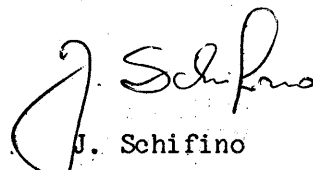## THE COLLISIONAL BEHAVIOUR OF
Mg, Ca AND Sr [nsnp(^3P_J)]
FOLLOWING EXCITATION BY A
PULSED DYE LASER

BY

JOSE SCHIFINO

PEMBROKE COLLEGE

CAMBRIDGE

A dissertation submited for the certificate of
post-graduate studies in the University of Cambridge

The work described in this dissertation was carried out by the author except were acknowledgment is made in the text

J. Schifino
June 1981

2

ACKNOWLEDGMENTS

CONTENTS

1. GENERAL INTRODUCTION

The direct study of the collisional behaviour of atoms in specific electronic states, particularly electronically excited atoms, is an area that has developed in recent years from both the experimental and fundamental view points. The study of fluorescence quenching of strongly-allowed, emitting atomic states in the steady mode, following excitation using the mean radiative lifetime as an "internal clock", through the agency of a Stern-Volmer plot is well established[1] and is not dealt with in this dissertation other than to indicate the existence of such studies.

Recent years have seen a large development of the direct investigation of excited states arising from the overall electronic structure of the ground state configuration. This is an area that has been extensively reviewed[2-8].

One experimental reason for the development of such an area arises from the optical metastability of the atomic state once generated, as the lifetime of the state is dominated by collisional removal, including energy transfer and chemical reaction, and this brings the state readily within the time-range of modern electronics and data handling apparatus in order to carry out kinetic measurements in "real time" rather than using the "internal clock" in the steady mode experiments of the Stern-Volmer type.

It is useful to note briefly some of the experimental methods that have been used to monitor directly these electronically excited, optically metastable states. These include[2-8]:

(i) Time-resolved atomic resonance absorption following the generation of the electronically excited state by pulsed irradiation. In this application of the flash photolysis technique, the excited atom is usually derived from the photodissociation of a stable molecule and its decay is then monitored by attenuation of radiation using photoelectric detection. This can be employed either in the "single-shot" mode or in the

"repetitive" mode. In the former, atomic particle densities are generated in sufficiently high concentration in order that the measured atomic decay from a single experiment may be used to obtain a satisfactory signal-to-noise ratio and hence, to use such decays to generate kinetic data. In the repetitive mode it is customary, though not absolutely necessary to employ a slow flow system, kinetically equivalent to a static one. In such experiments the atomic decay is rapid compared with the residence time and the time between succesive experiments. The function of the flow is simply to change the reactant mixture and this repetitive technique involves various methods of signal averaging and data analysis. An example of the former technique is that described for $Pb(6\ ^3P_{1,2})$[9] and of the latter, the study of the atmospherically important $O(2\ ^1D_2)$ is an example of current interest[10].

(ii) <u>Time-resolved resonance fluorescence</u> is a technique that is well established for various ground state atoms. Husain et al have described a set of studies of the ground states of group V atoms, $np^3(4\ ^4S_{3/2})$, by this method[11-15].

By contrast, the use of this method, particularly for the study of electronically excited atoms, has not been as extensively applied as that of resonance absorption. One example, is the recent work of Donovan on the electronically excited iodine atom $I[5\ p^2(^2P_{1/2})]$[16]. In general terms, this method involves the pulsed generation of the excited atom from photodissociation of a stable molecule. The lower ground state or optically metastable state is then excited via an allowed transition derived from a continuously running atomic resonance source. The fluorescence from the optically excited higher state in the reaction system is them monitored in "real time". This technique involves the justified assumption that whilst the upper emitting state is put in steady state on account of its high Einstein coefficient, the lower state from which it is optically derived, is not. This enables the time dependence of the fluorescence from the upper state to be employed to monitor the decay of the lower state from which it is derived[11-15]. As with time-resolved resonance absorption, this technique may be employed either in the single-shot mode or repetitive mode.

(iii) Time-resolved emission from the optically metