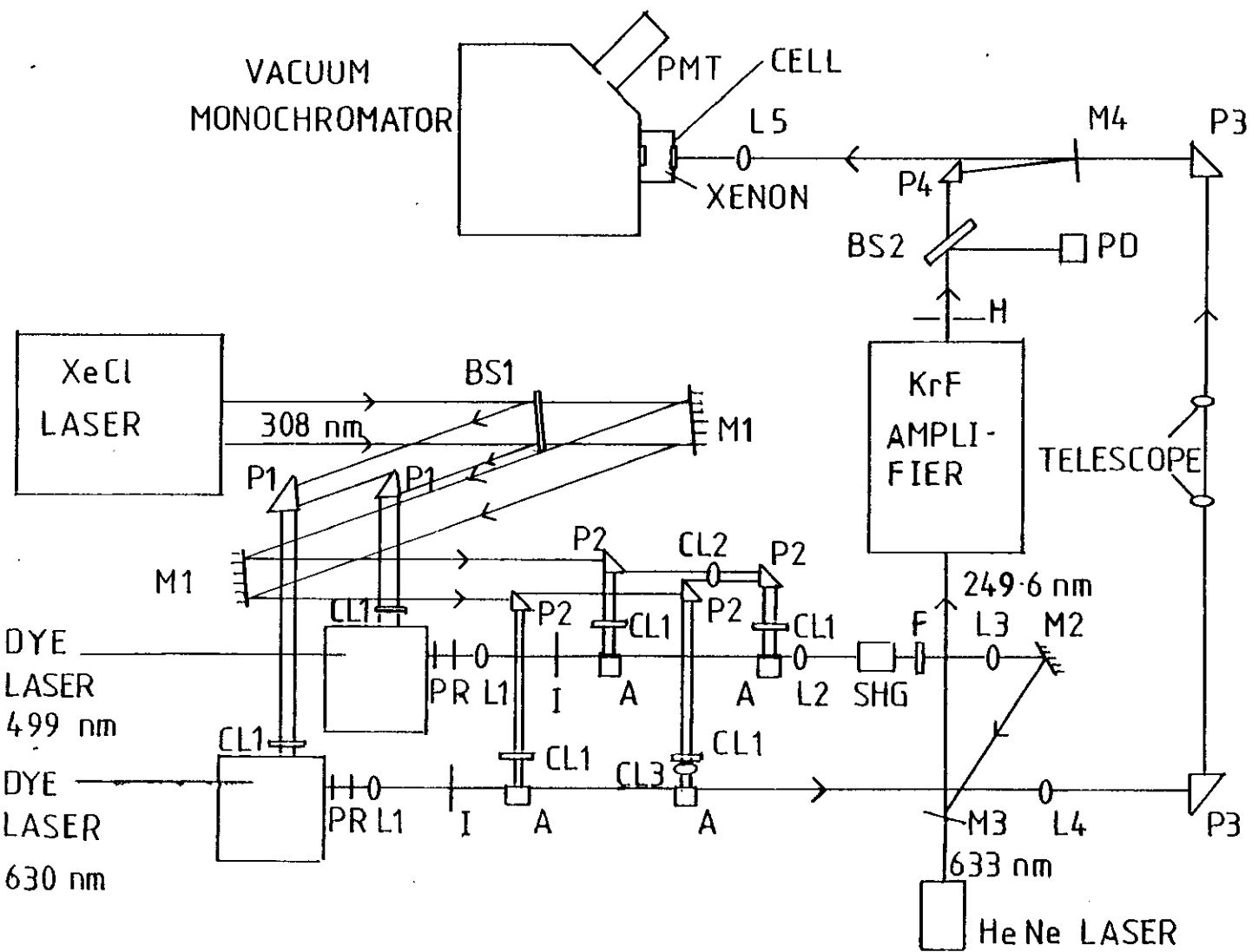
The experiment requires two narrowband, powerful (several kW) high quality laser beams to be produced, one of which must be accurately tuned to the two photon resonance in Xenon at 249.6 nm, and to be brought to a common focus inside a cell containing Xenon gas. The vacuum ultraviolet radiation then produced must be detected in order to analyse the process taking place.

The experimental arrangement is as shown in Fig. 4.1, which will be referred to throughout this chapter. A Lambda Physik EMG 101 discharge pumped excimer laser, operating at 308 nm (XeCl) and giving ~ 100 mJ in a 20 ns pulse, was used to pump two narrowband dye laser oscillators, each with two subsequent amplifiers (A in Fig. 4.1). One laser, operated with Coumarin 307 dye, was tuned to 499 nm and the second, using Rhodamine 101, was tunable between 610 and 650 nm.

The 499 nm dye laser beam was focused by a 25 cm focal length lens (L2) into a Potassium Pentaborate (KB5) frequency doubling crystal (SHG). The second harmonic radiation of wavelength 249.6 nm, generated with an efficiency of $\sim 1\%$, was recollimated and amplified in a discharge pumped KrF excimer amplifier with a gain of up to 100 synchronized to the XeCl pump laser.

The amplified beam was combined and made colinear with the second dye laser beam, whose wavelength was left at 630 nm during the course of the experiment, using a dielectric coated mirror (M4). A telescope inserted in the 630 nm beam enabled compensation to be made for the dispersion of the 20 cm lens

FIG. 4.1



The experimental arrangement

P1-P4 - Prisms, BS1, BS2 - Beam splitters, M1-M4 - Mirrors, L1-L5 - Lenses, CL1-CL3 - Cylindrical lenses, P - Polarizing filter, R - Half-wave plate, I - Iris, A - Amplifier, F - Filter, SHG - Second harmonic crystal, H - Aperture, PD - Photodiode, PMT - Photomultiplier tube.

(L5) used to focus the two beams into the centre of an 8 cm long cell, containing Xenon gas, mounted on the front of an Acton Research Corporation VUV monochromator. The input powers of the 630 nm and 249.6 nm pulses were 30 kW and up to 25 kW respectively, which, after focusing, corresponded to maximum intensities of 8 GW cm^{-2} and 5 GW cm^{-2} respectively. The VUV radiation generated by nonlinear four wave mixing was detected by a solar-blind photomultiplier (EMR model 541G-08-18) and the signals processed by a Tektronix 7912 AD transient digitiser and CP 1164 mini-computer.

The various parts of the apparatus are described in detail in the rest of this chapter.

4.1 The Narrowband Dye Lasers

4.1.1 The Oscillators

Discharge pumped excimer lasers are increasingly being used as pumps for dye lasers because of their high powers, repetition rates and their ability to pump dyes lasing over a wide region of the spectrum from the infrared to the ultra-violet⁽¹⁰³⁾. However, due to the short pulse duration of these excimer laser ($\sim 20 \text{ ns}$) and the N_2 lasers also used for dye laser pumping, the number of cavity round trips is limited and reliable narrowband operation in a single frequency mode is difficult to achieve.

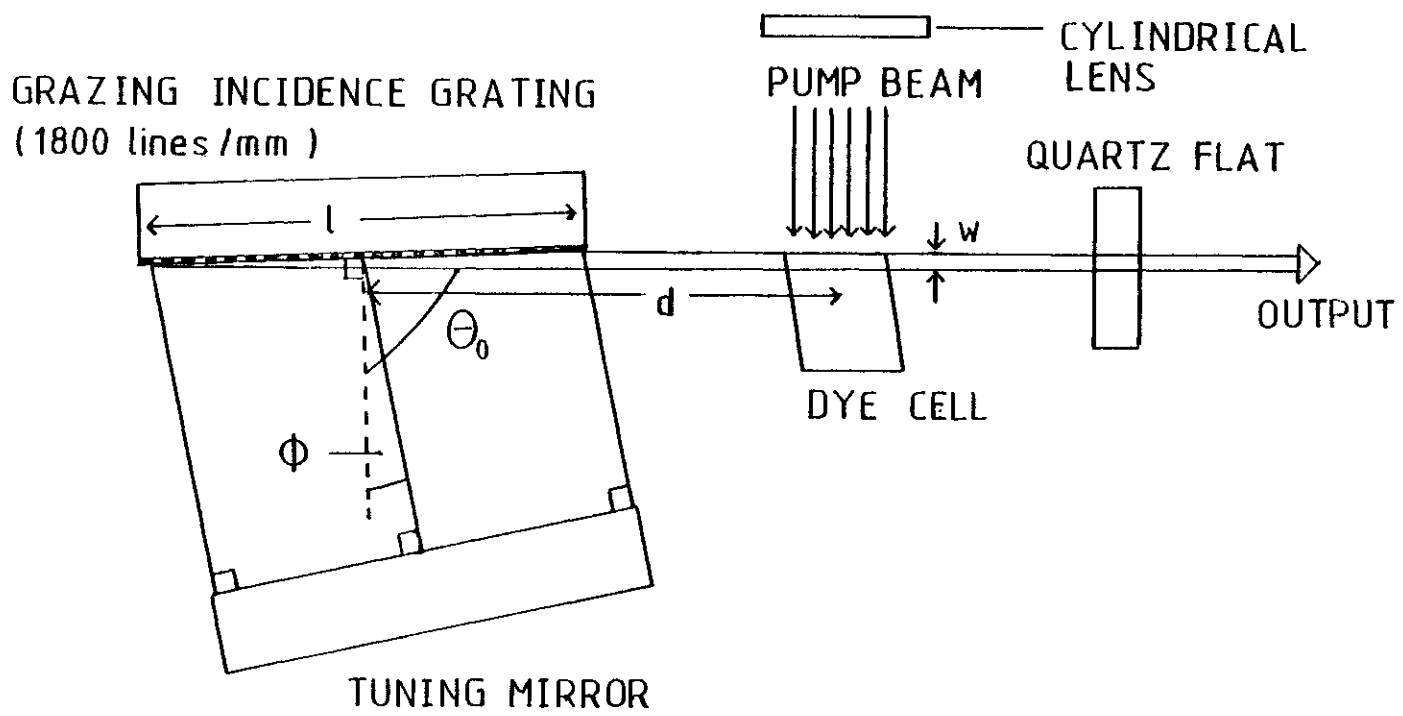
The first operation of a nitrogen laser pumped dye laser was reported by Hansch⁽¹⁰⁴⁾ in 1972. A grating was used as the dispersive element in the cavity and the number of lines illuminated increased by the use of an intra-cavity telescope. In 1977 Shoshan et al⁽¹⁰⁵⁾ reported on a much simplified cavity design where the telescope was eliminated by using a grating at grazing incidence to automatically provide beam expansion. This

also makes alignment easier, reduces the number of surfaces in the cavity and hence the reflection losses, and allows the cavity to be more compact, giving more round trips within the duration of the pump pulse.

This design was used by Littman and Metcalf⁽¹⁰⁶⁾ and Corney, Manners and Webb⁽¹⁰⁷⁾ when pumping with an Nd:YAG and XeCl laser respectively. This is the design used for the 500 nm dye laser built for the experiment, as shown in Fig. 4.2, the other dye laser being a modified version which will be discussed presently. A cylindrical lens (CL1 in Fig. 4.1 and also shown in Fig. 4.2) of 10 cm focal length focuses the pump beam to a fine horizontal line just inside the front face of the dye cell. The pump energy for both oscillators is provided by the 8% reflection from a quartz beam-splitter (BS1) which is divided and directed to the oscillators by two prisms (P1). The pump energy entering the dye cell was ~ 2 mJ. The side faces of the dye cell were angled with respect to the front face to prevent feedback between them, and the dye was flowed through to reduce instability in the output due to temperature dependent refractive index changes and the accumulation of ultra-violet irradiation induced decomposition products. An 1800 line mm^{-1} holographic grating was used at grazing incidence, tuning being provided by a 100% dielectric mirror whose angle was adjusted to reflect light of the desired wavelength back along the same path through the cavity. The half width of the dispersion envelope for the grating and mirror arrangement in Fig. 4.2 is given by⁽¹⁰⁶⁾

$$\Delta\lambda = \frac{\lambda \cos\theta_0}{2(\sin\theta_0 + \sin\phi)} \left[\left(\frac{l \cos\theta_0}{2d} \right)^2 + \left(\frac{W}{d} \right)^2 \right]^{1/2} \quad (4.1)$$

FIG. 4.2



The 500 nm excimer laser pumped dye laser oscillator

where W is the depth of the excited region in the dye cell, d is the distance between the dye cell and grating, l is the length of the grating, θ_0 is the angle of incidence of light onto the grating measured from the grating normal, and ϕ is the angle of the diffracted light, i.e. the perpendicular to the tuning mirror again with respect to the grating normal. Therefore it emerges that $\Delta\lambda$ is minimized for

$$d = L_R = \frac{\pi W^2}{\lambda} \quad (4.2)$$

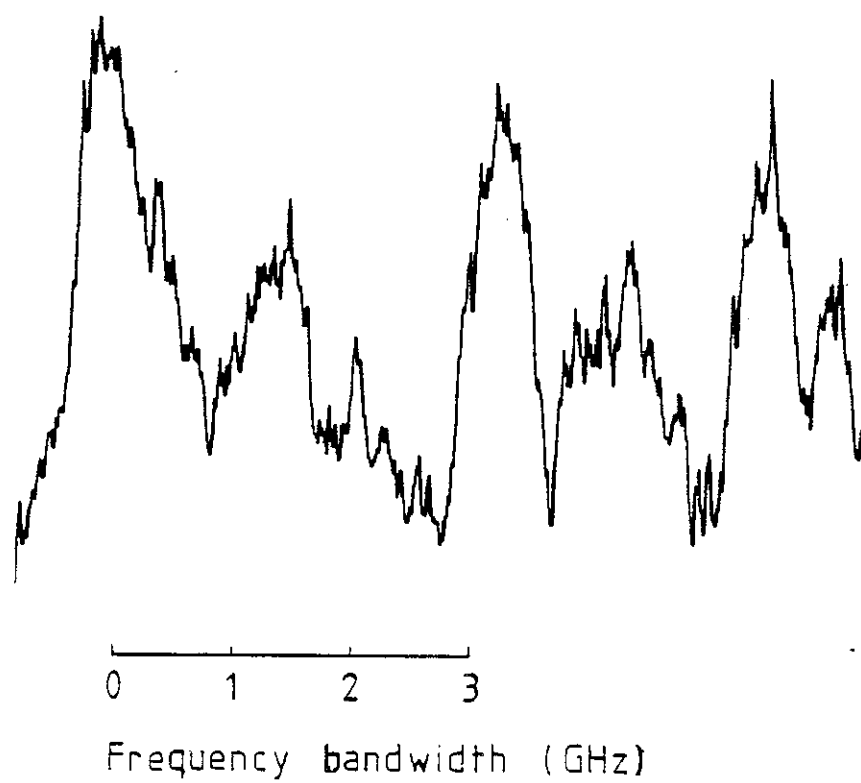
where L_R is the Rayleigh distance. Physically this is the distance at which the principal diffraction lobe of the slit function corresponding to the excited dye region just fills the grating. For $\lambda = 500$ nm and $W = 0.1$ mm the Rayleigh distance is ~ 6 cm. This therefore limits how compact such a cavity can be made. The cavity length of the laser as used in the experiment was ~ 15 cm, giving a longitudinal mode separation

$$\Delta\nu = \frac{c}{2L} \simeq 1 \text{ GHz}$$

where L is the total cavity length.

A glass flat was used as the output coupler of the oscillator, as shown in Fig. 4.2. Coumarin 307 dye of concentration 10^{-2} g moles l^{-1} dissolved in ethanol was used to give an output wavelength tunable around 500 nm. The output power was ~ 400 W and from a microdensitometer trace of Fabry-Perot fringes shown in Fig. 4.3 it can be seen that the laser operated in two longitudinal frequency modes, giving a linewidth of ~ 1 GHz. The laser output is horizontally polarized, due to the orientation of the grating.

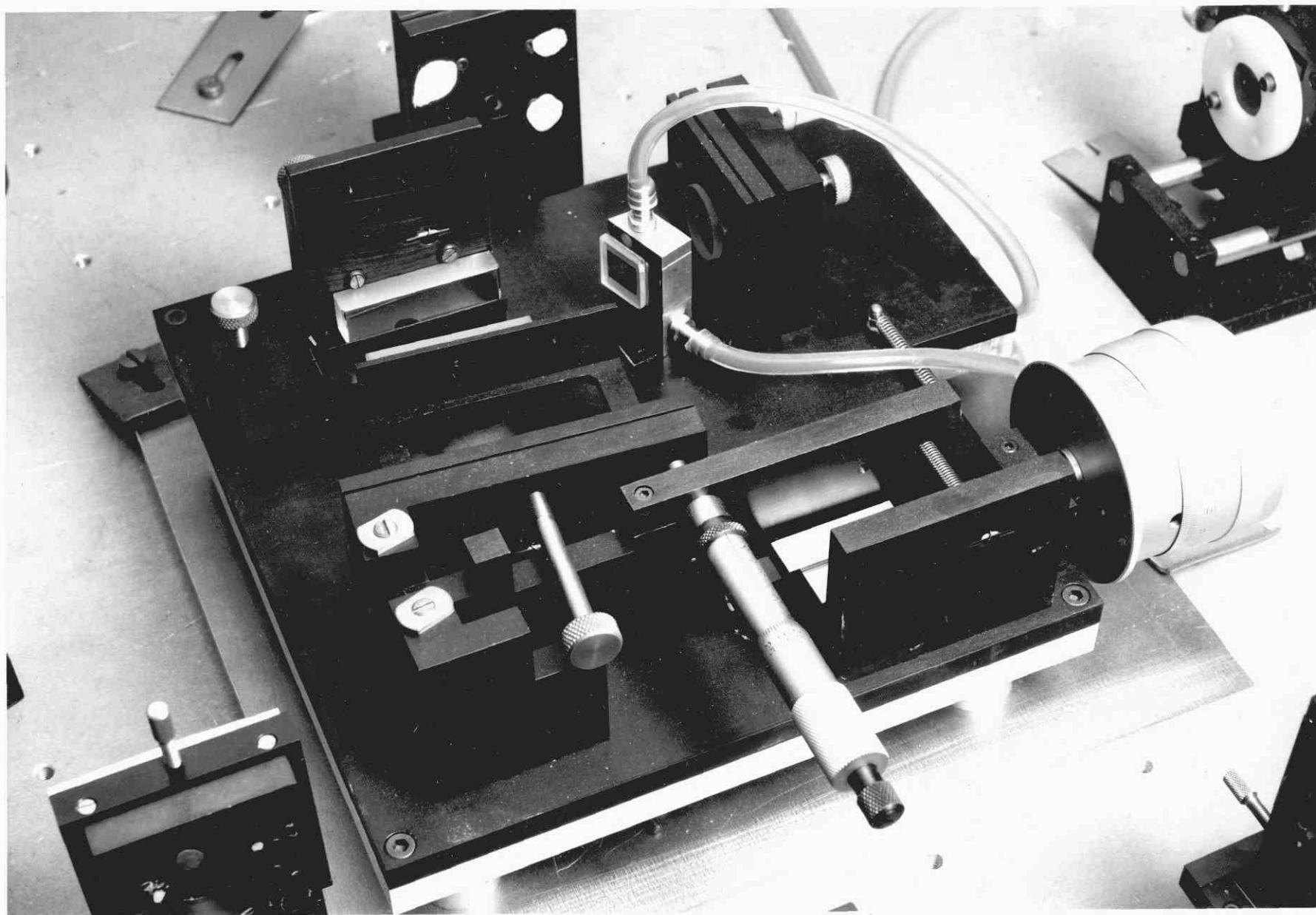
Fig. 4.4 shows a photograph of the dye laser. The coarse



Fabry-Perot fringes of 500 nm dye laser beam

FIG. 4.4 (plate)

The narrowband dye laser oscillator



and fine tuning controls (the small and large micrometers respectively) can be seen. Both act by pivoting the 100% tuning mirror opposite the grating. The first acts directly on the mount while the second (the fine tuning) pushes a 2° wedge, which contacts with a bearing on the mirror mount, providing precise adjustment.

The second dye laser (630 nm) used in the experiment had been the subject of some development work⁽¹⁰⁸⁾, and the modified design is shown in Fig. 4.5. The major modification is the use of a four prism beam expander^(109,110). Since some beam expansion is provided by the prisms, the angle of the grating can be reduced, improving its efficiency. The other modification was to replace the tuning mirror with a Littrow grating⁽¹¹¹⁾. The grating is correctly aligned to reflect light of wavelength λ back along its path, as shown in Fig. 4.5 when

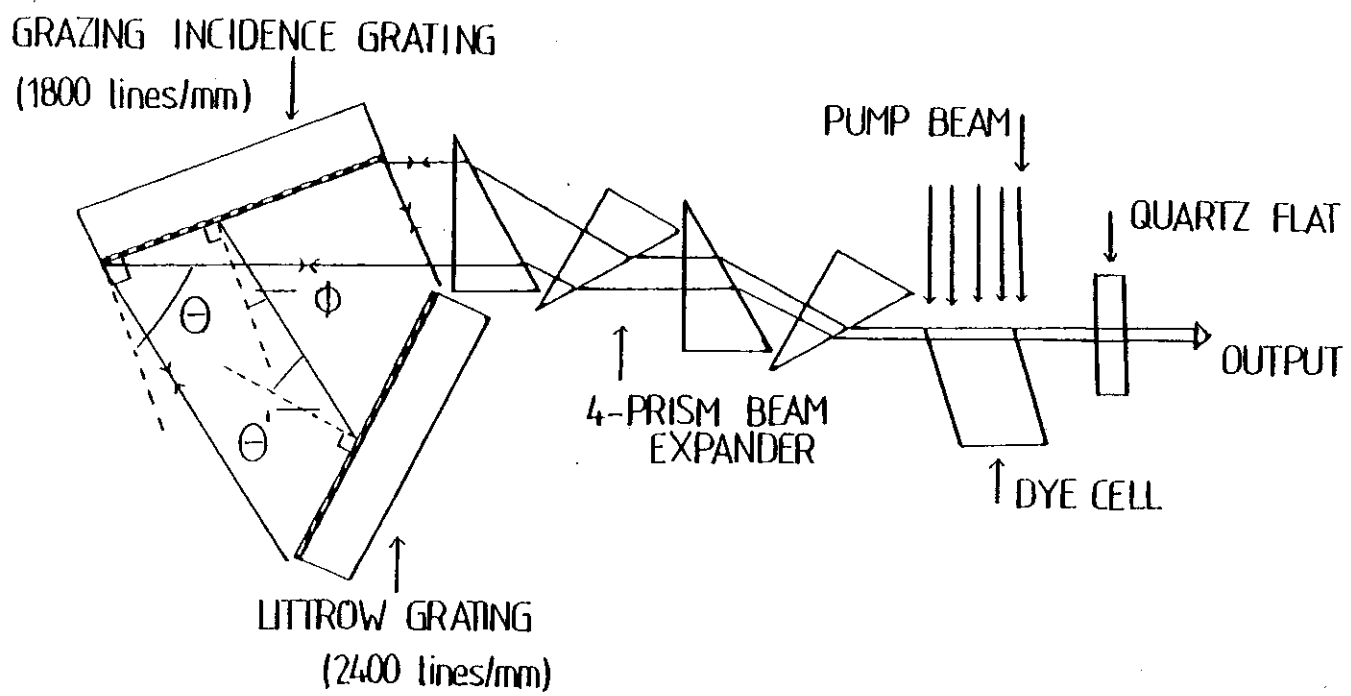
$$2d_2 \cos \theta' = m_2 \lambda \quad (4.3)$$

where d_2 is the line spacing of the Littrow grating, θ' is the angle of incidence and m_2 is an integer.

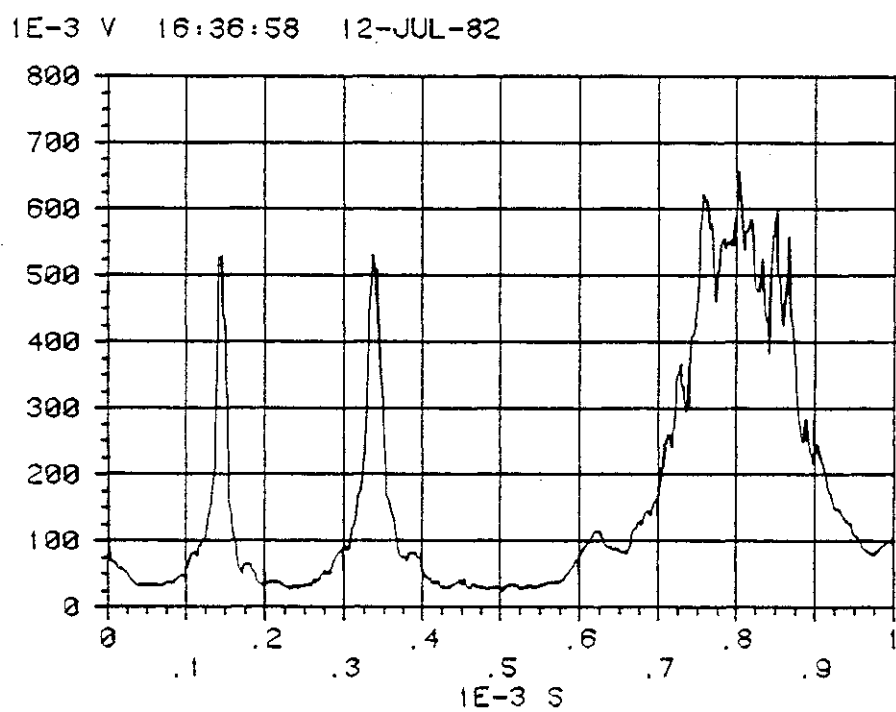
The dye cell, which in this case did not have a dye-flowing system, was filled with Rhodamine 101 dye dissolved in ethanol at a concentration of 10^{-3} gm. moles l^{-1} . Fabry-Perot fringes detected by a Reticon diode array are shown in Fig. 4.6⁽¹⁰⁸⁾, which show that the oscillator was operating in a single frequency mode, and hence the linewidth of the laser as used during the experiment was < 500 MHz.

There was insufficient time to make similar modifications to the 500 nm dye laser before the experiment was carried out, and so it remained as shown in Figs. 4.2 and 4.4.

FIG. 4.5



Modified design used for 630 nm dye laser



Fabry-Perot fringes of 630nm dye laser beam

4.1.2 The Amplifiers

The narrowband, but low power, output pulses from each dye laser oscillator are amplified in a chain of two amplifiers (A in Fig. 4.1) pumped by the remaining 90% of the 308 nm beam. An optical delay of 5 ns is introduced into this pump beam by two 100% reflecting aluminized mirrors (M1) in order to allow time for laser action to build up in the oscillators before pump energy reaches the amplifiers.

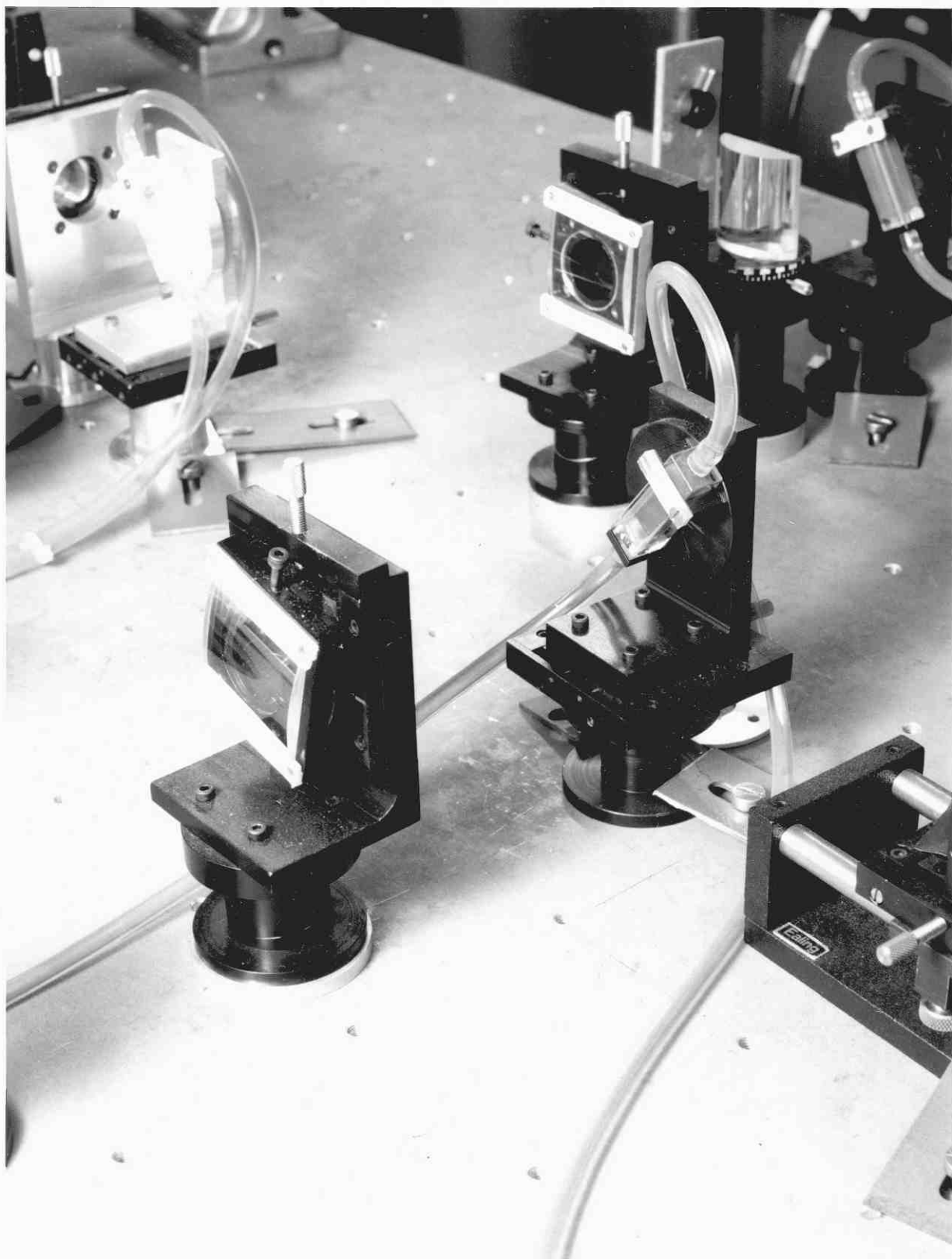
The pump beam is split and directed to the amplifiers by four 45° prisms (P2), which select successive sections across the width of the beam which has a rectangular cross section. The second amplifiers of the two chains receive a greater proportion of the pump energy than the first amplifiers. Cylindrical lenses (CL2 and CL3) are therefore necessary to condense the beam in the horizontal direction down to the dimensions of the dye cells.

Fig. 4.7 is a photograph of one amplifier. Dye is flowed through a 10 mm square section quartz dye cell (Hellma (UK) Ltd.). The cell is angled to prevent feedback between the faces. A 10 cm focal length cylindrical quartz lens (CL1) focuses the pump beam to a line just inside the dye cell at an angle set by rotation of the lens. The line of the excited dye region must be offset slightly from the beam line, otherwise broadband amplified spontaneous emission from the dye cell can be reflected from the output coupler of the oscillator and be reamplified, reducing the gain available for the narrowband beam.

The dye cell must be positioned so that the beam line passes along the inside of its front face. It is mounted on a translation stage which allows it to be moved across the beam line, and it must also be rotated to make the dye cell face parallel with the beam. The cylindrical focusing lens (CL1)

Fig. 4.7 (plate)

A dye laser amplifier comprising a cylindrical quartz focusing lens and a quartz dye cell with dye flowing system.



must be positioned vertically by the translation stage shown in Fig. 4.7 to position the focus at the same height as the dye laser beam.

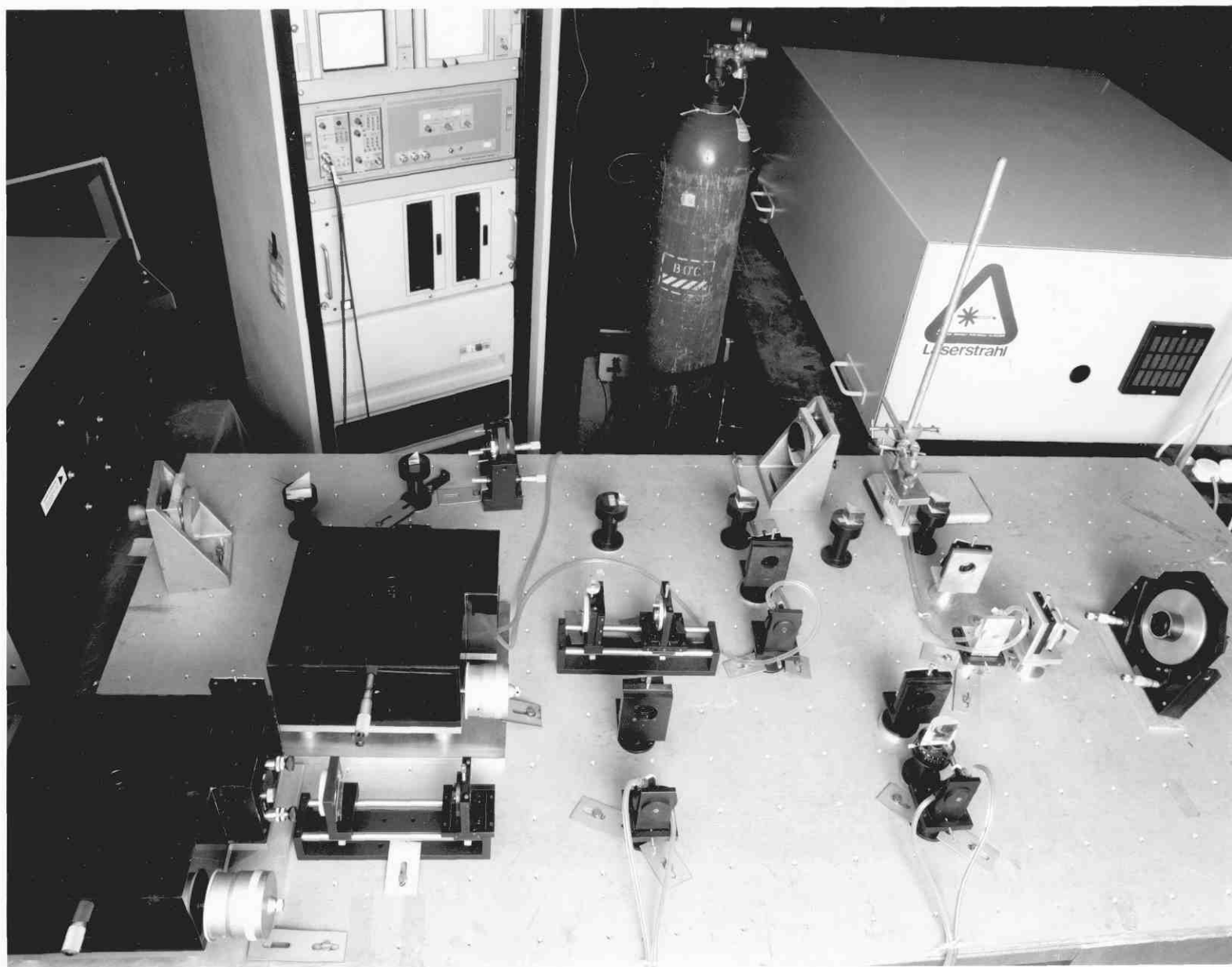
Fig. 4.8 is a photograph of the dye laser table shown schematically in part of Fig. 4.1. The output beam from each narrowband oscillator is horizontally polarized and is accompanied by broad band, divergent unpolarized amplified spontaneous emission from the dye cell. A polarizing filter (P) orientated to allow through the output beam is useful in that it attenuates the A.S.E. A 25 cm focal length lens (L1) brings the beam to a focus just before the first amplifier and an iris (I) blocks most of the remaining A.S.E. Since the dye cells of the amplifiers are tilted in the vertical direction, there would be a large reflection loss for horizontally polarized incident light. Therefore, a half-wave plate (R) is used to rotate the polarization of the beam to the vertical direction before amplification.

The dye concentration in the first amplifier of each chain is the same as in the respective oscillator, i.e. 10^{-2} gm. moles l^{-1} of Coumarin 307 and 10^{-3} gm. moles l^{-1} of Rhodamine 101, ethanol being the solvent in both cases. This allows a common dye flow system to be used for the oscillator and first amplifier, although this had only been arranged for the 500 nm (Coumarin 307) arm, the dye in the other oscillator being unflowed.

After the first stage of amplification, the beam continues to diverge away from the focus of the 25 cm lens (L1), so that the beam radius is ~ 1 mm at the second amplifier. To match the size of the pumped region to the larger beam the pump beam is slightly defocused at the dye cell surface, and the dye

Fig. 4.8 (plate)

The complete dye laser system and second harmonic crystal (far right).



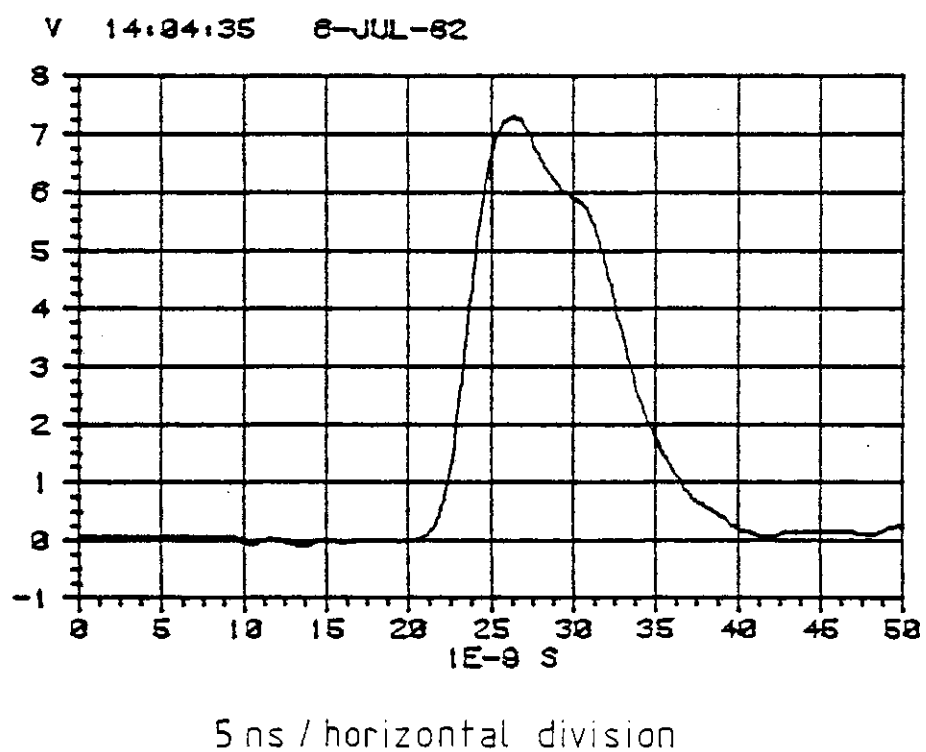
concentration is reduced by a factor of 3-4, with respect to that in the first amplifier, i.e. the concentrations are $\sim 3 \times 10^{-3}$ gm. moles l^{-1} and $\sim 3 \times 10^{-4}$ gm. moles l^{-1} for Coumarin 307 and Rhodamine 101 respectively. The second amplifiers, therefore, each have an exclusive dye flowing system.

Gain saturation occurs in the second amplifier, i.e. the pulse reaches an intensity where it can severely deplete the number of dye molecules in the upper laser level so that the gain is no longer exponential with distance. For the 500 nm beam the gain drops from x80 in the first amplifier to x8 in the second. The output energy was 2.5 mJ, giving an average power for a 10 ns pulse of 250 kW. The temporal profile of the dye laser output pulse is shown in Fig. 4.9.

Most of the 308 nm pump energy was directed to the second amplifier of the 500 nm dye laser since the output was to be used for frequency doubling. The reduced energy available for the other (630 nm) dye laser therefore meant that its pulse energy was only ~ 1.5 mJ, giving an average power of 150 kW.

4.2 Second Harmonic Generation in Potassium Pentaborate

Potassium Pentaborate ($KB_5O_8 \cdot 4H_2O$) was first shown to be useful as a frequency doubling crystal for wavelengths as short as 217.3 nm in 1975⁽¹¹²⁾. Until 1973 Ammonium Di-Hydrogen Phosphate (ADP) first used in 1962⁽¹¹³⁾ had been the most frequently used doubling crystal for short wavelength generation, its birefringence being sufficient for phase matching down to 244.2 nm⁽¹¹⁴⁾. In 1973 low power second harmonic generation was observed in Lithium Formate Monohydrate⁽¹¹⁴⁾ at wavelengths down to 225 nm. However, the conversion efficiency was limited by the crystals' UV absorption.



Dye laser output pulse after second amplifier

Dewey⁽⁷¹⁾ demonstrated second harmonic generation in Potassium Pentaborate (KB5) from 217.1 to 315.0 nm, and such a crystal was available (Cleveland Crystals) for the experiment. Fig. 4.10 shows the crystal orientation used for second harmonic generation where the refractive indices n_a , n_b , n_c for light polarized in the direction of the crystal axes labelled a, b and c respectively are shown as a function of wavelength in Fig. 4.11. An incident beam polarized in the ab plane generates its second harmonic polarized 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 radiation must be phase matched, i.e. their velocities of propagation must be equal. The velocity of the fundamental beam propagating in the ab plane at an angle Φ to the b axis is $c/n(\omega)$ where the refractive index $n(\omega)$ is given by

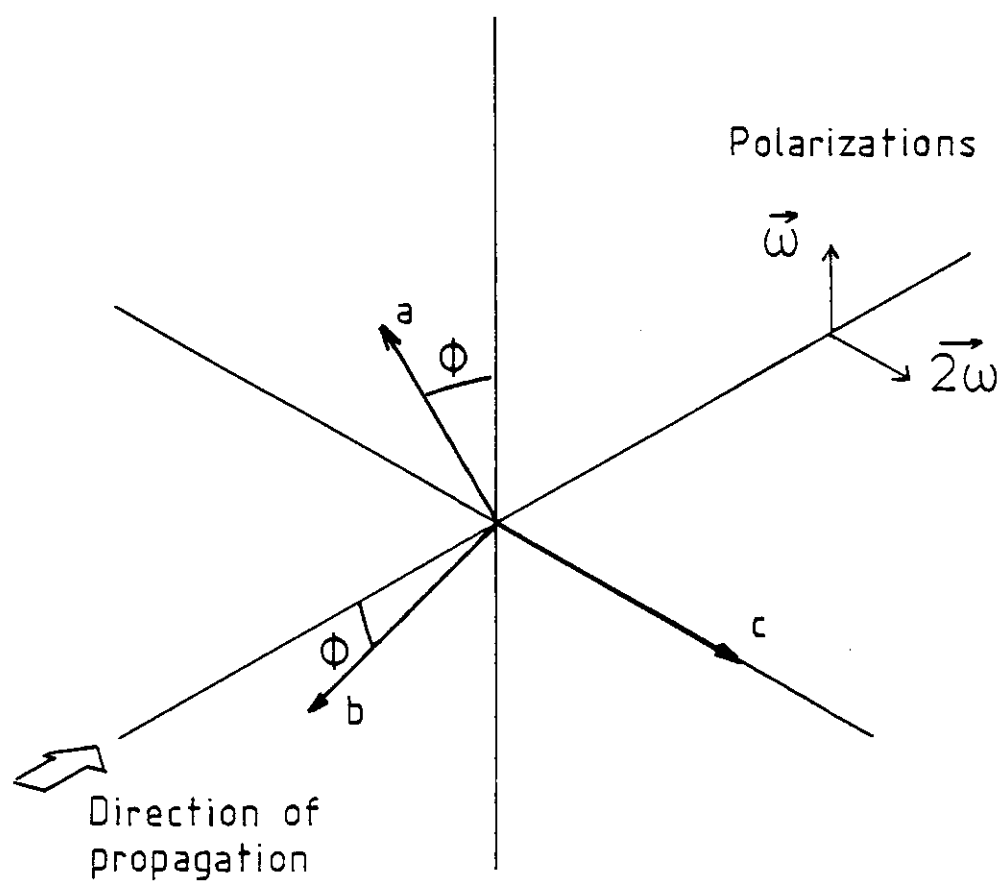
$$[n(\omega)]^{-2} = [n_b(\omega)]^{-2} \sin^2 \Phi + [n_a(\omega)]^{-2} \cos^2 \Phi \quad (4.4)$$

Therefore the velocities are equalized when $\Phi = \Phi_m$, the phase matching angle, where

$$\sin^2 \Phi_m = \{[n_c(2\omega)]^{-2} - [n_a(\omega)]^{-2}\} \{[n_b(\omega)]^{-2} - [n_a(\omega)]^{-2}\}^{-1} \quad (4.5)$$

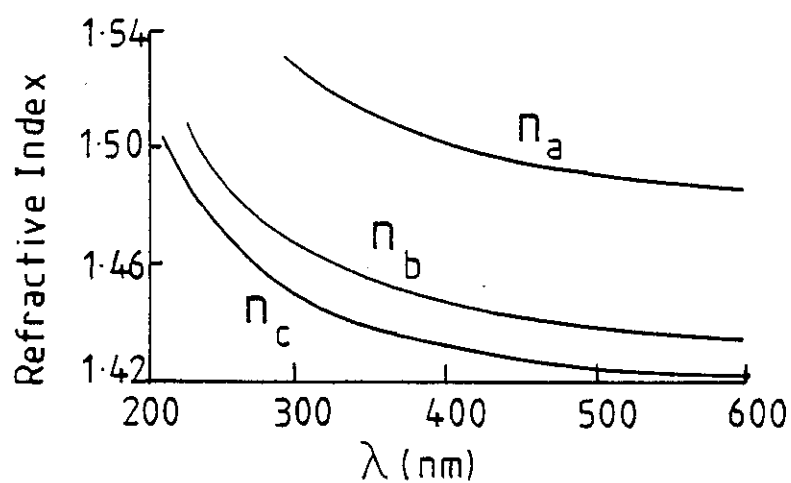
Fig. 4.12⁽⁷¹⁾ shows the required phase matching angle for generating wavelengths between 217 and 315 nm. The crystal used in the experiment was originally cut for generating a shorter wavelength than 249 nm and had to be angled at 15° to generate that wavelength. The mount for the doubling crystal can be seen

FIG. 4-10



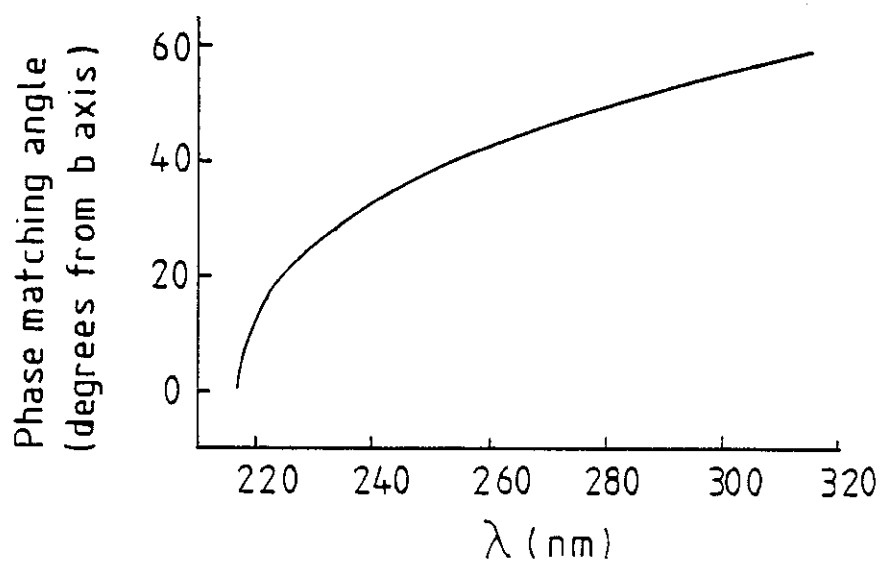
Orientation of KBr crystal for second harmonic generation

FIG. 4.11



Refractive indices of KBr (from Ref. 112)

FIG. 4.12



Phase matching angle against output wavelength for KBr crystal (from Ref. 71)

at the far right of Fig. 4.8.

The crystal itself was a cube of side ~ 10 mm, mounted in a cell with quartz windows and immersed in phase matching fluid which also prevented attack by moisture since the crystal is hygroscopic. The 250 kW output from the Coumarin 307 dye laser tuned to 499.2 nm was focused by a 25 cm lens (L2 in Fig. 4.1) into the crystal (SHG). (When a shorter focal length lens had been used the intensity produced was found to be sufficient to damage the crystal). The 499.2 nm fundamental beam was removed by an UV filter (F) after traversing the crystal, leaving the 249.6 nm second harmonic radiation. Losses due to reflections from the 15° angled windows and crystal faces and also absorption in the UV filter meant that, despite the crystal having an actual conversion efficiency of $\sim 1\%$, the output power at 249.6 nm was ~ 300 W.

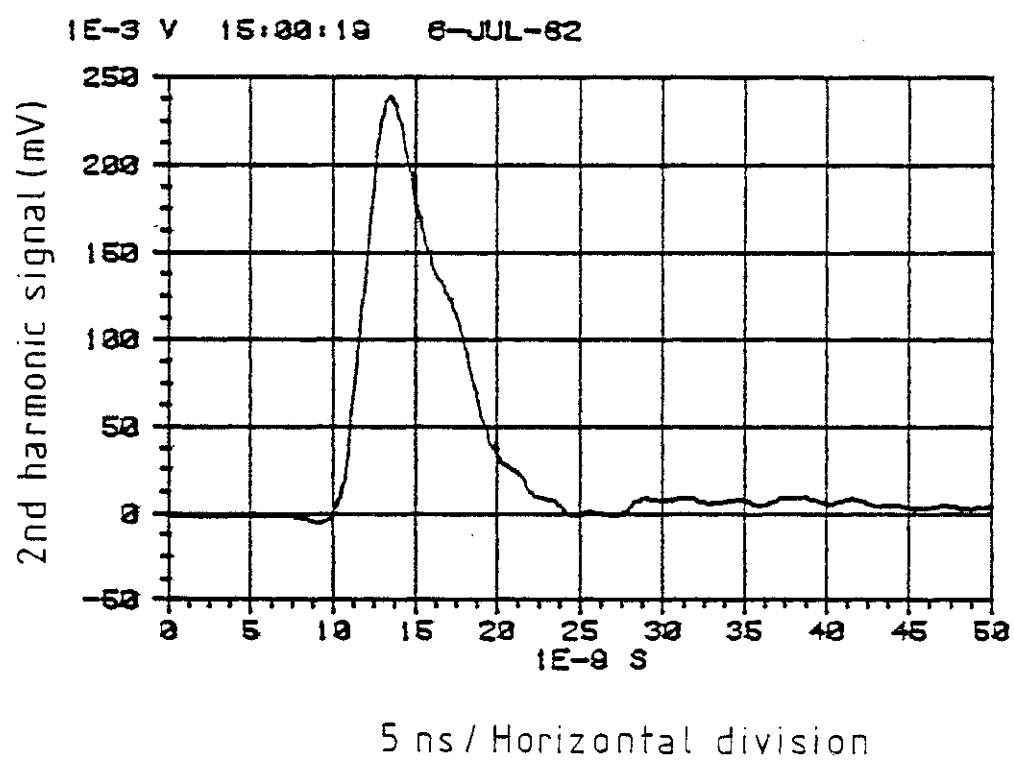
Due to the quadratic dependence of the output intensity of the second harmonic radiation on the intensity of the fundamental beam, the duration of the second harmonic pulse is shorter than that of the fundamental, having a half-width of ~ 5 ns, as can be seen from the photodiode trace in Fig. 4.13.

The second harmonic radiation at $\lambda = 249.6$ nm was recollimated by a 25 cm focal length quartz lens (L3) ready for amplification in the discharge pumped KrF amplifier.

4.3 The Discharge Pumped KrF Amplifier

The narrowband low power pulses at a wavelength of 249.6 nm were amplified in a discharge pumped KrF excimer amplifier to increase the pulse energy to several kW for appreciable output from the four wave mixing experiment. Previously, narrowband output from excimer lasers has been

FIG. 4-13



Photodiode trace of second harmonic pulse

achieved by using a narrowband excimer laser oscillator with frequency selective optics in the resonator and injection locking the output into another excimer laser, either with an unstable resonator cavity⁽¹¹⁵⁾ or used as a ring amplifier⁽¹¹⁶⁾. The approach used here has advantages over these systems, namely:

a) A narrower linewidth can be achieved with a dye laser, due to the far greater number of round trips achieved in the smaller cavity within the duration of the excimer laser pulse.

b) In the case of a narrow linewidth excimer laser, the losses introduced by the frequency selective optics are such that at wavelengths in the "wings" of the excimer laser transition the gain is not sufficient for the laser threshold condition to be achieved. Therefore the tuning range is narrower than when amplifying the second harmonic of a dye laser which is broadly tunable. The power output will be reduced in the "wings" of the transition, but lasing action will not stop. In this way it is possible to tune to 249.6 nm in a KrF amplifier where the centre of the transition is at 248.6 nm.

The discharge laser used as an amplifier for this experiment was constructed at this laboratory and is of the type described in Chapter 1 (Section 1.1.2) and shown schematically in Fig. 1.5. A thyatron was used as the High Voltage switch in the amplifier since synchronization with the Lambda Physik EMG 101 laser to within a few nanoseconds was required. However, this caused problems, since the high inductance of the thyatron, and hence its long risetime compared to a spark gap or grounded grid thyatron, resulted in a low power output and poor shot to shot reproducibility. When operated as an oscillator with a

back mirror and its windows aligned, the output energy was no more than ~ 60 mJ compared to ~ 250 mJ from the Lambda Physik EMG 101 with the same gas mixture (45 Torr of 10% F_2 /90% He, 90 Torr Xe and 1700 Torr He). Gas fill lifetime was also limited to ~ 5000 shots.

Synchronization was achieved between the amplifier and the EMG 101 with a jitter of ~ 10 ns. Appreciable gain is available from the amplifier for a period of ~ 15 ns. Since the double transit time for the amplifier would be ~ 10 ns the synchronization was not good enough to maintain two passes of the amplifier within the required time window. When this was attempted the shot to shot reproducibility was extremely poor. Therefore the 249.6 nm radiation was amplified in a single pass through the amplifier.

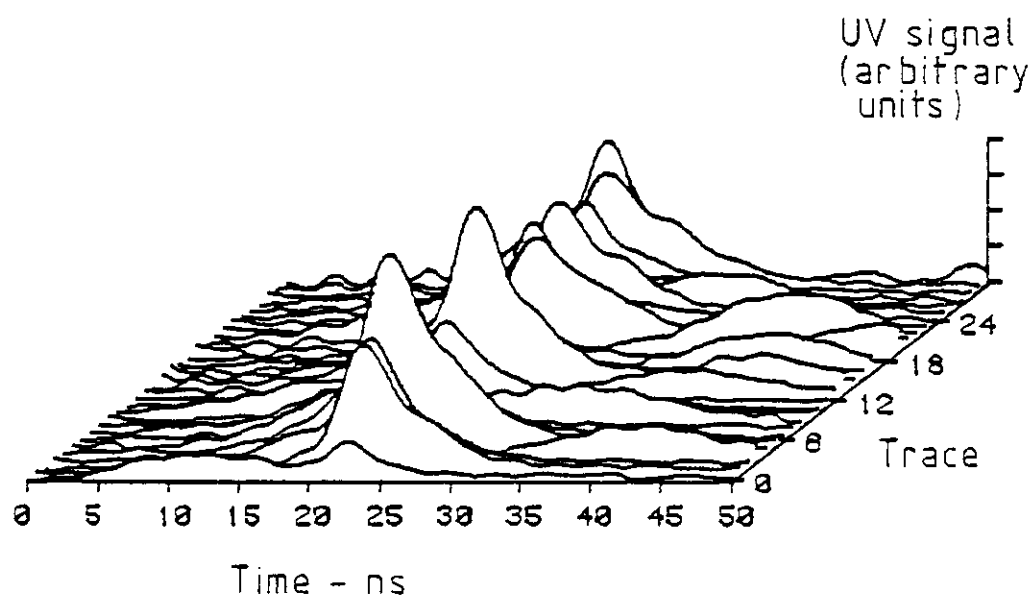
A He-Ne laser (shown in Fig. 4.1) was directed along the centre of the discharge in the amplifier to provide a reference for alignment of the second harmonic radiation from the KB5 crystal. This 249.6 nm radiation was then aligned with the He-Ne beam by adjustment of two mirrors (M2 and M3), the second of which was dielectric coated for $\sim 100\%$ reflection at 249 nm and transmitted the HeNe reference beam. The collimating lens (L3) after the KB5 crystal was adjusted so that the 249.6 nm beam diverged sufficiently to match its diameter to the height of the discharge volume in the amplifier in order to extract the maximum possible amount of energy. The end windows of the amplifier were angled in the horizontal plane to prevent feedback between them without affecting the height of the beam. An aperture (H) positioned after the amplifier removed the unwanted amplified spontaneous emission, and an uncoated quartz flat (BS2) acted as a beam splitter to provide a monitor of the amplified output on the photodiode

(PD). Attenuators placed in front of the photodiode ensured that the amplified signal remained within the limits of the linear response of the photodiode, so that the gain could be estimated. The maximum gain achieved at $\lambda = 249.6$ nm was ~ 100 . Fig. 4.14 shows an isometric plot of a series of amplified UV pulse waveforms demonstrating the variability of the pulse power. Some amplified spontaneous emission from the amplifier is detected, and this is useful in synchronizing the two discharge lasers. The gain was found to be approximately doubled near line-centre (248.6 nm), and with an amplifier with performance similar to that of commercial discharge lasers gains of up to ~ 1000 should be possible.

4.4 Beam Combination and VUV Detection

To generate VUV radiation by four wave mixing it was necessary to align the 249.6 nm amplified second harmonic and the 630 nm beams and bring them to a common focus to achieve the type of geometry described in Chapter 3 (see Fig. 3.1).

The two beams were combined at a dielectric coated mirror surface (M4 in Fig. 4.1) which was nearly 100% reflecting at 249.6 nm and transmitted $\sim 50\%$ of the red (630 nm) beam. This mirror was mounted on an optical bench at a right angle to the amplified beam from the discharge pumped amplifier, as shown schematically in Fig. 4.1. A 45° right angled prism (P4) turned the 249.6 nm beam and directed it at almost normal incidence onto the mirror (M4). This reflected the beam down the optical bench to a 20 cm focal length quartz lens (L5), which brought it to a focus at the centre of the 8 cm long cell containing Xenon gas.



Isometric plot of amplified UV pulse waveforms

The red beam (630 nm) was directed around the path defined by the prisms (P3) shown in Fig. 4.1, which equalized the optical delay in the two beams, and was transmitted through the mirror (M4) and down the optical bench to the same focusing lens (L5). To compensate for dispersion between the two beams in the focusing lens a telescope was mounted in the red beam between the two prisms (P3). The telescope was adjusted to bring the red beam to a focus at a distance greater than that between the telescope and the Xenon cell, so that its focus after the 20 cm lens (L5) would occur at the same point as that for the ultra-violet (249.6 nm) beam.

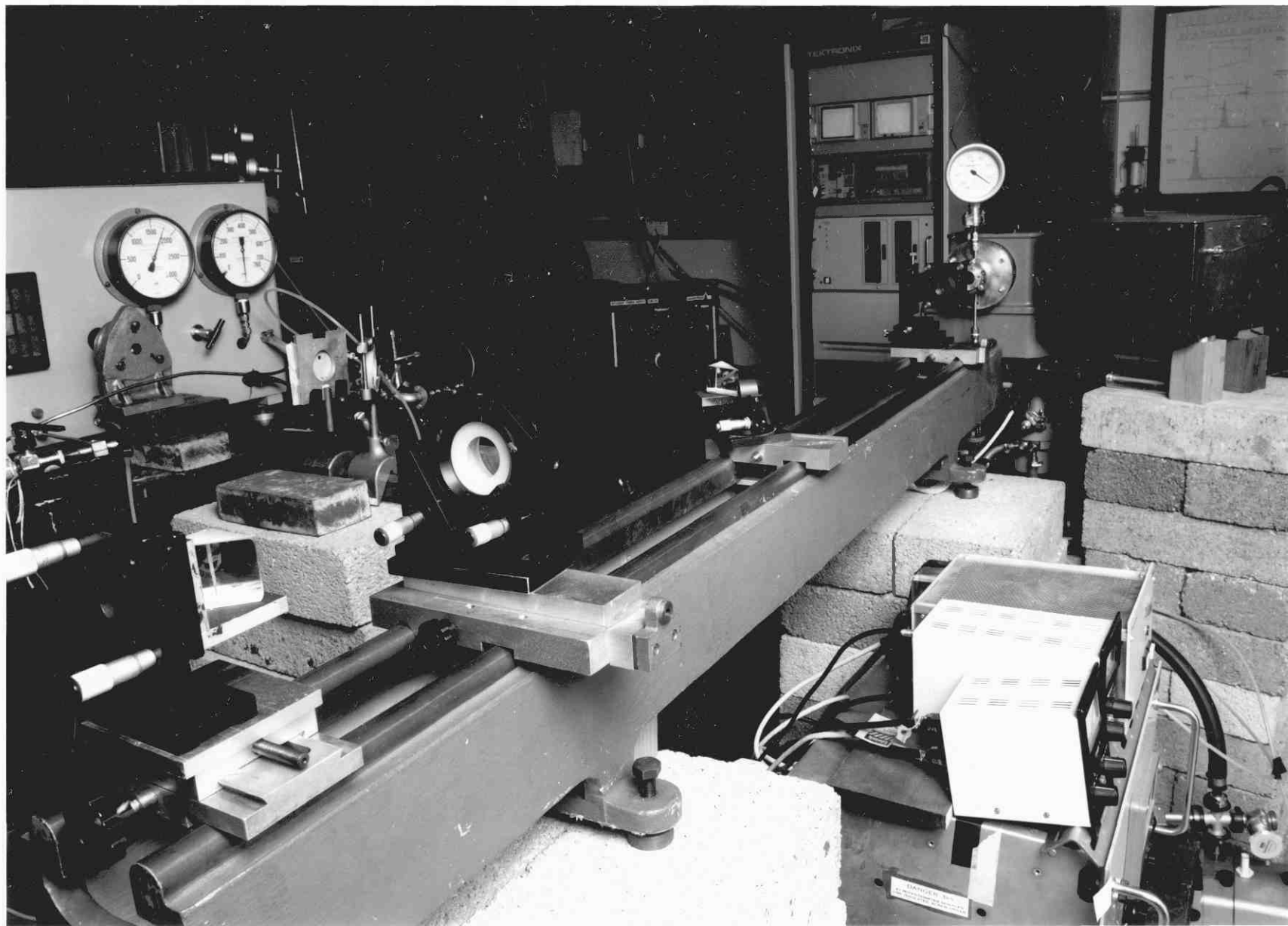
The alignment of the two beams was accomplished by the use of a pinhole of diameter 2.5×10^{-5} m, which was mounted on the optical bench at the focus of the 20 cm lens. By ensuring that both the 249.6 nm and 630 nm beams were transmitted through the pinhole while the lens and pinhole were tracked along the optical bench the two beams were known to be colinear and parallel to the optical bench.

Using the 25 micron precision pinhole (Ealing Corporation) as a calibration, the spot sizes were estimated from the images after focusing through the pinhole to be 25 microns for the 630 nm beam and 20 by 15 microns for the slightly asymmetrical ultraviolet beam. The beam divergence calculated from the spot size was $\sim 10^{-4}$ rads for both beams.

Fig. 4.15 is a photograph of the beam combining bench seen from the end opposite the Xenon cell, which is just behind the focusing lens and its mount and is mounted on the input of the monochromator in the background. The cell was evacuated to $\sim 10^{-2}$ Torr and filled with Research Grade Xenon (BOC Special Gases Division). The input window was a quartz flat and the output window a CaF_2 flat of ~ 1 mm thickness.

Fig. 4.15 (plate)

The beam combining optics, focusing lens, mixing cell and monochromator.



The 0.5 m Vacuum Monochromator (Acton Research Corporation) was evacuated to $\sim 10^{-6}$ mbar by a turbo-molecular pump. A solar blind photomultiplier (EMR model 541G-08-18) was mounted on the output of the monochromator and enclosed in a mild steel casing to reduce electrical noise. Signals from the photomultiplier were passed to a Tektronix 7912 AD Transient Digitiser and the digitized waveforms acquired could be read off by a Tektronix CP1164 mini-computer for processing or storage on hard and floppy discs.

Chapter 5

The Four-Wave Mixing Experiment : Results and Analysis

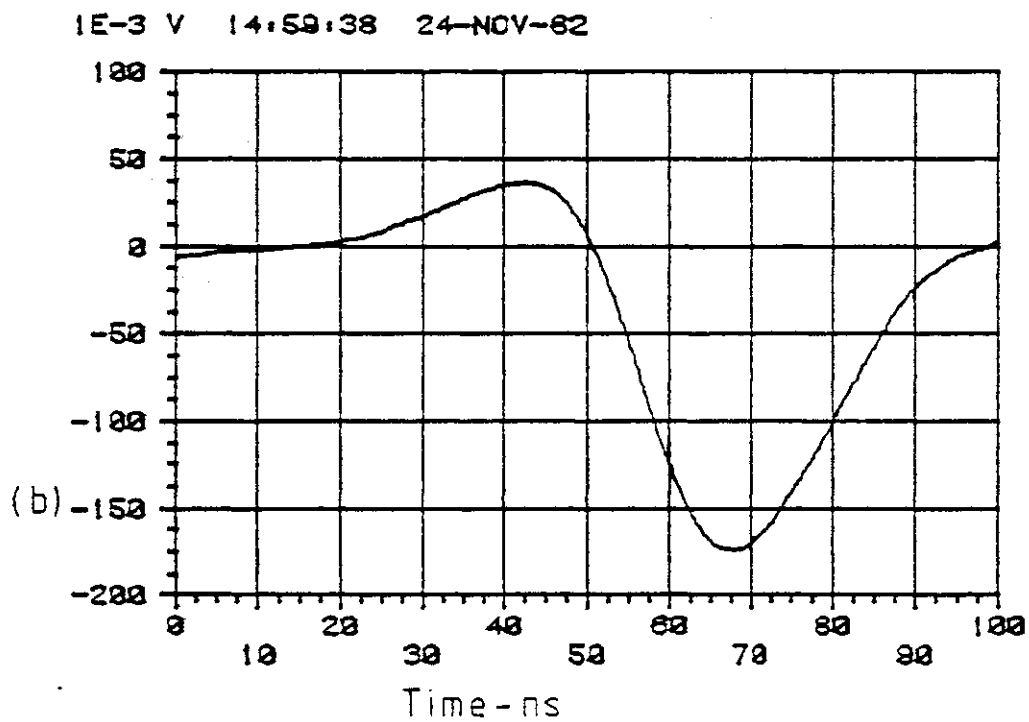
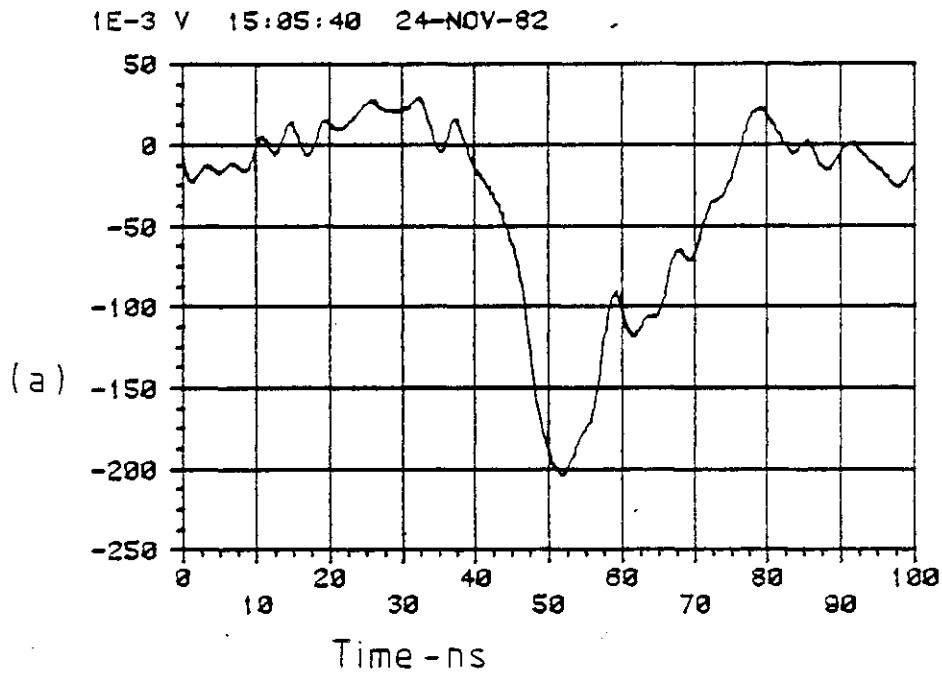
5.1 The Experimental Procedure

The apparatus used for the four-wave mixing experiment has been described in the previous chapter. During the course of the investigation of the physics of the four-wave mixing process in Xenon the wavelength of the visible dye laser was set at approximately the centre of its tuning range at 630 nm, producing VUV radiation at 155.6 nm when mixed with the 249.6 nm beam, these wavelengths being far off any single photon resonances which could affect the results.

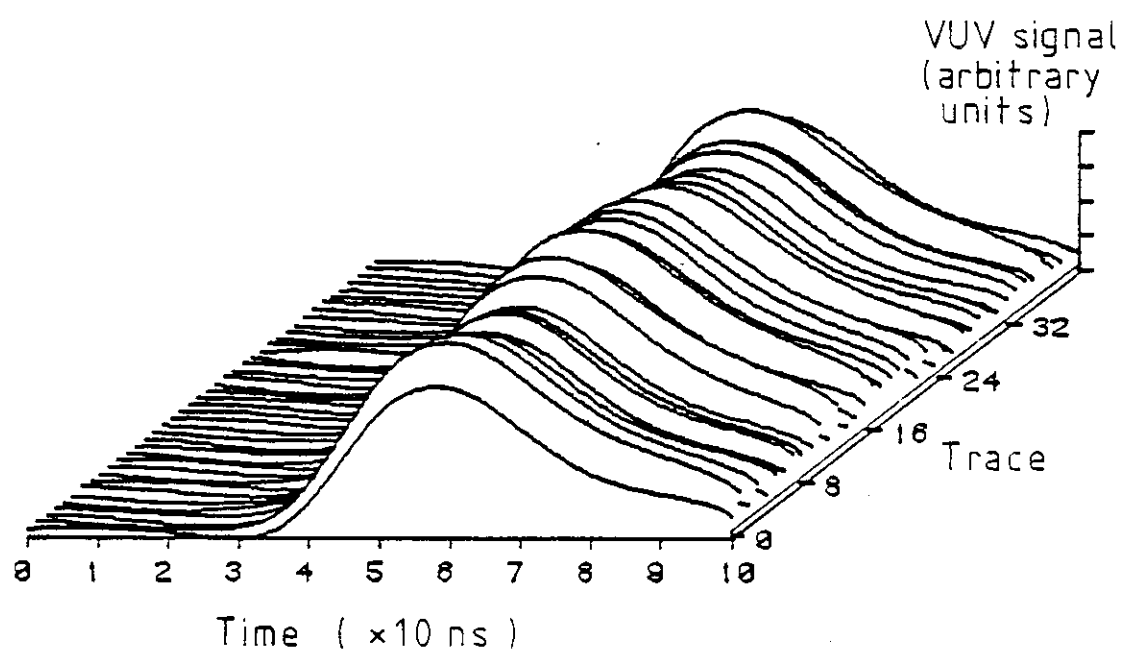
A waveform stored by the Tektronix CP1164 minicomputer showing a signal from the photomultiplier detecting the VUV radiation is reproduced in Fig. 5.1a. High frequency noise is evident in this waveform and so, to improve the reliability of pulse height determination, the bandwidth limiting facility of the Tektronix 7912 AD transient digitiser was used, filtering out transients of frequency greater than 20 MHz and producing the type of trace shown in Fig. 5.1b. This was desirable since the power output in the VUV region was, for the purposes of the experiment, characterized by the pulse height, assuming that the pulse duration was approximately constant.

The shot to shot variation of the UV input power to the mixing cell due to the KrF amplifier performance has been mentioned in Chapter 4 (see Fig. 4.14). This leads to a corresponding shot to shot variation in the VUV output power, as shown in the isometric plot in Fig. 5.2. The variation is not as severe as that in the UV power due to saturation effects which will be discussed in this chapter. A typical signal

FIG. 5.1



VUV signal (a) without bandwidth limiting
(b) with bandwidth limiting



Isometric plot of a series of VUV signals

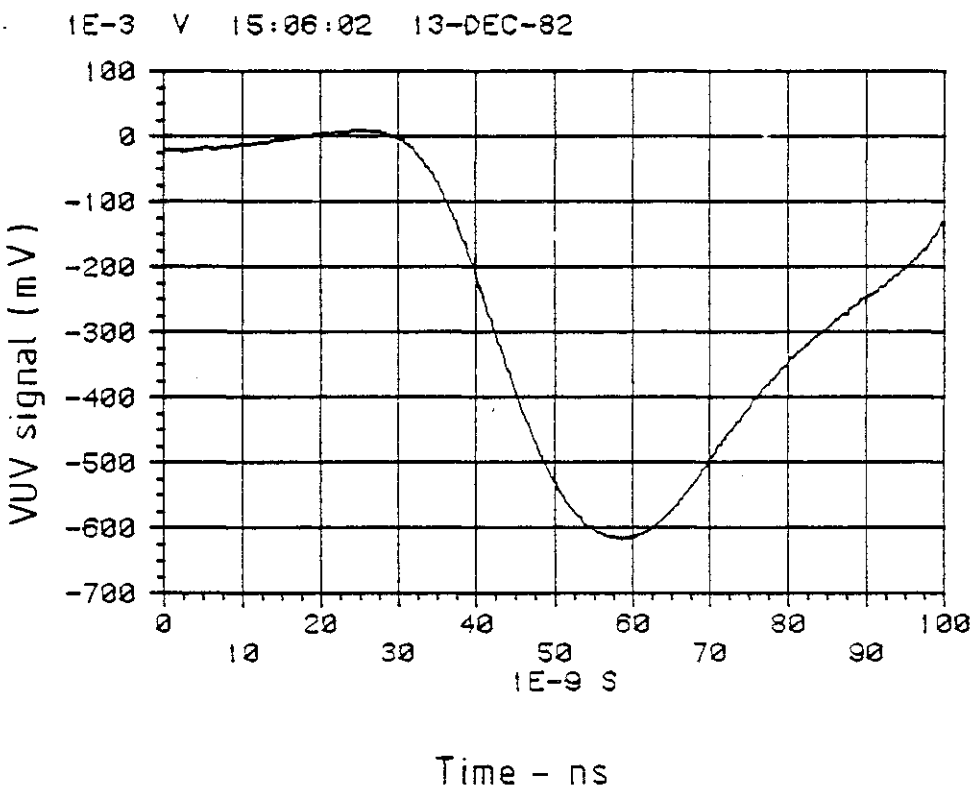
obtained is shown in Fig. 5.3.

In order to perform an analysis of the experimental results it was necessary to be able to determine the VUV power for a specific UV power. Therefore the peak height of the VUV signal (extracted from the waveform acquired by the transient digitiser) and the signal height of the amplified UV radiation (as detected by an ITL UV photodiode and Tektronix 7834 Storage Oscilloscope) for the same shot were recorded. A series of these shots allowed the VUV output to be determined for a spread of UV powers, as shown in Fig. 5.4. In order to produce a graph of VUV output against parameters other than the UV power, one of these curves was required for each data point. Approximately twenty points were obtained for each VUV against UV power curve. This allowed a sufficient number of data points to be obtained within the "lifetime" of one gas fill of the KrF discharge amplifier (approximately 2 hours at 0.5 Hz). Due to temperature changes in the laboratory, the alignment of the optical system and in particular the stabilization of the wavelength of the 249.6 nm radiation could not be maintained over long periods. However, normalization with respect to the VUV power enabled accurate comparisons to be made.

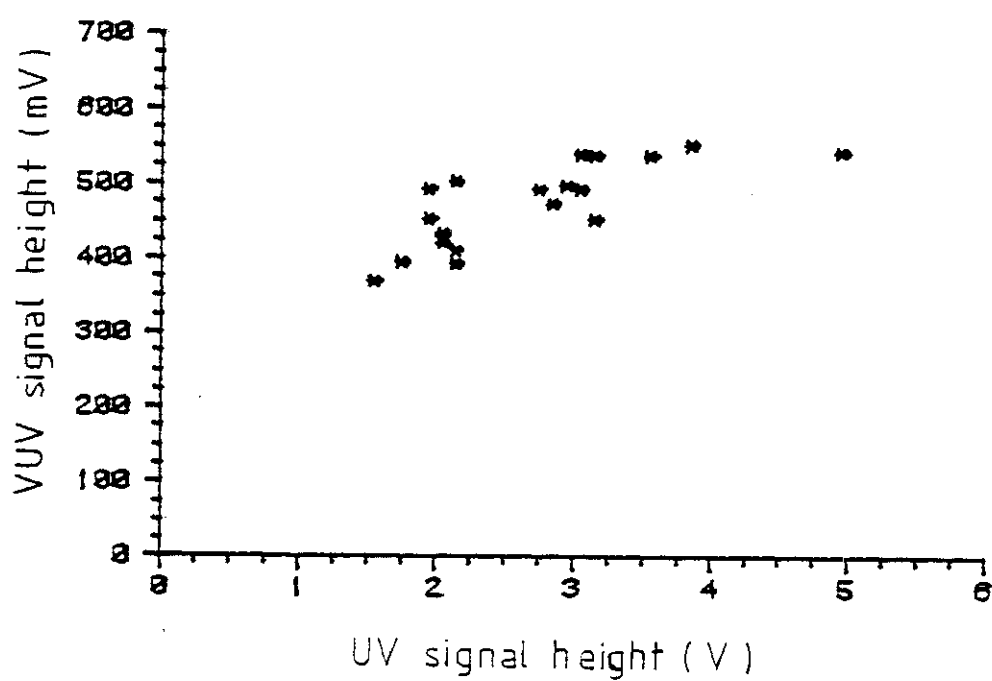
Other parameters whose effect on the VUV power were studied were the Xenon pressure, the power of the radiation at 630 nm and the detuning of the 249.6 nm radiation from the two photon resonance. The VUV power was plotted against these parameters for a range of UV powers.

Results

Fig. 5.5 shows the dependence of the peak height of the VUV signal (on the photomultiplier - mV) on the amplified UV

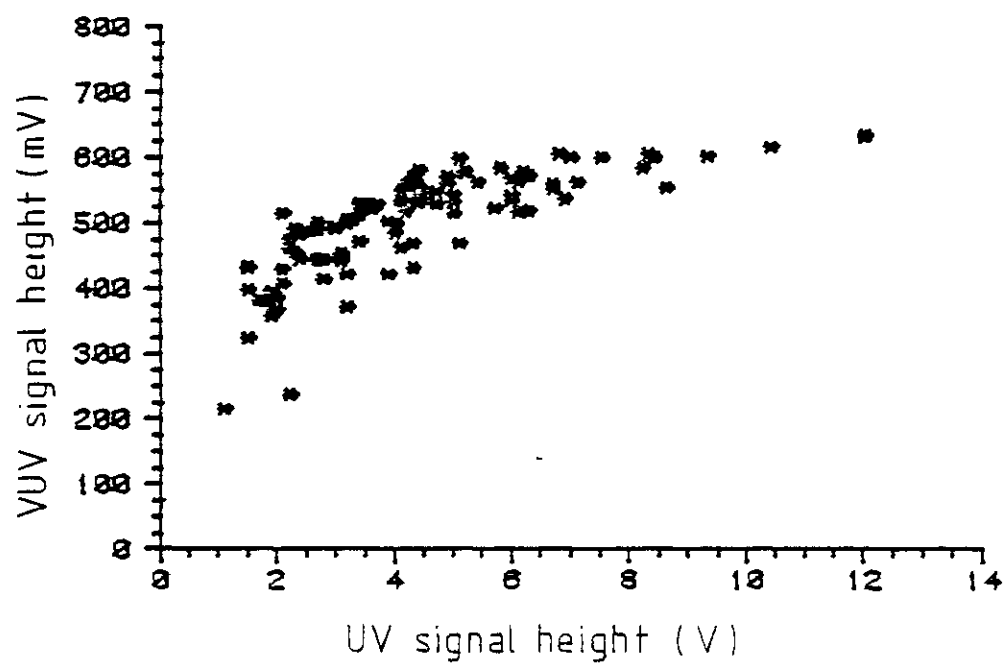


A typical VUV signal



A graph of VUV signal height (mV) against peak UV signal height (V) for the same shot

FIG. 5.5

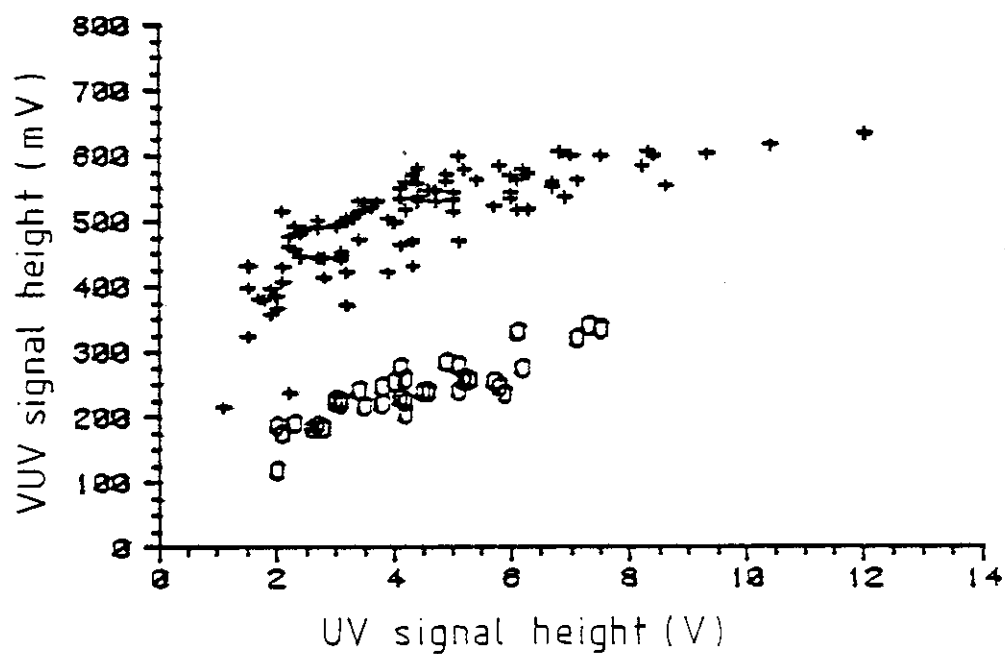


A graph of VUV signal height (mV) against peak UV signal (V) for a Xenon pressure of 50 Torr

signal peak height (on the photodiode—V) at a Xenon pressure of 50 Torr. Saturation is evident from this graph and to ensure that this was not due to saturation of the photomultiplier the entrance and exit slits of the monochromator, which had been fully open to improve the collection efficiency, were closed down until the VUV signal was reduced by approximately a factor of two. The results shown in Fig. 5.6 were then taken, which shows the spread of points obtained with the reduced slit width (circles) compared to the results in Fig. 5.5 (crosses) for which all other experimental conditions were the same. The saturation phenomenon is observed in both, suggesting it is caused by processes occurring in the nonlinear medium and not in the detector.

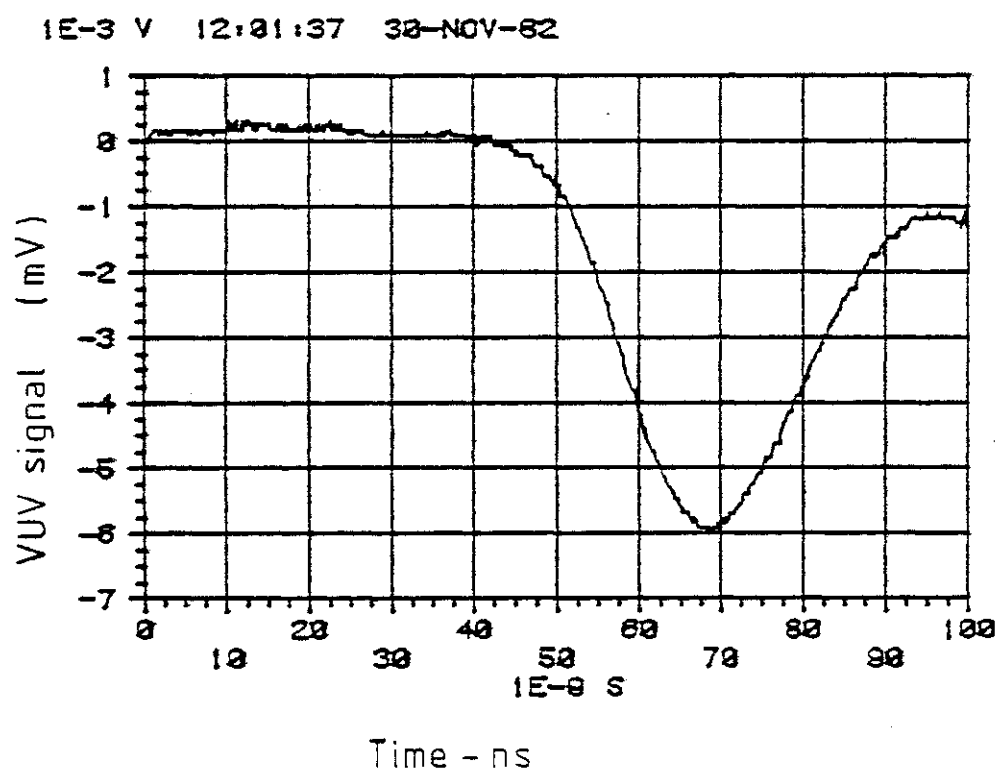
Fine tuning of the alignment of the laser system and of the wavelength of the Coumarin 307 dye laser was achieved by optimization of the VUV signal and it is of interest to note that when this fine tuning had been achieved it was just possible to detect a VUV signal, even without amplification of the 249.6 nm radiation. Such a VUV signal obtained under these conditions is shown in Fig. 5.7.

By measuring the energy of the amplified UV pulses with a calorimeter and using the temporal profile of the pulse (see Fig. 4.14) it was possible to estimate the peak power of the UV pulses. This enables the abscissae in Figs. 5.4, 5.5 and 5.6 to be expressed in power units with a conversion factor of $\sim 1.5 \text{ kW V}^{-1}$. As the spot size, when focussed by the 20 cm lens in front of the mixing cell is ~ 20 by $15 \mu\text{m}$, this implies a conversion factor for the peak intensity at the focus of $0.5 \text{ GW cm}^{-2} \text{ V}^{-1} \pm 40\%$, the error taking into account the difficulty in measuring the small UV pulse energies ($\sim 0.05 \text{ mJ}$)



Comparison of VUV signal with (O) and without (+) monochromator slits closed down

FIG. 5-7



VUV signal on photomultiplier with unamplified
UV input pulse

accurately and also the errors in estimating the spot size. An approximate intensity scale could then be substituted for the UV monitor voltage. By the same method the peak intensity, I_{VIS} , of the red dye laser (630 nm) was estimated to be $5 \text{ GW cm}^{-2} \pm 15\%$ at the focus for the following results (except for Fig. 5.10 where realignment of the dye laser system meant that I_{VIS} was $7 \text{ GW cm}^{-2} \pm 15\%$).

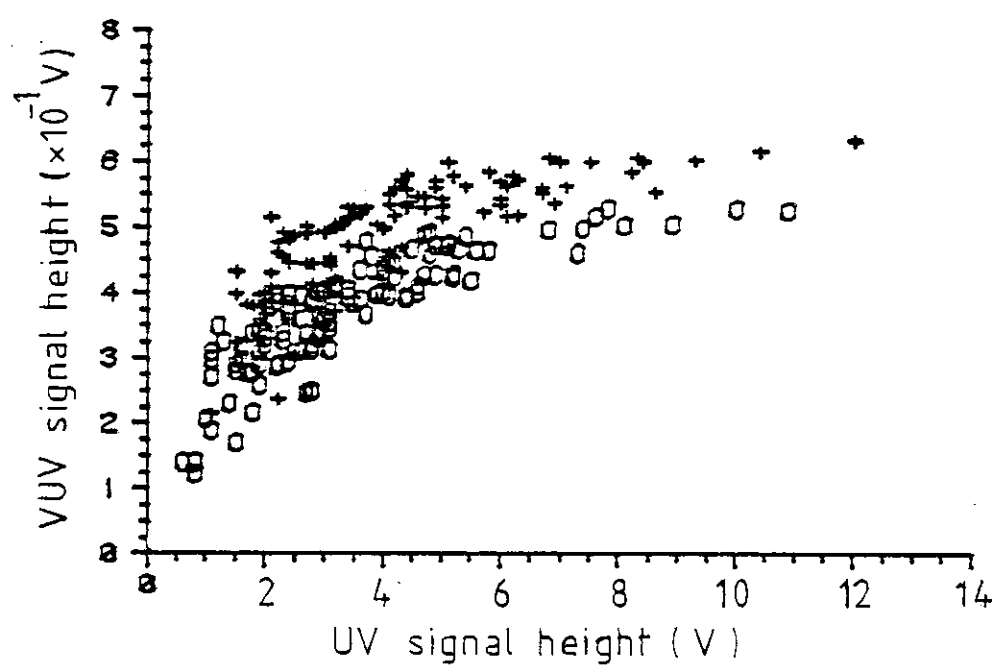
Therefore, from the results shown in Fig. 5.8 of VUV signal height against UV signal height at pressures of 50 Torr (crosses) and 20 Torr (circles) the graph shown in Fig. 5.9 of VUV intensity, I_{VUV} (arbitrary units) against UV intensity, I_{UV} (GW cm^{-2}) for the two pressures could be obtained. Strong saturation is indicated by the marked departure of the dependence of I_{VUV} from I_{UV}^2 which would be expected from theoretical predictions, not taking into account saturation phenomena.

Fig. 5.10 shows the experimentally determined variation of output power with Xenon pressure for the three values of I_{UV} shown with I_{VIS} fixed ($\sim 7 \times 10^9 \text{ W cm}^{-2}$) and the wavelength of the amplified UV tuned into the two photon resonance. The optimum pressure was found to be 55 Torr for the three values of I_{UV} . Also plotted is the theoretical pressure dependence

$$I_{VUV} \propto P^2 \exp(-KP) \quad (5.1)$$

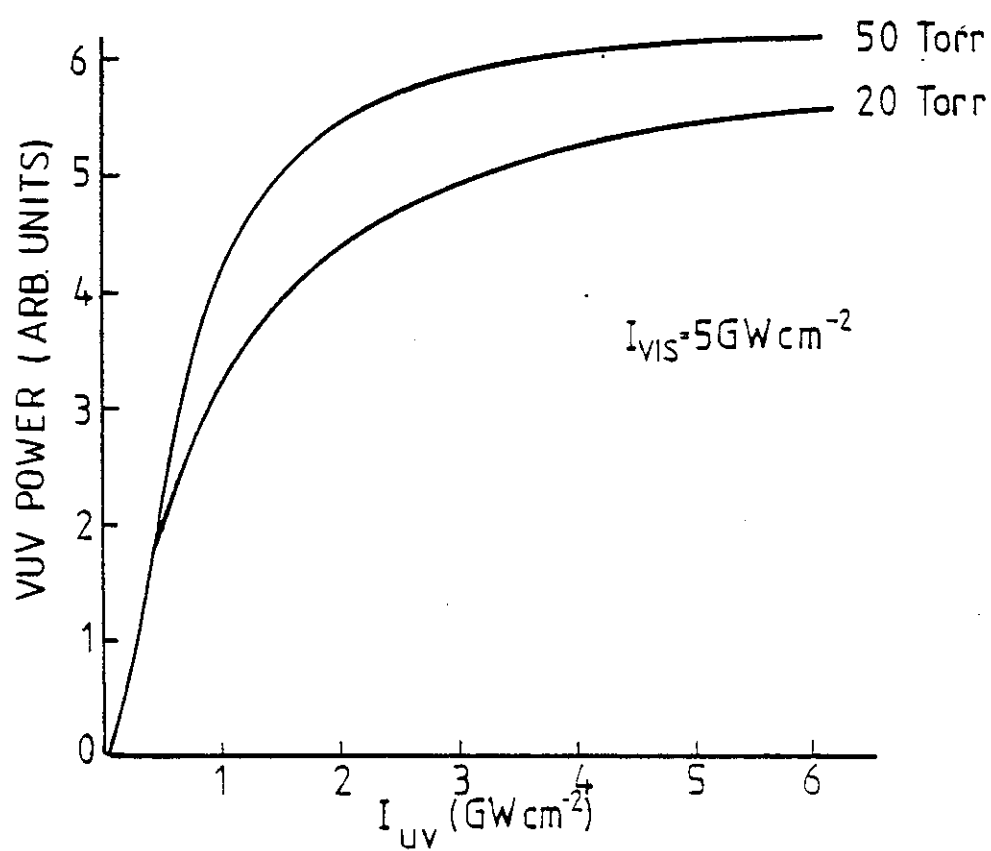
where $K = b \Delta k / P$

and is calculated from the calculated dispersion of atomic Xenon (Fig. 3.5a) and given a confocal parameter (b) of 2 mm, as calculated from the measured spot sizes of the beams. While there is good agreement with the theoretical prediction at low pressures (< 40 Torr) there is a marked departure at

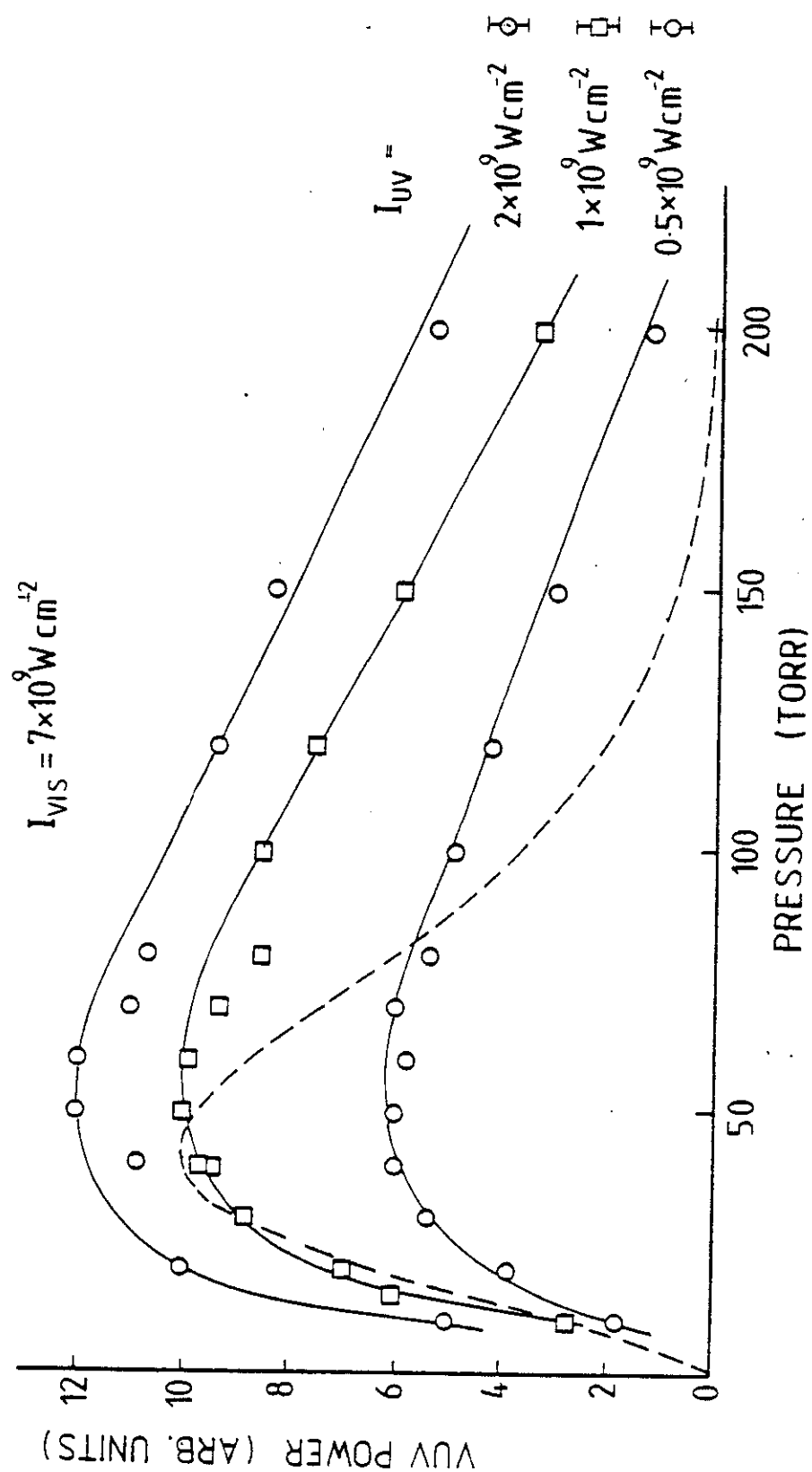


VUV signal height against UV signal height for pressures of 50 Torr (+) and 20 Torr (O)

FIG. 5.9



VUV Intensity(arbitrary units) against UV Intensity (GW.cm^{-2}) for pressures of 50 and 20 Torr



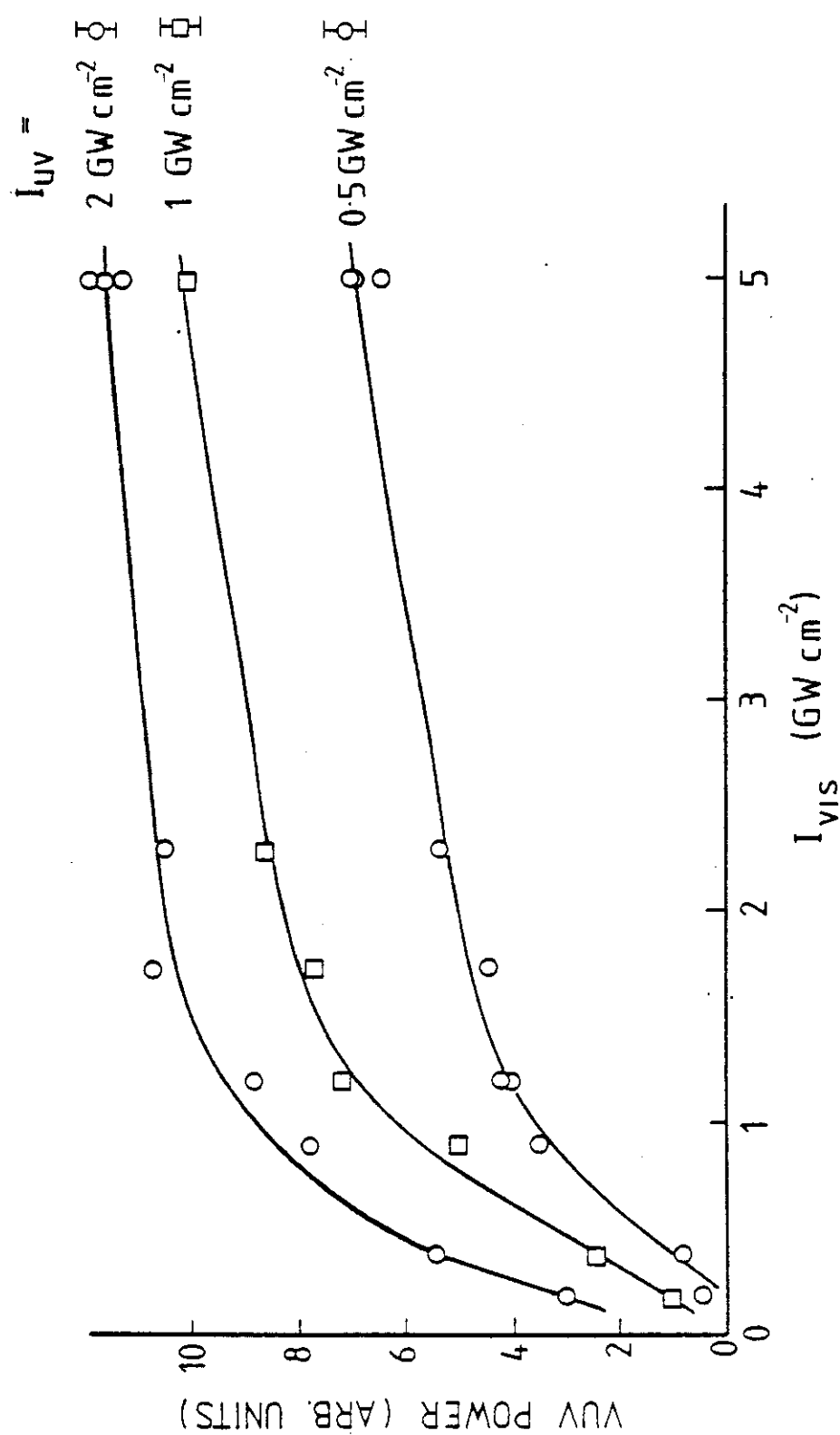
VUV Intensity against Xenon pressure for UV Intensities of 0.5, 1 and 2 GW/cm^2 with the theoretical curve shown for comparison (dashed curve)

high pressures, the reasons for which will be discussed in the next section.

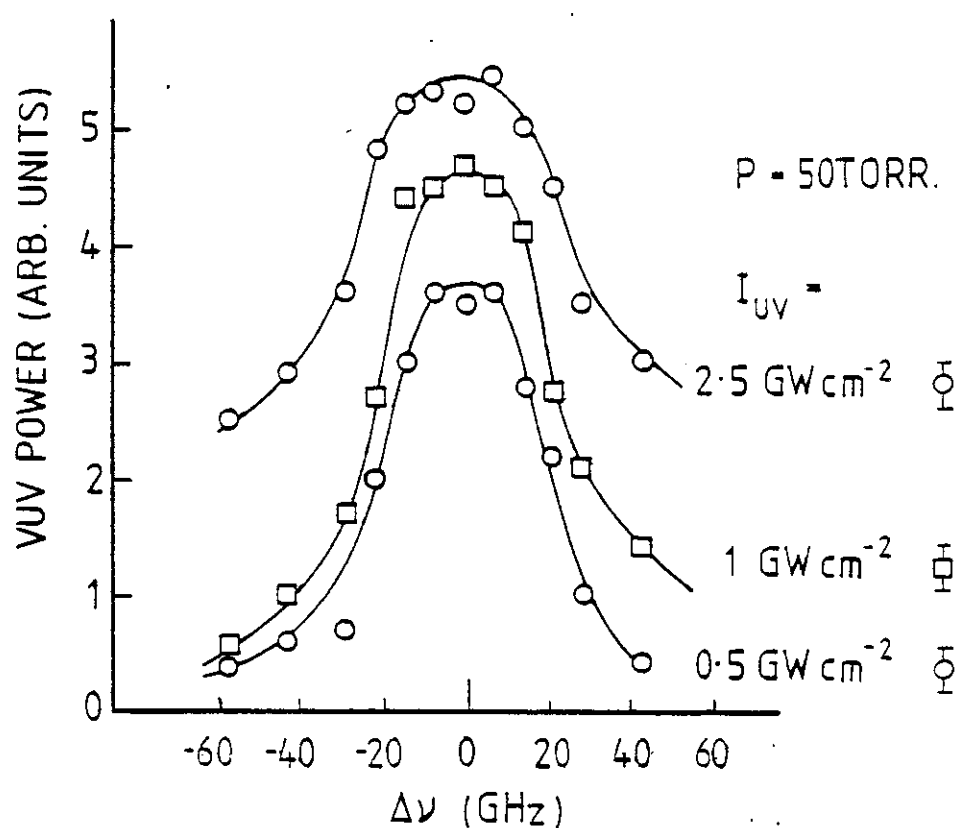
The dependence of the VUV output on the intensity, I_{VIS} , of the 630 nm radiation was also investigated. Attenuators calibrated for use at 630 nm were inserted in the beam to give the results shown in Fig. 5.11 for peak UV intensities of 0.5, 1 and 2 GW cm^{-2} . As with the UV intensity dependence, saturation is indicated by the departure from the expected linear dependence on I_{VIS} predicted by equation (3.30).

Finally, the influence of detuning of the 249.6 nm radiation from the two photon resonance was experimentally determined. This presented problems since the fine tuning micrometer of the 499 nm dye laser was found to exhibit back-lash. To negate the effect of this, the tuning micrometer was turned only in one direction, the wavelength of the UV radiation being tracked across the two-photon resonance. As can be seen from Fig. 5.12, the widths of the detuning curves for the three values of I_{UV} shown are much broader than both the spectral width of the two photon resonant laser radiation (~ 1.5 GHz) and the two photon state whose pressure broadened and Doppler linewidths are both ~ 1 GHz⁽⁹⁷⁾. The width of the detuning curve is seen to increase with increasing I_{UV} . These results will be discussed in the next section.

An estimate was made of the maximum VUV power obtained by using the spectral response curve supplied by the manufacturers of the photomultiplier and its sensitivity at 249.6 nm calculated from the previously determined UV power. Again, the accuracy is limited by the difficulty in measuring the small UV pulse energy precisely with a calorimeter and also the wavelength of 249.6 nm is at the extreme limit of the response of the photomultiplier where the error in the response curve is greatest.



VUV Intensity against Intensity of the 630 nm fundamental beam for UV Intensities of 0.5, 1 and 2 GW cm^{-2}



Variation of VUV Intensity with detuning of the 249.6 nm radiation from the two photon resonance (GHz) for UV Intensities of 0.5, 1 and 2.5 GW / cm^2

The maximum VUV output power was estimated to be 100 W $\pm$ 40% (at $I_{UV} > 5 \text{ GW cm}^{-2}$) by this method, but shortening of the pulse duration due to saturation and the breaking of phase matching would imply that this is a lower limit.

5.3 Discussion of Results

The processes that are the most probable causes of the saturation effects evident in Figs. 5.9 and 5.11 are two photon absorption into the 6p state and multiphoton ionization (as illustrated by Fig. 3.7). The two photon absorption cross section for the 5p-6p transition in Xenon and the photoionization cross section from the 6p state at 249 nm are $\sim 10^{-28} \text{ cm}^4 \text{ W}^{-1}$ and $\sim 10^{-18} \text{ cm}^2$ (97) respectively. These cross sections are high enough for this process alone to be responsible for appreciable depopulation of the 5p ground state within the duration of the laser pulses used in this experiment. The rate of two photon absorption is

$$\frac{\alpha(V_1) I_1^2 N_g}{\hbar \omega_1}$$

where N_g is the ground state population, $\alpha(V_1)$ is the cross section, and I_1 ($= I_{UV}$) is the UV intensity. For $I_1 = 1 \text{ GW cm}^{-2}$

$$\frac{\alpha(V_1) I_1^2}{\hbar \omega_1} = 1.26 \times 10^8 \text{ s}^{-1}$$

Therefore this process could depopulate the ground state by 20% in only $\sim 2 \text{ ns}$. The rate of photoionization from the 6p state at the same intensity is even greater, being equal to

$$\frac{\sigma_{pi} I_1 N_g}{\hbar \omega_1} = 1.26 \times 10^9 N_g \text{ s}^{-1}$$

where σ_{pi} is the photoionization cross section. The photoionization therefore reduces the population of the two photon resonant level, so that it is unlikely to be the cause of saturation at this intensity. However, since the rate of two photon absorption scales as I_1^2 , whereas that for photoionization scales linearly with I_1 , the build-up of population in the two photon resonant state may be come a major contribution to the saturation at higher UV intensities.

The ground 5p state can also be depopulated by multiphoton ionization. The saturation of the VUV intensity with the visible intensity I_{VIS} (Fig. 5.11) suggests that this is a dominant factor, although the cross sections are not known. Multiphoton ionization can occur, involving two photons at 249.6 nm, which would provide resonant enhancement of the process, and either another 249.6 nm photon or two at 630 nm. The quadratic dependence of the rate for this latter process would explain the strong saturation of I_{VUV} with I_{VIS} since the unsaturated dependence of I_{VUV} on I_{VIS} is only linear (equation 3.30). Similarly, the rate of multi-photon ionization via the absorption of three 249.6 nm photons would have a cubic dependence on I_{UV} compared to the quadratic dependence of the VUV generation.

Depopulation of the 5p ground state caused by photoionization will have two main effects, as can be seen from equation (3.30).

$$P_4 = 1.580 \times 10^{-4} \frac{k_0^4 k_1^2 k_3^2 N^2 |X|^2 P_1^2 P_3^2}{k_4^2 k'} F(b \Delta k) \quad (3.30)$$

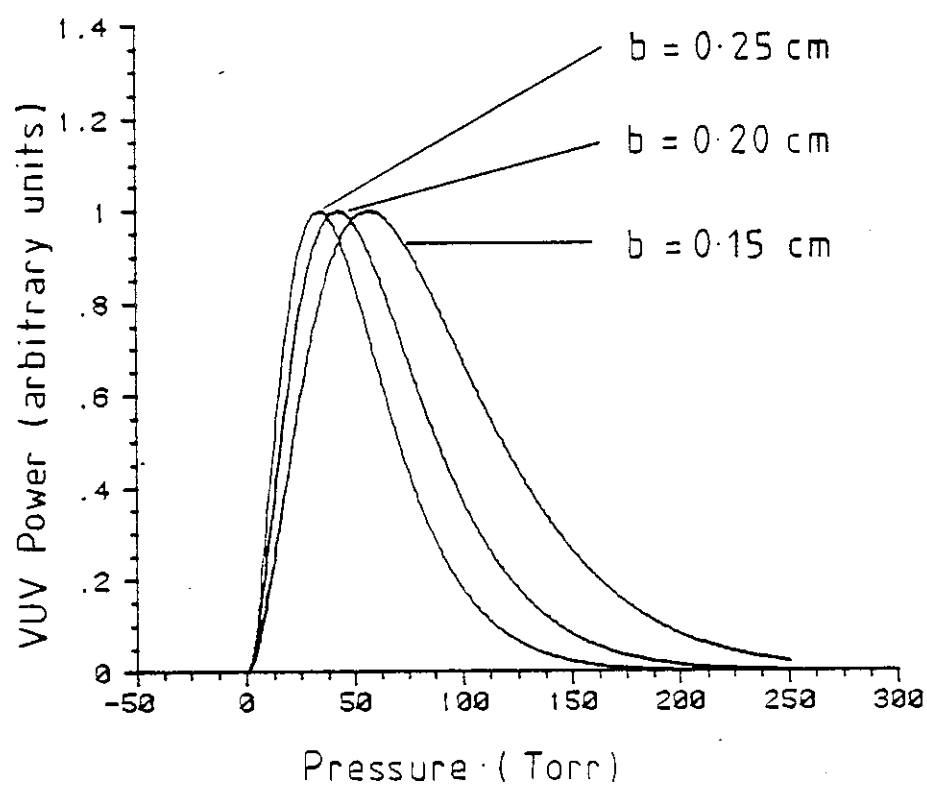
The VUV power generated, P_4 , is proportional to N^2 , where N

is the number density of ground state Xenon atoms and so will be reduced by ground state depopulation. Also, the term $F(b\Delta k)$ (as defined by Bjorkland⁽⁸⁴⁾) depends on N , since

$$F(b\Delta k) \propto \exp(-b\Delta k)$$

and Δk , the phase mismatch parameter, is proportional to N . Therefore the optimum pressure for VUV generation would be expected to increase from its value for negligible ground state depopulation since the number of ground state atoms available for the mixing process per unit volume of Xenon gas originally in the mixing cell would be reduced. The value of $\Delta k/P$ has been calculated and is shown in Fig. 3.5 plotted against the generated wavelength. Using the value for $\lambda_4 = 155.6 \text{ nm}$ from this graph ($0.235 \text{ cm}^{-1} \text{ Torr}^{-1}$), the theoretical pressure dependence curves for confocal parameters $b = 0.15, 0.20$ and 0.25 cm and zero ground state depopulation are as shown in Fig. 5.13. For a confocal parameter of 0.2 cm (as has been calculated for the beams in the experiment) it can be seen that the optimum Xenon pressure is predicted to be 40 Torr. When compared with this, the experimentally determined optimum pressure of $\sim 55 \text{ Torr}$ (Fig. 5.10) suggests a ground state depopulation of $\sim 30\%$. Since the photoionization process will steadily reduce the ground state population during the transit of a UV pulse with a consequent reduction in the efficiency of the nonlinear process, it must be expected that the temporal profile of the VUV pulses will be shortened with respect to that of the UV pulses.

Since, according to the above result, the ratio of ions to atoms in the nonlinear medium may exceed 40%, it is possible that the phase mismatch parameter, Δk , will no longer have a



Theoretical Pressure dependence of VUV Power for confocal parameters (b) of 0.15, 0.20 and 0.25 cm

linear dependence on the ground state density, N , due to the contribution to the refractive index from the ions in the medium whose magnitude is unknown. Further modification of the temporal profile of the VUV pulses may result. The temporal resolution of the photomultiplier used in the experiment was insufficient to be able to determine the pulse duration, so no direct evidence is available for pulse shortening.

In Fig. 5.10 it can be seen that the experimental pressure dependence curves show a marked departure from the theoretical curve (the dotted line) at high pressures. This can only partly be attributed to the shift induced by ground state depopulation. One reason for this inconsistency is that the function $F(b\Delta k)$ is only strictly equal to $\pi^2 \exp[-b|\Delta k|]$ (see equation 3.32) for tightly focused single mode gaussian beams when

$$k''/k' = 1$$

$$\text{i.e.} \quad 2k_1 - k_3 = 2k_1 + k_3$$

$$\text{since} \quad k'' = 2k_1 + k_3$$

$$k' = 2k_1 - k_3$$

where k_1 and k_3 are the wavenumbers of the ultra violet and visible fundamental beams respectively. As can be seen from Fig. 3.2a, when, as in this case, $k'' \neq k'$, the function $F(b\Delta k)$ must be numerically determined⁽⁸⁴⁾ and is less highly peaked. Experimentally, $k''/k' = 1.5$ and the curve of $F(b\Delta k)$ against $b\Delta k$ for this value is shown in Fig. 3.2a. Therefore $F(b\Delta k)$ will be relatively larger at higher values of $b\Delta k$, i.e. pressure. Additionally, the fundamental beams are not exactly Gaussian modes. This, as well as the fact that the confocal parameters of the two fundamental beams cannot be exactly matched due to their different wavelengths means that the conditions assumed in deriving equation (3.30) are not completely

satisfied. The mismatch of the confocal parameters will also give rise to complex mode structure in the output beam which, even in the ideal case, for four wave difference frequency mixing, will have a ring shaped far field diffraction pattern as discussed in Chapter 3, section 3.2.3. Also, excited dimer formation may occur at high pressures (Chapter 3, section 3.3.4) modifying the dispersion of the nonlinear medium.

The Doppler width of the two photon resonant transition is calculated to be 2.6 GHz at 300 K and the pressure broadened linewidth is also ~ 1 GHz⁽⁹⁶⁾. It can be seen from Fig. 5.12 that the experimentally determined detuning curve is substantially broader than these values and its width increases with increasing intensity. The saturation already mentioned, caused by two photon absorption and multiphoton ionization, is the probable cause of most of the observed broadening. Ward and Smith⁽¹⁰⁰⁾ showed that, for third harmonic generation, the plot of the intensity of the generated radiation against detuning from resonance would have a complex dependence on the fundamental intensity. However, they considered saturation to be occurring due to population of the two photon resonant level, whereas in the case of this experiment, at the UV intensities considered, this is likely to be reduced by photoionization, the saturation being caused mainly by depopulation of the ground state.

Another possible broadening mechanism is Stark broadening due to photoelectrons produced by photoionization. If, as is suggested by the VUV power versus Xenon pressure curve (Fig. 5.10), the depopulation of the ground state reaches $\sim 30\%$ and all the atoms so lost are singly ionized, at a pressure of 50 Torr $\sim 5 \times 10^{23}$ electrons m^{-3} will be produced. Assuming that only the 6s state has an appreciable contribution to the calculation and taking the dipole moments μ from this state to

the 5p and 6p states to be $3.4 \times 10^{-30} \text{ cm}^{(97)}$, equation (3.72) i.e.

$$\gamma = 22.8 \left(\frac{C_4}{\hbar} \right)^{2/3} (\bar{v})^{1/3} N \quad (3.72)$$

where

$$C_4 = \left(\frac{Z e}{4 \pi \epsilon_0} \right)^2 \sum_a \frac{|\langle b | \mu_{ab} | a \rangle|^2}{E_b - E_a}$$

indicates that for a mean electron velocity ($\bar{v}$) of $5 \times 10^5 \text{ ms}^{-1}$ the FWHM of the Stark broadened line profile (γ) will be 10 GHz. This compares with a FWHM of $\sim 80 \text{ GHz}$ at an UV intensity of 1 GW cm^{-2} obtained from Fig. 5.12. It should be noted that the x axis in Fig. 5.12 denotes detuning of the 249.6 nm radiation from resonance, so the detuning at 125 nm is double that shown.

Therefore, although the Stark broadening can make an appreciable contribution, the dominant broadening mechanism appears to be saturation due to depopulation of the ground state at these intensities. Since both the number of ions present and the ground state depopulation depend on various processes with quadratic and cubic relationships to the UV intensity, it is hardly surprising that the broadening does not follow any simple power dependence.

As has been mentioned in Chapter 3 (section 3.3.2), Scheingraber and Vidal⁽¹⁰⁰⁾ predicted from their numerical calculations on third harmonic generation that at high input intensities the Stark shift of the two photon resonant level could produce an asymmetry in the detuning curve and even a minimum in the generated power at resonance. This is not observed in Fig. 5.12. The expected Stark shift can be

calculated from equations (3.66) and (3.67), given by Elgin and New⁽⁹⁹⁾

$$\delta \Omega_s = (\zeta_2 - \zeta_1) I_1 \quad (3.66)$$

where

$$\zeta_i = (2c \epsilon_0 \hbar^2)^{-1} \sum_k \frac{2 \Omega_{ik} |\mu_{ki}|^2}{\Omega_{ik}^2 - \omega^2} \quad (3.67)$$

Assuming, again, that the 6s state provides the main contribution in the calculation of the Stark shift and with the dipole moments equal to 3.4×10^{-30} cm⁽⁹⁷⁾, the Stark shift for an UV intensity of 1 GW cm^{-2} is calculated to be ~ 1 GHz. This is approximately equal to the bandwidth of the lasers used in the experiment and is much less than the broadened two photon resonant transition linewidth, so it would be impossible to detect and is therefore consistent with the results in Fig. 5.12.

From equation (3.30), i.e.

$$P_4 = 1.580 \times 10^{-4} \frac{k_0^4 k_1^2 k_3}{k_4^2 k'} N^2 |\chi|^2 P_1^2 P_3 F(b \Delta k) \quad (3.30)$$

where powers are in Watts, N is in atoms cm^{-3} , χ is in ESU/atom and wavenumbers are in cm^{-1} , with a knowledge of the VUV power P_4 generated for known input powers, it should be possible to estimate the magnitude of the nonlinear susceptibility for the difference frequency mixing process,

In the unsaturated regime of the graphs in Figs. 5.9 and 5.11 an output power of $\sim 8\text{W}$ can be expected for an UV power, P_1 , of 1.5 kW and a visible power, P_3 , of 2.5 kW. At 50 Torr the number density N is $1.8 \times 10^{18}\text{cm}^{-3}$ and $F(b\Delta k)$ from Figs. 3.2a and 3.5a is ~ 0.8 . The refractive index of the gas is assumed to be near unity, so

$$k' = 2k_1 - k_3 = k_4$$

and $k_4 = k_0$.

Therefore, making a correction for the overlap of the focii of the ultraviolet and visible beams the magnitude of the nonlinear susceptibility is calculated to be $\sim 5 \times 10^{-32}$ ESU/atom at zero detuning from the two photon resonance. This would suggest an enhancement of over two orders of magnitude over the off-resonance susceptibility calculated in Chapter 3 (Section 3.2.4) ($\sim 3 \times 10^{-34}$ ESU/atom), which would result in an increase of the generated power by four orders of magnitude.

The FWHM of the detuning curve (Fig. 5.12) at the lowest UV intensity is approximately 65 GHz; i.e. $\Gamma \sim 400\text{ rad s}^{-1}$. The resonant enhancement varies inversely with the linewidth Γ (section 3.2.4). For $\Gamma = 400\text{ rad s}^{-1}$ the resonant enhancement of $|X|$ over the value calculated for $\Delta\omega = 5 \times 10^{13}\text{ rad s}^{-1}$ would be expected to be 1.25×10^2 , and hence an increase of 1.5×10^4 in the generated power would result. Therefore the resonant enhancement of the experimentally determined power output over the theoretically determined off-resonance value is consistent with the transition linewidth deduced from the observed detuning curve.

The highest VUV power obtained was $\sim 100\text{W}$ at input powers of 25 kW in the UV and 30 kW in the visible. This equates to a power conversion efficiency of $\sim 0.2\%$ when comparing the VUV

power obtained with the total input power. However, since in the case of difference frequency mixing, visible photons are actually produced, an alternative measure of the conversion efficiency is the ratio of VUV power to input UV power, $\sim 0.4\%$.

With the bandwidth of the UV radiation equal to ~ 1.5 GHz the bandwidth of the VUV radiation would be expected to be ~ 2 GHz. The fundamental limitation on the bandwidth of the generated radiation is given by the uncertainty principle

$$\Delta\nu \Delta t \sim 1 \quad (3.70)$$

so the pulse duration of the generated radiation (~ 3.5 ns without pulse shortening due to saturation) would have to be less than a nanosecond before this limit was reached. Pulse shortening is expected due to the reduction in the efficiency of the nonlinear process caused by two photon absorption and multiphoton ionization leading to saturation. If both dye lasers used in the experiment operated in a single longitudinal mode with a bandwidth of ~ 300 MHz, these effects might lead to the fundamental limit being approached at high powers.

Chapter 6

Conclusions and Applications

6.1 The Vibrational Relaxation and Gain Recovery Time

Experiment

6.1.1 Conclusions

It was possible to conclude from this experiment that, under conditions which are typical of electron-beam pumped lasers, vibrational relaxation occurs in KrF^* on a sub-nanosecond timescale. In particular, an upper limit of 450 ps was set on the vibrational relaxation time for the case of an Argon buffer at a pressure of 3.5 bar. This information is beneficial for the study of the amplification of pulses of ~ 1 ns duration since energy can be extracted from higher vibrational levels in the bound KrF^* state during a pulse of that duration.

The time in which the gain of a KrF laser system recovers after the passage of a saturating pulse has been shown to have only a very weak dependence on the vibrational relaxation time and is approximately equal to the fluorescence lifetime of the upper laser level (which can be calculated from the spontaneous emission probability of that level and the rate constants for quenching of KrF^* in two and three body collisions with the component gases of the laser medium). The fluorescence lifetime and hence the gain recovery time is ~ 1 ns for typical gas mixtures. Therefore a single KrF amplifier could efficiently amplify a series of short (~ 1 ns) pulses separated by only a few nanoseconds, permitting sequential extraction from the amplifier.

6.1.2 Further Work

The experiment has not provided a "direct" measurement

of the vibrational relaxation time of KrF^* since it is much shorter than the duration of the probe laser used and also, in any case, would not be temporally resolved by the detection system. A possible method for obtaining such a measurement would be to form KrF^* in a higher lying vibrational level by selective photolysis of KrF_2^* (59) on a picosecond timescale and then monitor the build up of fluorescence at the longer wavelengths corresponding to transitions from the lower levels, also on a picosecond timescale, e.g. with a streak camera.

A direct measurement of the intrinsic gain recovery time i.e. the recovery time of the gain after the passage of a saturating pulse of duration less than or approximately equal to the fluorescence lifetime would require short (~ 1 ns) extremely powerful pulses (> 100 MW) to achieve significant depletion of the upper state population. This should be possible with the new generation of powerful e-beam pumped KrF lasers (12) that are being developed.

6.2 The Four Wave Mixing Experiment

6.2.1 Conclusions

It has been demonstrated that two photon resonantly enhanced four-wave difference frequency mixing in Xenon offers a method of producing very narrow bandwidth, relatively high power, tunable VUV radiation. An output power of ~ 100 W has been obtained at a wavelength of ~ 155 nm. By using a narrow-band dye laser tunable between 610 and 650 nm in the mixing process the output wavelength is tunable between 154.5 and 157 nm and, by the use of alternative dyes lasing in the range 350 - 900 nm, it will be possible to extend the tuning range to $\sim 145 - 195$ nm. By utilizing the three photon resonance at 147 nm (5p - 6s) higher power outputs may be possible over a

limited wavelength range. However, absorption and the alteration in the phase matching conditions around this resonance mean that there may be gaps in the range of wavelengths available by this process which is otherwise continuously tunable over the whole range mentioned above. The resolving power, i.e. $\Delta\lambda / \lambda$, of the system is $\sim 10^6$, better than conventional spectrometers, and hence higher spectral brightness can be achieved than by the use of synchrotron sources.

From the investigation carried out into the dependence of the VUV power generated on the input laser powers saturation effects are evident. Firstly, saturation with respect to the visible dye laser power is probably due to depopulation of the ground state density by two photon resonantly enhanced multi-photon ionization involving two ultraviolet and two 630 nm photons. Also, saturation with respect to the ultraviolet power could be caused by a combination of ground state depopulation by three photon ionization at 249.6 nm and two photon absorption into the resonant 6p state. This state can itself be depopulated by photoionization by either a single UV photon or two 630 nm photons, providing another mechanism for ground state depopulation. At high UV intensities the build up of population in the two photon resonant state may also contribute to saturation since the rate constant for two photon absorption has a quadratic dependence on the UV power.

The FWHM of the curve showing the dependence of VUV power on detuning of the 249.6 nm fundamental beam from the two photon resonance in Xenon is much broader than the Doppler or collisionally broadened width of that line. Most of the broadening is thought to be due to the saturation of the transition but a significant fraction ($\sim 10\%$) can be accounted

for by Stark broadening due to photoelectrons produced by photoionization.

The dependence of the VUV power on the Xenon pressure agrees with the theoretical prediction except for a departure at high pressures. The reasons for this include a shift in the curve due to ground state depletion and, more importantly, the departure of the experimental conditions from the theoretical assumption of two tightly focused, Gaussian, fundamental beams with beam waists of the same size.

The nonlinear susceptibility is calculated from the experimental results to be $\sim 5 \times 10^{-32}$ ESU/atom when the process is resonantly enhanced, which is consistent with the theoretically calculated off-resonance susceptibility ($\sim 3 \times 10^{-34}$ ESU/atom) and the resonant enhancement that could be expected, given the linewidth of the two photon transition deduced from the experimentally determined detuning curve (~ 65 GHz).

The maximum VUV power obtained equated to a power conversion efficiency from fundamental to generated radiation of $\sim 0.2\%$. The bandwidth of the VUV radiation is likely to be determined by the dye laser bandwidth in the absence of severe pulse shortening due to saturation and hence is ~ 2 GHz.

6.2.2 Possible Refinements to the Experiment

A number of refinements are possible to the laser system that has been described here. First, by the insertion of beam expanding prisms and the substitution of a Littrow mount grating for the tuning mirror, the dye laser operating at ~ 500 nm could be brought up to the specification of the other visible dye laser (630 nm) giving a narrower linewidth, single mode output, hence reducing the bandwidth of the VUV radiation generated. A discharge amplifier for the 249.6 nm radiation with better shot to shot reproducibility would be desirable, allowing more

precise fine tuning of the optical alignment and 500 nm dye laser wavelength as well as simplifying data acquisition. Also, it could, along with the saturation effects observed, give a stable VUV power output.

The 500 nm dye laser suffered from poor wavelength calibration. This could be improved by maintaining a constant temperature in the laboratory or the laser environment preventing expansion and contraction of mechanical components and also by utilizing a micrometer with less "backlash" in the tuning mechanism.

The dependence of the VUV power, P_4 , on the Xenon number density N is of the form

$$P_4 \propto N^2 \exp(-b \Delta k) \quad (6.1)$$

where b is the confocal parameter and Δk is the phase mismatch parameter which is proportional to N

$$\Delta k = K_1 N \quad (6.2)$$

Therefore the optimum value of P_4 occurs for

$$N = \frac{2}{b K_1} \quad (6.3)$$

which gives the dependence of the optimum VUV output, $P_{4\text{opt}}$ on the confocal parameter b as

$$P_{4\text{opt}} \propto \frac{4}{b^2 K_1^2} e^{-2} \quad (6.4)$$

Therefore, according to (6.4), by tighter focusing (reducing b) higher power outputs are possible. However, the reduced spot size of the focused beams would result in alignment being more difficult and the increased intensity for the

same input powers might result in more pronounced saturation limiting the benefits that could be obtained. Further work is required to determine the optimum focusing geometry. The use of the sum frequency mixing process

$$2\omega_1 + \omega_3 \longrightarrow \omega_4$$

should also be investigated for the generation of even shorter wavelengths down to ~ 100 nm. This work would present further difficulties since the wavelengths generated are close to or beyond the cut-off of the transmission of VUV window materials. Also, the more stringent phase matching conditions (an anomalously dispersive medium is required) would mean that the range of wavelengths that could be generated would be limited.

6.2.3 Applications

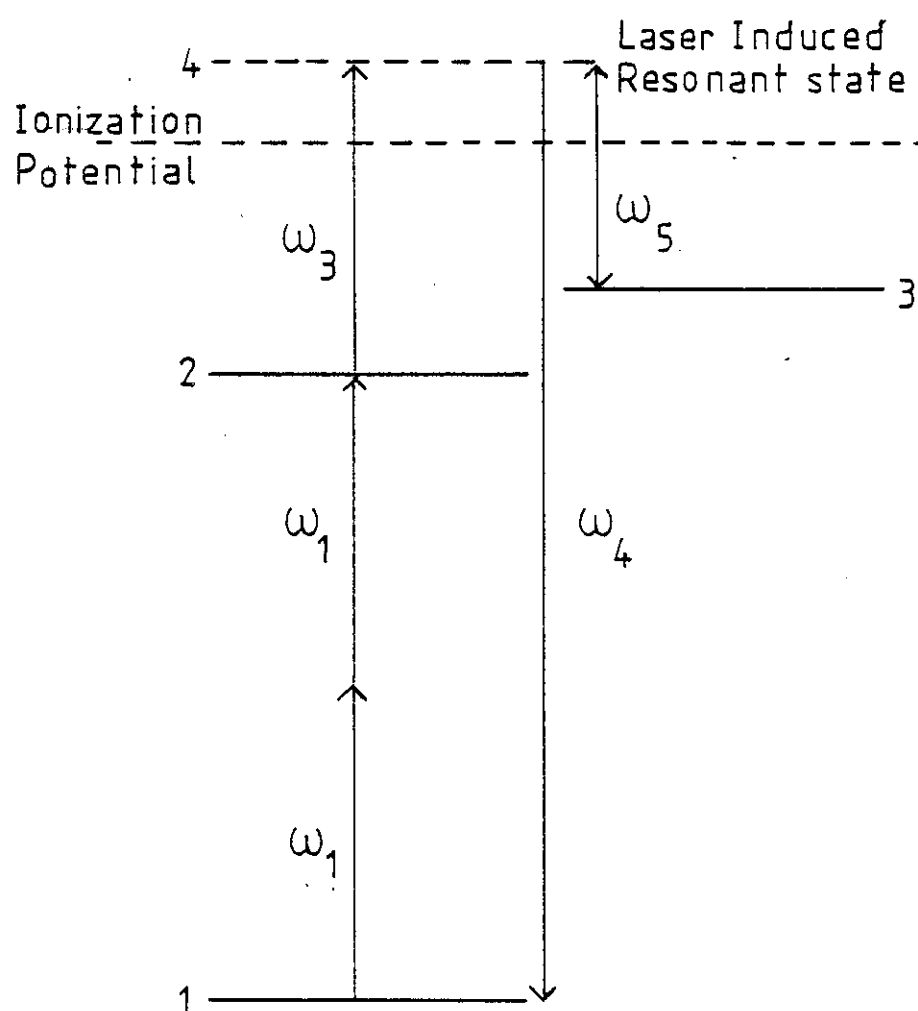
The experiment that has been described in this work has demonstrated a novel source of coherent radiation in the VUV. Some examples of the applications of this type of source are mentioned here.

One example which demonstrates the usefulness of the narrow bandwidth and precise tunability of the system is the study of emission spectra from molecular states selectively excited by the VUV radiation. Excimer lasers have already been used for this technique, in particular emissions from single vibronic states of NO and O₂ have been studied after excitation by an ArF laser at 193 nm⁽²⁴⁾. However, even finer rotational structure exists within these vibrational levels⁽¹¹⁷⁾ which could possibly be selectively excited with the narrowband VUV, facilitating the extraction of further data about the structure of these molecules. The wide tunability of the VUV source would allow similar experiments to be carried out with a wide variety of molecular species.

Techniques for laser spectroscopy in the VUV include simple absorption spectroscopy, the wide tunability allowing an unbroken spectrum to be obtained. Also, photoionization spectroscopy, where the number of electrons produced by photoionization as a function of wavelength is detected, would allow the photoionization spectrum of a gas and its presence, even in small quantities, to be determined. The ionization potential of molecules could also be accurately determined by this method because of the VUV source's tunability and fine structure near the continuum edge⁽¹¹⁸⁾ could be resolved. This type of experiment has been done on CO and NO using the third harmonic of a dye laser⁽¹¹⁹⁾. The source described here would allow other molecules to be investigated due to its extended wavelength range.

Another possible use of the laser system is a technique proposed by White⁽¹²⁰⁾ for inducing photodissociation in a molecular species by forming that species by collisional transfer with another atom or molecule. There is the possibility of producing a population inversion by forming an excited state of an atom in the photodissociation. Laser assisted collisions in CO have been observed⁽¹²¹⁾, and this molecule could possibly be used in such a process with collisional transfer from Xenon atoms excited by resonantly enhanced absorption in a system similar to the one described here.

The possibility exists of enhancing the sum frequency mixing process in Xenon when the generated photon energy lies above the ionization potential by inducing a nonlinear resonance in the continuum with another laser. The technique has been discussed by Coleman et al⁽¹²²⁾, and enhancement of third harmonic generation has been observed by Dimov et al⁽¹²³⁾. Fig. 6.1 shows the transition scheme for the process. The



Transition scheme for laser induced resonant enhancement of sum frequency mixing in Xenon.

frequency ω_5 induces a resonance, signified by level 4 in the photoionization continuum, by radiative coupling with the bound state 3. The generation of frequency $\omega_4 = 2\omega_1 + \omega_3$ then experiences enhancement when it approaches the frequency of the transition $4 - 1$.

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Appendix

Publications

High efficiency generation of
narrow bandwidth tunable VUV radiation

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Frequency tunable VUV radiation has been generated using excimer lasers and very narrow bandwidth dye lasers by two-photon resonant difference-frequency mixing in xenon. Conversion efficiencies of 0.1% have been achieved.

Introduction

The generation of coherent vacuum ultraviolet radiation by third-order nonlinear processes has been studied for several years, (1-3) but recently it has become possible to produce frequency tunable radiation with pulsed powers of up to 10KW in the VUV with conversion efficiencies of up to 1% (4,5) using metal vapours or the noble gases as the nonlinear medium. Complete spectral coverage of the range 110 and 210nm can be achieved with a single laser system (6) and, by the use of very narrowband dye lasers to provide the fundamental driving frequencies, VUV radiation with very narrow bandwidths can be produced with a spectral brightness many orders of magnitude greater than that of synchrotron radiation and effective resolving powers in excess of 10^7 . (7,8)

The efficiency of four-wave mixing may be increased by two-photon resonant enhancement of the third order nonlinear susceptibility (9). Although a degree of tunability may be obtained using a single laser and its Stokes shifted frequency obtained by stimulated Raman Scattering, (8) to provide a widely tunable source of VUV radiation requires the use of two independently tunable lasers. Although the conversion efficiency to the VUV can be further enhanced by three photon resonant enhancement, this severely restricts the tuning range at which the highest powers are obtained to the regions close to the resonance lines of the nonlinear medium (4). In this paper, we report a system which produces narrow bandwidth coherent VUV radiation which is widely tunable with conversion efficiencies of 0.1%.

The generation of VUV radiation by sum frequency mixing i.e.

$\omega_4 = \omega_1 + \omega_2 + \omega_3$ requires the dispersion of the medium to be negative i.e.

$$\Delta k = k_4 - \sum_{i=1}^3 k_i < 0$$

for tightly focussed beams⁽¹²⁾. This restricts the choice of the nonlinear medium and the tuning range available. However, difference frequency mixing by the process $\omega_4 = \omega_1 + \omega_2 - \omega_3$ is possible for values of k which are either positive or negative and the scheme for VUV generation by difference frequency mixing in xenon is shown in figure 1. The susceptibility for four wave mixing is enhanced by tuning to the $5p^1S - 6p[0^1_2]$ two photon transition ($\lambda = 249.6\text{nm}$) and continuously tunable VUV radiation is obtained by mixing with tunable radiation from a second dye laser.

Apparatus

A diagram of the experimental arrangement is shown in Fig. 2. The output from a discharge pumped XeCl laser (Lambda Physik, EMG 101) was used to pump two narrow bandwidth dye laser oscillators, each with a chain of two amplifiers.

The pump radiation reflected from a quartz flat was split by prisms and used to pump the two dye laser oscillators. One oscillator, operated with Coumarin 307 dye, was tuned to 499nm and the second dye laser using Rhodamine 101 was tunable between 610 and 650nm. The oscillators used a grazing incidence grating for both dispersion and beam expansion.⁽¹¹⁾ The resonator of the first

oscillator consisted of a 1800 lines/mm grazing incidence grating and 100% mirror with an uncoated flat as output coupler. The output consisted of two longitudinal frequency modes giving a linewidth of ~ 1 GHz. The Rhodamine 101 oscillator differed from this in that it included a four prism beam expander between the dye cell and grating and also used a grating of 2400 lines/mm in the Littrow configuration instead of the 100% mirror. This oscillator operated reliably in a single longitudinal mode and had a frequency bandwidth estimated to be $< 500\text{MHz}$ using a Fabry Perot interferometer.

The remaining 90% of the XeCl pump beam was used to pump two amplifiers in each arm of the dye laser system. The amplification achieved was X80 in the first amplifier and X8 in the second giving output energies of 2.5 mJ at 499nm and 1.5 mJ at 630 nm. The pulse duration was 10ns and the beam divergence of both lasers was measured to be $\sim 10^{-4}$ rads.

The 499nm dye laser beam was focussed by a 25cm focal length lens into a Potassium Pentaborate (KB5) frequency doubling crystal, (Cleveland Crystals). The second harmonic radiation, generated with an efficiency of $\sim 1\%$, was recollimated and amplified in a discharge pumped KrF excimer amplifier. Although discharge lasers can have a single pass gain of 1000 when operated at their line centre, the gain in this case at the wavelength $\lambda = 249.6$ nm which is in the wing of the transition was 100. In such a system, synchronization between the pumping XeCl laser and the KrF amplifier is important. Jitter times of 10ns were achieved using thyatron switches in the discharge circuits of the two excimer lasers.

The amplified 249.6nm beam was combined and collimated with the

630nm beam using a dielectric coated mirror. A telescope inserted in the 630nm beam enabled compensation to be made for the dispersion in the 20cm focal length quartz focussing lens. The confocal parameters of both beams were $\sim 0.2\text{cm}$.

The two beams were focussed into the centre of an 8cm long cell mounted on the front of a VUV Monochromator (Acton Research Corporation) The input powers of the 630nm and 249.6nm pulses were 30 kW and 25 kW respectively, which, after focussing corresponded to maximum power densities of 8 GW/cm^2 and 5 GW/cm^2 respectively. The VUV radiation was detected with a solar blind photo-multiplier (EMR model 541G-08-18) and the signals were processed by a Tektronix 7912AD transient digitiser and CP1164 mini computer.

Results

At low intensities the power of the VUV radiation (P_{vuv}) is given by $P_{\text{vuv}} \propto N^2 \chi^{(3)2} P_{\text{uv}}^2 P_{\text{vis}} F(b\Delta k)$ where P_{uv} and P_{vis} are the powers of the incident UV and visible radiation, N is the xenon number density and $\chi^{(3)}$ is the third-order nonlinear susceptibility. $F(b\Delta k)$ is a function which describes the effect of the phase mismatch Δk on the efficiency for beams of confocal parameter b . For a single component medium, $\Delta k \propto N$ and so the maximum

conversion efficiency occurs at the gas pressure for which $\Delta k^2 F(b \Delta k)$ is a maximum. The form of $F(b \Delta k)$ is given by Bjorklund⁽¹⁰⁾ and indicates that for a value of $b \sim 0.2$ mm, and a calculated value of $\Delta k = 0.235 \text{ cm}^{-1} \text{ torr}^{-1}$, the optimum gas pressure is ~ 40 torr.

The experimentally determined variation of output power with gas pressure is shown in figure 3. In this case the UV laser was tuned to the two-photon resonance and the intensity of the visible laser (I_{vis}) was fixed ($\sim 7 \times 10^9 \text{ Wcm}^{-2}$). For the three values of I_{uv} shown, the optimum pressure was found to be 55 torr. In the absence of saturating processes, for a TEM₀₀ mode laser tightly focussed into the medium, the VUV power is related to the pressure by (10)

$$I_{\text{vuv}} \propto p^2 e^{-Kp}$$

where $K = b \Delta k / p$. The predicted form of I_{vuv} calculated from the dispersion of atomic xenon is shown by the dashed curve in figure 3. The departure of the experimental results, particularly at high pressure, may be due to population of the two photon state, photoionisation which can deplete the ground state and dimer formation at high pressures which modifies the dispersion of the gas. The form of the pressure dependence is also modified by departures of the radial intensity distribution from Gaussian.

The dependence of the output power on I_{uv} and I_{vis} is shown in figures 4 and 5 respectively. In both cases strong saturation is indicated by the marked departure of the dependence from I_{uv}^2 and I_{vis} expected for weak input pulses. The effects of saturation are also obvious in figure 6 which shows the measured dependence on the

output power as a function of detuning from the exact two-photon resonance. In the absence of saturating processes the width of the detuning curve should be determined by the spectral widths of the two photon resonant laser radiation and the two photon state. The pressure broadened and Doppler linewidths of this state are both $\sim 1\text{GHz}$ ⁽¹⁷⁾ which is substantially narrower than the measured linewidths which were found to increase with increasing I_{uv} .

The output power of the VUV radiation ($\lambda = 155\text{ nm}$) was estimated from the relative amplitudes of signal produced when the vacuum monochromator was tuned to 249.6 nm and 158 nm using the measured spectral response of the photomultiplier as supplied by the manufacturer. At the highest input powers used the VUV output power was found to be $\sim 100\text{W}$, corresponding to an efficiency of conversion of $\sim 0.2\%$. However, it is anticipated that these values of power and efficiency will be very significantly increased in the spectral region close to the single photon $5p^1s - 6s [1/2]$ ($\lambda = 147\text{ nm}$) resonance line. ⁽⁴⁾

Discussion

Saturation effects which are evident in the preceding results can arise in several ways. In a two-photon resonant system the dispersion of the gas may be modified by redistribution of the population of the xenon atoms by two-photon absorption and by photoionisation. Power broadening (14,15) and A.C. Stark shifting (15,16) of the two photon state can also lead to saturation. However, in this case photoionisation of the two-photon state both by a single photon process for the UV radiation and by a two-photon

process for the visible radiation is expected to be the dominant mechanism. The rate coefficient for two-photon absorption at the line centre is $2 \times 10^{-28} \text{ cm}^4 \text{ W}^{-1}$ for a laser of $\sim 1 \text{ GHz}$ bandwidth and the photoionisation cross-section is $\sim 10^{-18} \text{ cm}^2$. (17) Thus the population of the ground state is severely depleted during the passage of the 5 ns input pulses and the two-photon state is substantially broadened by the rate of photoionisation and possibly by Stark broadening by the photoelectrons.

In conclusion it has been demonstrated that two-photon resonantly enhanced four-wave difference frequency mixing in xenon offers a method of producing continuously tunable, very narrow bandwidth VUV radiation of relatively high power over a wide spectral range. Although saturation will produce some spectral broadening of the VUV radiation, effective resolving powers of $\sim 10^6$ are to be expected. The system is therefore capable of higher resolution than conventional spectrometers and has immediate applications in atomic and molecular Spectroscopy.

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Figure Legends

Figure 1. Energy level diagram of xenon. The two-photon resonant state is $5p^5 6p[0\frac{1}{2}]$.

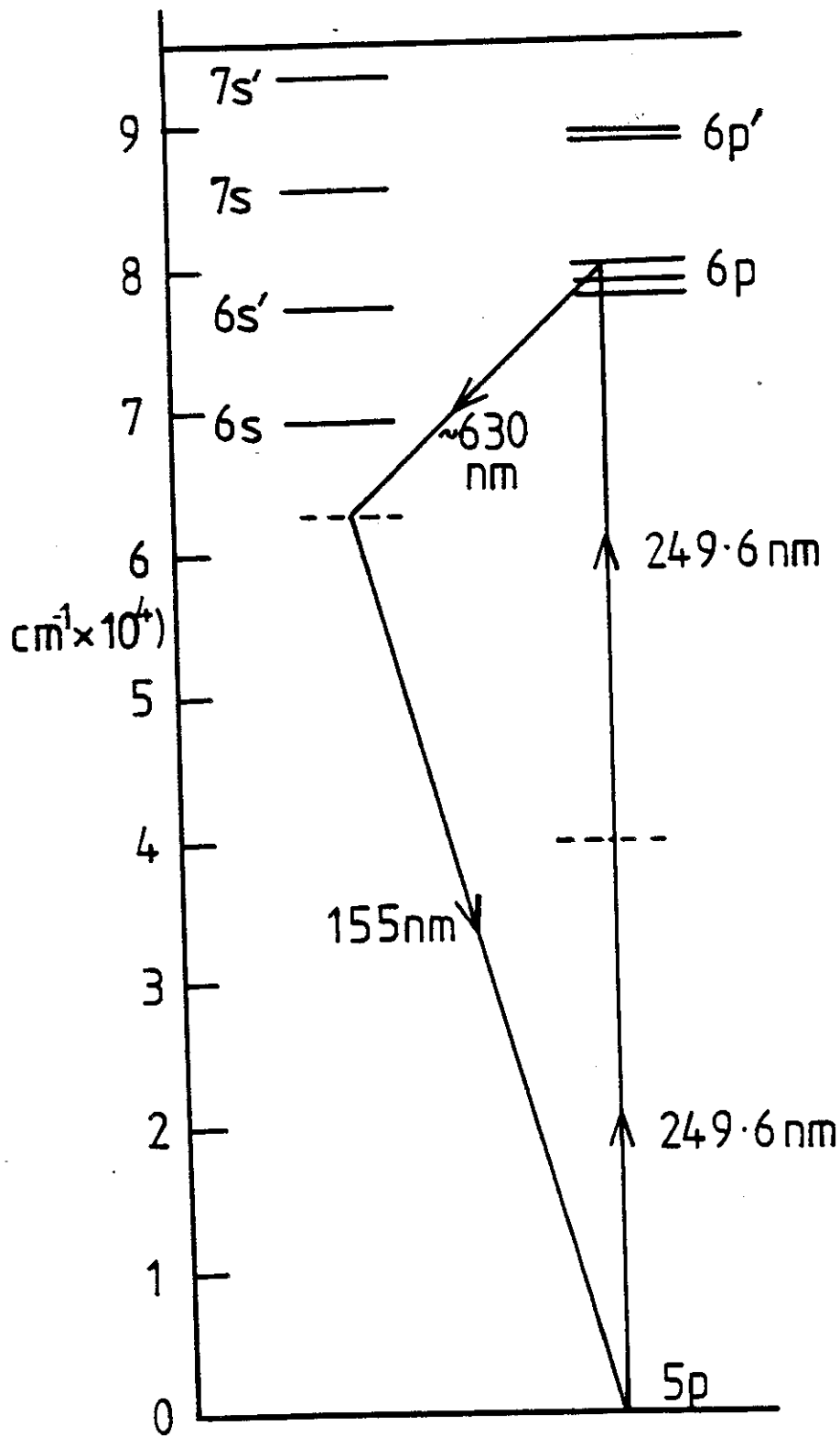
Figure 2. Laser system used for VUV generation. P-polarising filter, R-half wave plate, L-spherical lens, CL-cylindrical lens, A-amplifier, M-mirror, I-iris, SHG-second harmonic crystal, F-filter.

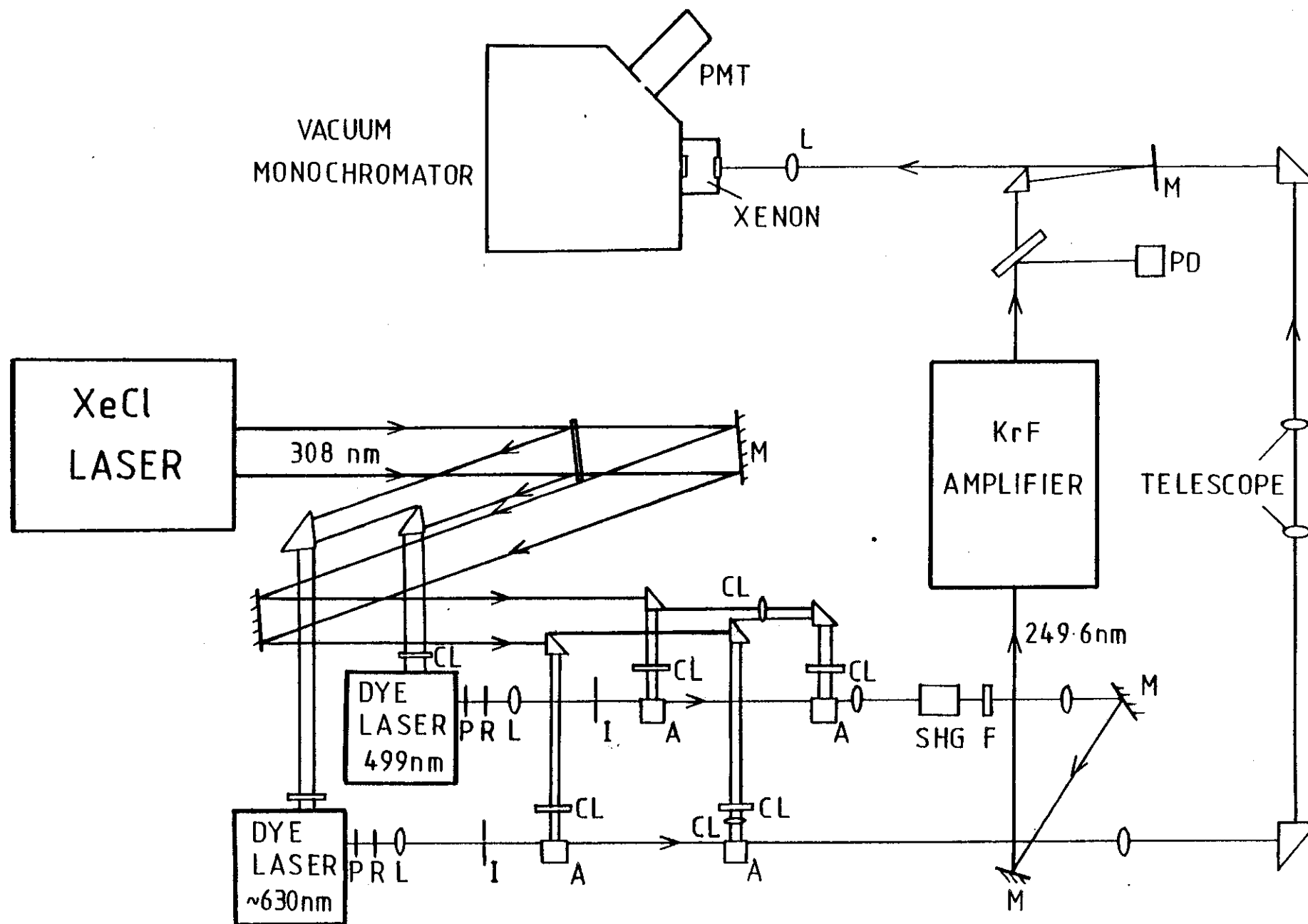
Figure 3. Pressure dependence of I_{vuv} . The solid lines are measured for $I_{\text{vis}} \sim 7 \times 10^9 \text{ Wcm}^{-2}$. The dashed line is the theoretical form using the calculated dispersion.

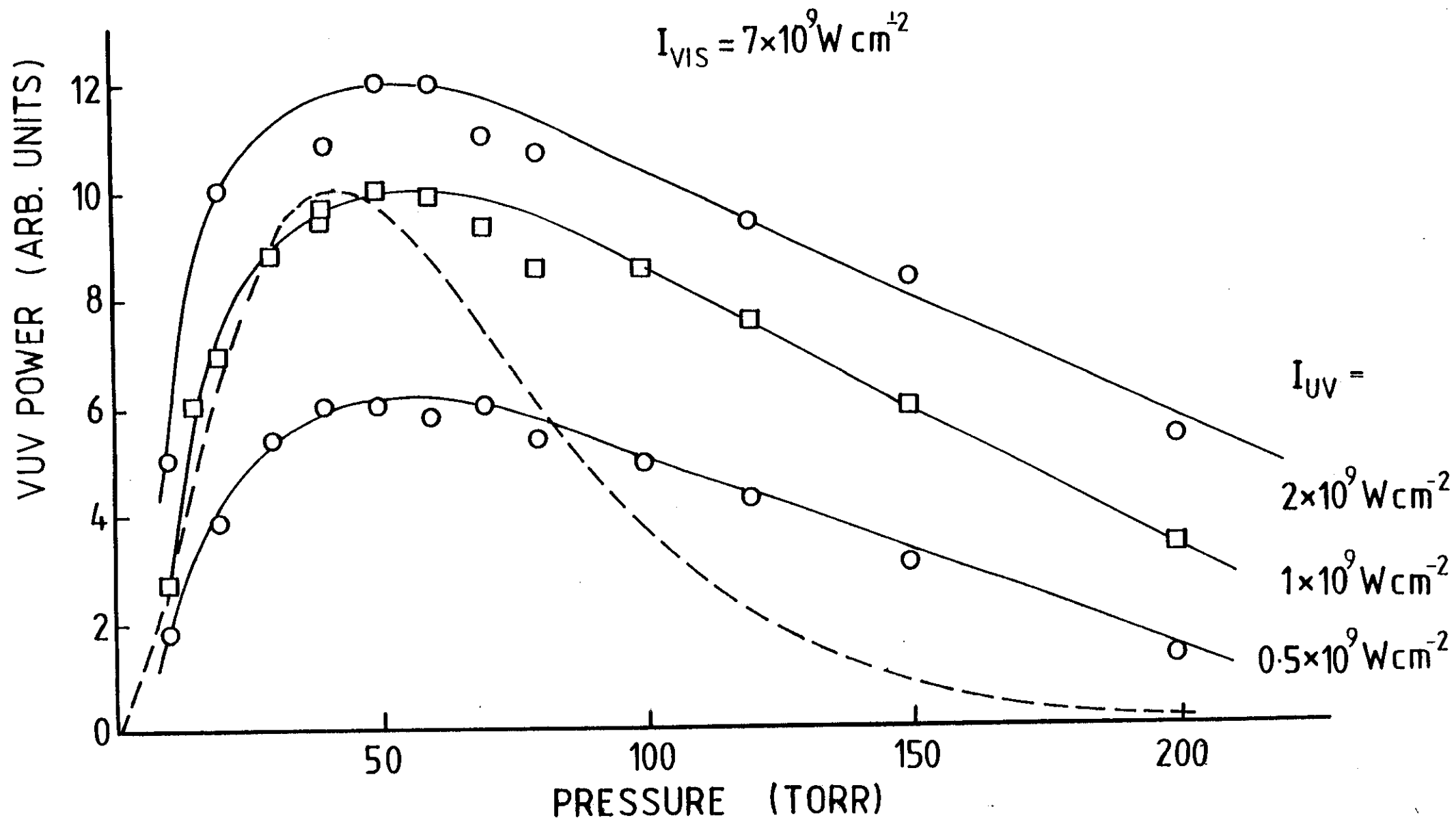
Figure 4. Measured variation of I_{vuv} with I_{uv} for $I_{\text{vis}} = 5 \times 10^9 \text{ Wcm}^{-2}$ and $p = 20 \text{ torr}$ and 50 torr .

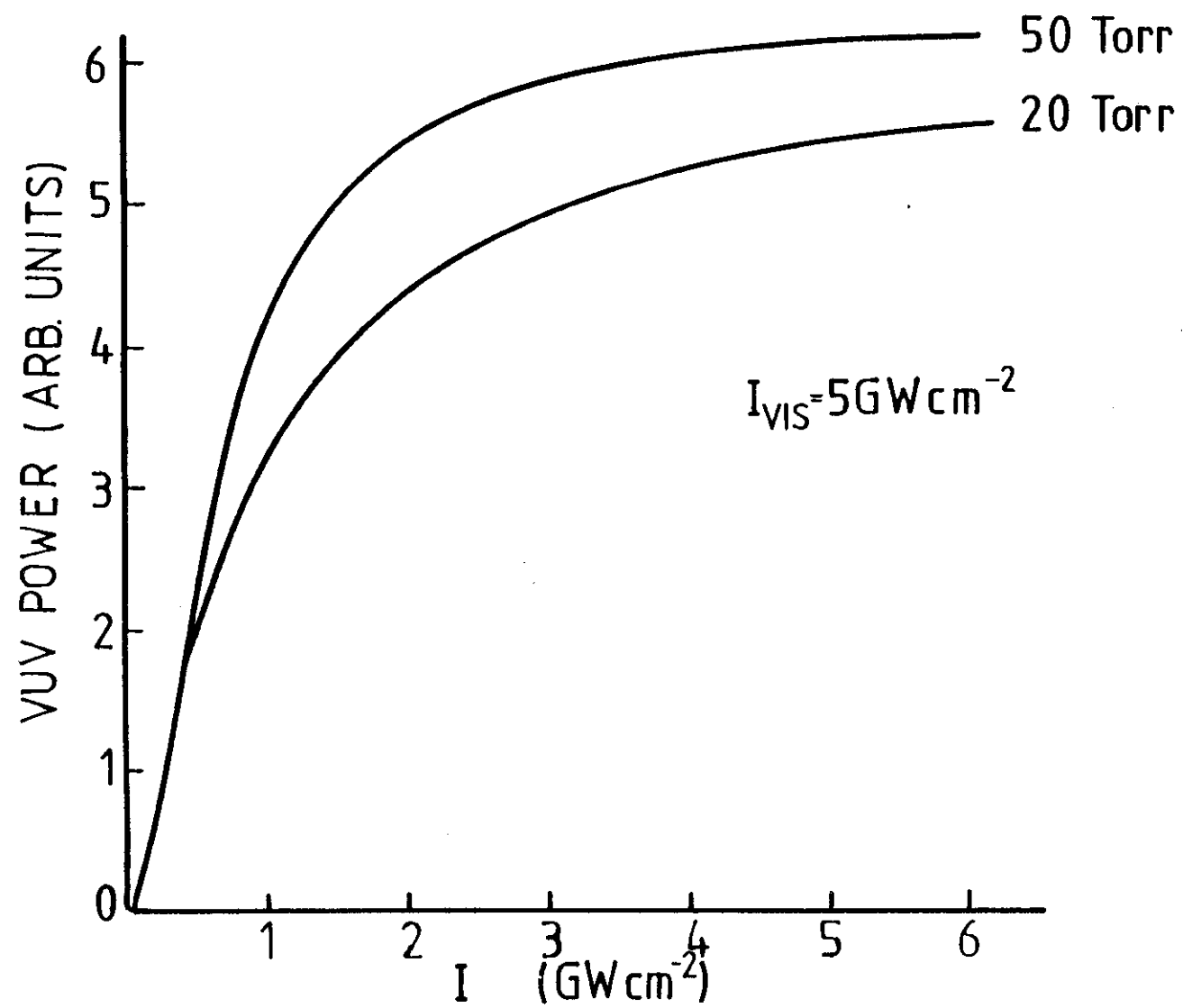
Figure 5. Measured variation of I_{vuv} and I_{vis} for $P = 50 \text{ torr}$ and $I_{\text{uv}} = 0.5, 1.0$ and $2.0 \times 10^9 \text{ Wcm}^{-2}$.

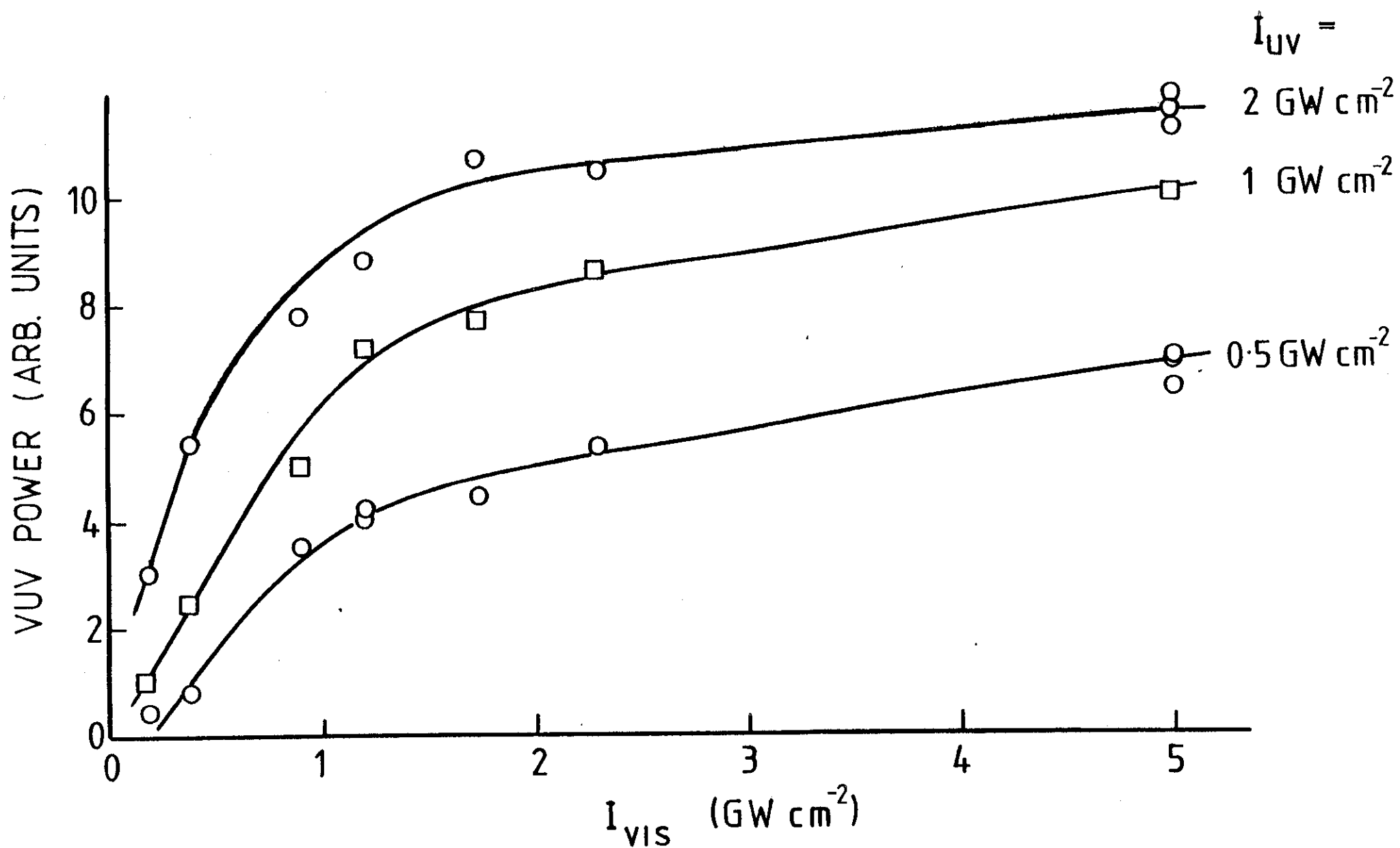
Figure 6. Variation of I_{vuv} with detuning ($\Delta\nu$) of the 249.6nm radiation from two-photon resonance ($5p - 6p[0\frac{1}{2}]$).

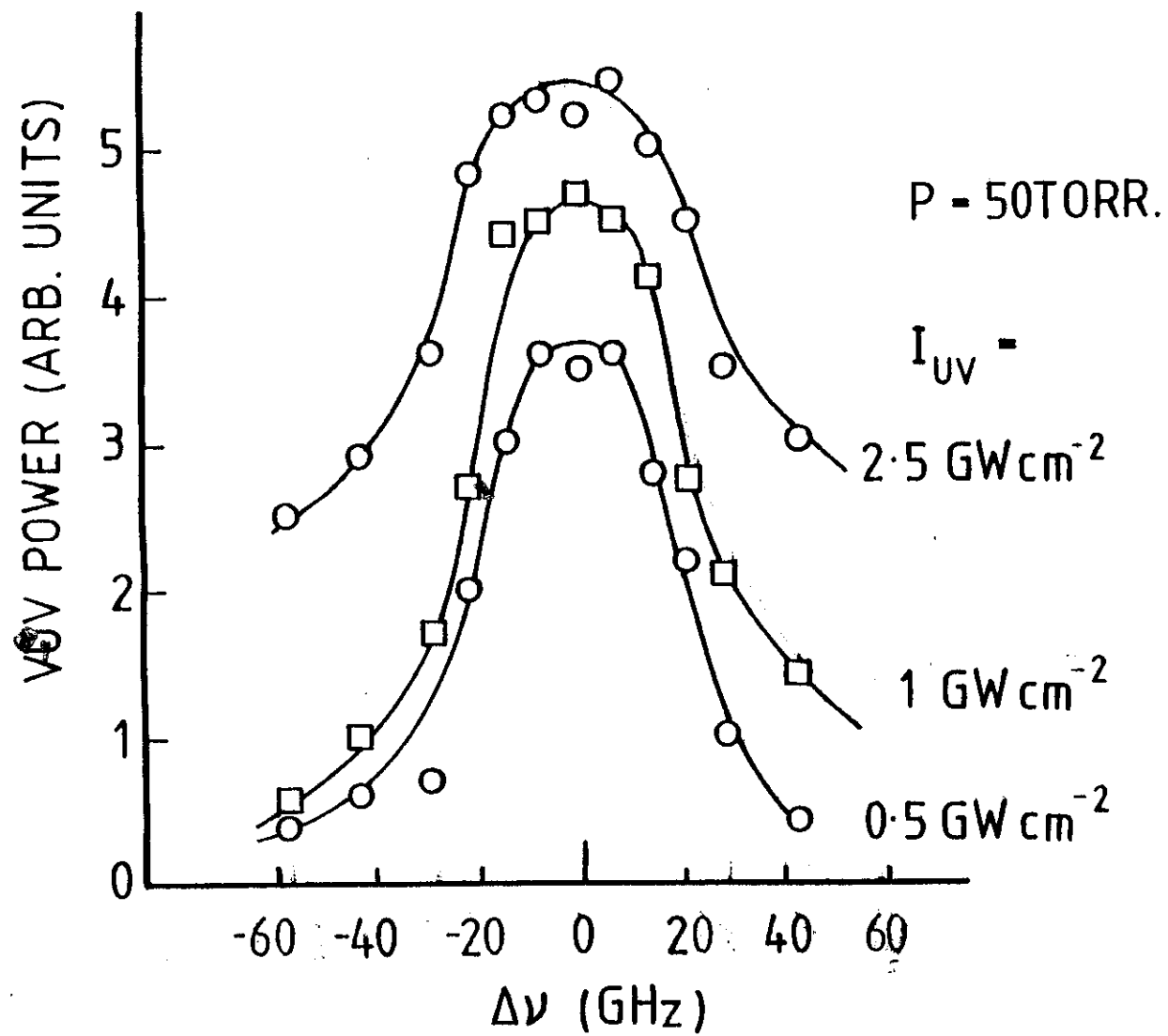












VIBRATIONAL RELAXATION STUDIES IN ELECTRON-BEAM EXCITED KrF ***K.T.V. GRATTAN, M.H.R. HUTCHINSON and K.J. THOMAS***Optics Section, Blackett Laboratory, Imperial College, London SW7 2BZ, UK*

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The recovery of the gain in electron-beam pumped krypton fluoride has been investigated following saturation with a pulse from a discharge pumped KrF laser. Vibrational relaxation in KrF* is found to occur on a subnanosecond timescale under typical laser conditions and the gain recovers in a time which is approximately equal to the fluorescence decay time.

1. Introduction

Recent theoretical studies [1] of laser-plasma interactions have suggested a marked increase in energy coupling to the plasma with the use of laser wavelengths shorter than 1 μm . Experimental work [2] in this field has also found that using 0.53 μm and 0.35 μm radiation produced by second and third harmonic generation with Nd : glass lasers, a substantial increase in ablation pressure may be achieved with shorter wavelength lasers. It is envisaged that there will be a need for a short pulse (~ 1 ns), high power (~ 1 TW) laser for compression studies utilizing KrF* as the active medium ($\lambda \sim 249$ nm). Such a laser is relatively efficient and energetically scalable [3], but pulse lengths for such operations are considerably longer than those believed useful for fusion studies and amplification of a single pulse of nanosecond duration is inefficient. This problem may be overcome by extracting the energy from the amplifier in a sequence of short pulses which are then made to strike a target simultaneously. Following saturated amplification of one such pulse, sufficient time must be allowed for the gain in the medium to recover so that the following pulse may be amplified. Furthermore, the vibrational relaxation time in the electronically excited KrF* molecule must be shorter than the duration of the pulse to be amplified, if efficient extraction of energy from high lying vibrational levels is to be achieved. It is important therefore to have information about both the gain recovery time and the vibra-

tional relaxation time for the design of high power laser amplifiers. Since significant disagreement exists in the published values of the vibrational relaxation time of KrF* [4–7], a new study of both this parameter and gain recovery time under typical amplifier conditions was undertaken.

2. Experimental

In order to investigate the vibrational relaxation in KrF*, the depletion of the sidelight fluorescence from electron-beam pumped krypton fluoride was monitored, when a saturating pulse from an external laser was introduced. Information was obtained from the maximum depth and the temporal change of the depletion observed under fixed experimental conditions. The experimental arrangement is illustrated in fig. 1. A ~ 10 ns pulse from a discharge pumped KrF* laser (Lambda Physik EMG 101) was focused into a cell containing a suitable mixture of F₂, Kr and Ar which was excited by a ~ 50 ns, 1.5 MeV pulse from a Febetron 705 generator. The laser pulse was synchronised to the fluorescence pulse, to within $\sim \pm 5$ ns. The power density of the laser was considerably in excess of the saturation requirement of ~ 1 MW cm⁻². The intense laser pulse can deplete the population of the lowest vibrational states of the excimer, which are then refilled from a reservoir set of higher lying vibrational states. The laser beam passes axially along a cylinder within the gas cell and the electron-beam

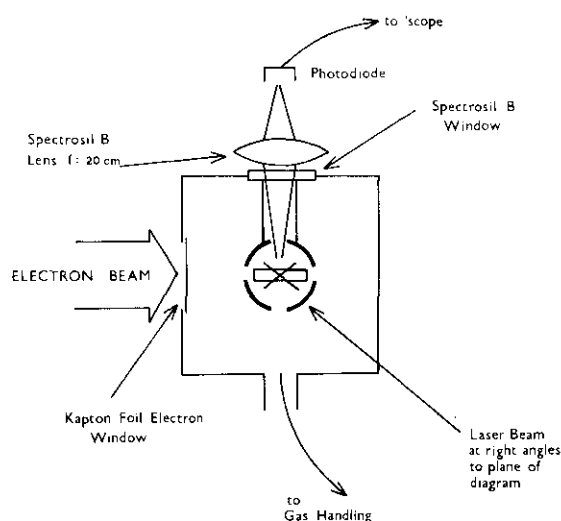


Fig. 1. Experimental arrangement.

pumped region is defined by an aperture which admits electrons only to a small volume of gas. The fluorescence from this volume perpendicular to the axis of the laser beam was collected using a lens which focused the light onto a fast response solar blind UV photodiode, both with and without the axial laser beam.

3. Theoretical background

When pumped by an electron beam, KrF^* is formed in a vibrationally excited state [4] and so collisionally induced vibrational relaxation must occur to populate the lowest vibrational states ($v' = 0, 1$) from which laser action occurs. This system may be modelled by assuming a time dependent pump-rate, $P(t)$, into an upper set of vibrational states of population $N_1(t) \text{ cm}^{-3}$. Collisional mixing occurs between this reservoir and the upper laser level of population $N_2(t) \text{ cm}^{-3}$. The rates of collisional mixing to the reservoir (τ_{v12}^{-1}) and from the reservoir (τ_{v21}^{-1}) to the lasing states are assumed to be similar and are made to equal to τ_v^{-1} , the inverse of the vibrational relaxation time. The fluorescence lifetimes of both states are given by τ_f . Stimulated emission to the repulsive ground state, assumed to have zero population, oc-

curs from the upper laser level. Hence, the rate of change of the populations of the upper vibrational level and the upper laser level are given by

$$\frac{dN_1(t)}{dt} = P(t) - \frac{N_1(t)}{\tau_f} - \frac{N_1(t)}{\tau_{v12}} + \frac{N_2(t)}{\tau_{v21}},$$

$$\frac{dN_2(t)}{dt} = \frac{N_1(t)}{\tau_{v12}} - \frac{N_2(t)}{\tau_{v21}} - \frac{N_2(t)}{\tau_f} - \sigma F(t) N_2(t),$$

where σ is the stimulated emission cross-section for the lasing transition (cm^2) and $F(t)$ is the instantaneous photon flux ($\text{photons cm}^{-2} \text{ s}^{-1}$). The upper level populations are assumed to be zero initially and the equations solved numerically. The falling edge of the laser pulse is approximated by a function of the form $A = A_0 \exp(-\tau_d t)$ where τ_d is the measured exponential decay time of the laser pulse used in the experiment. The temporal profile and maximum depth of depletion of the electron beam pumped fluorescence pulse is derived from the difference of the calculated $N_2(t)$ populations with a non-zero and zero laser flux. The gain recovery time (τ_r), is derived from the exponential increase in the $N_2(t)$ population as the laser power decays. The fluorescence lifetime, τ_f , used in the calculation was determined from published [8,9] two and three body quenching rates for the constituent gases at the pressures used experimentally. A stimulated emission cross-section of $2 \times 10^{-16} \text{ cm}^2 (\pm 10\%)$ [10] was assumed. The rate constant for electron quenching ($2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$) [11] is sufficiently small for this effect to be negligible at the electron number densities ($10^{12} - 10^{13} \text{ cm}^{-3}$) used.

4. Results and discussion

Initially a gas mixture of 6.5 mbar F_2 , 33 mbar Kr and 3.4 bar Ar, which is typical of electron-beam pumped lasers, was excited by the electron-beam. At these pressures the KrF^* fluorescence lifetime is 0.6 ns. Through this gas was passed light from the laser of fluence $\sim 75 \text{ mJ cm}^{-2}$ which was brought to a focus beyond the interaction region. The percentage of the volume excited which was intersected by the laser was $50 \pm 8\%$. A comparison of the temporal variation of the fluorescence when depleted and undepleted i.e. with the laser switched on and off respectively

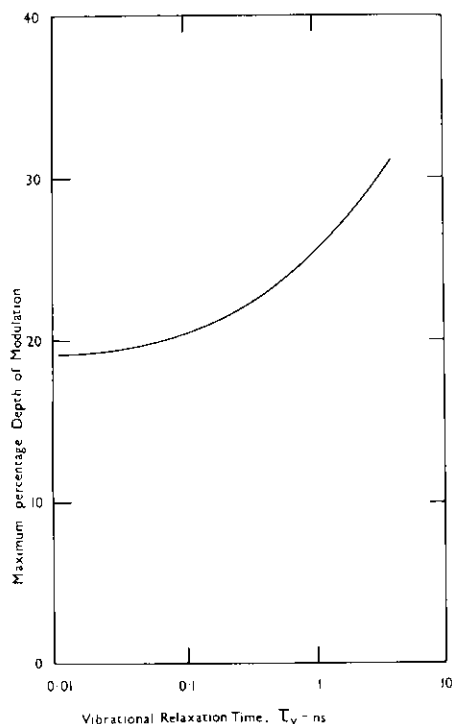


Fig. 2. Calculated maximum percentage modulation depth as a function of the vibrational relaxation time, τ_v , for $\tau_f = 600$ ps.

was obtained and an average maximum depth of modulation of $(9 \pm 1)\%$ was observed.

The maximum depth of modulation was calculated from the kinetic model and its variation with τ_v is shown in fig. 2. Allowing for the volume unpenetrated by the laser which contributed to a lowering of the observed depth of modulation, a maximum value of $(18 \pm 6)\%$ is concluded. Hence an upper limit of 450 ps is set on the vibrational relaxation time under the conditions of the experiment.

In order to slow the kinetic processes of the system, the electronbeam pumped cell was operated at near atmospheric pressure with a gas mixture of 1 mbar F_2 , 20 mbar Kr and 1.3 bar Ar. At lower argon pressures, the coupling of the electron energy to the gas is decreased with a consequent reduction in the amplitude of the fluorescence signal. Under these conditions, the calculated fluorescence lifetime of KrF^* is 2.5 ns [8,9]. By comparing the fluorescence signals with and without the saturating laser pulse present,

the fluorescence intensity was observed to recover to the unsaturated value from the maximum depletion depth with an exponential recovery time of 11.5 ± 3.0 ns. This is in agreement with the value of 8.0 ± 1.0 ns predicted from the kinetic model using the laser decay time which was measured to be 4.7 ± 0.3 ns and it was assumed that τ_v scales inversely with gas pressure as in a two-body process [4], using the maximum value of τ_v at the higher pressures (~ 3.5 bar) of 450 ps. The intrinsic gain recovery time of KrF^* may be obtained from the kinetic model by setting $\tau_q = 0$ and fig. 3 shows its dependence on the vibrational relaxation time under different conditions of pressure and hence of τ_f . Also shown is the variation with τ_v of the intrinsic gain depletion time i.e. the exponential time taken for the depletion to rise from zero to its maximum value produced by a saturating laser pulse with a fast rising edge. It is clear that both these gain depletion and recovery times are only weakly dependent on τ_v and that the gain recovers in a time which is approximately equal to the fluorescence lifetime τ_f .

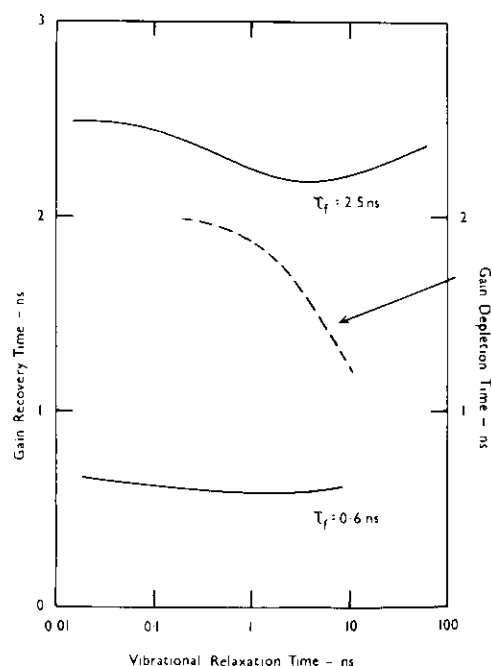


Fig. 3. Solid curves: Calculated intrinsic gain recovery times as a function of the vibrational relaxation time. Dashed curve: Calculated intrinsic gain depletion time as a function of the vibrational relaxation time.

The result obtained for τ_v (≤ 450 ps at 3.5 bar total pressure) is consistent with recent work by Jacob et al. [4] who quote a two-body rate constant for vibrational relaxation of $5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. This yields a value of τ_v of 180 ps (at 3.5 bar Ar) which may be reduced by three-body collisions. However, in a recent publication by Pummer et al. [5], a value of $\tau_v = 4 \pm 2$ ns is reported which was obtained from the decay of the fluorescence when saturated by laser action. As fig. 3 demonstrates, the fluorescence depletion and recovery times are very insensitive to τ_v and the reported depleted fluorescence temporal profile can be reproduced to a high degree of accuracy with values of τ_v as short as 450 ps.

5. Conclusion

In conclusion, therefore, it has been demonstrated that, under conditions which are typical of electron-beam pumped lasers, vibrational relaxation occurs in KrF^* on a sub-nanosecond timescale and amplification of a sequence of 1 ns pulses separated by several nanoseconds is expected to be efficient.

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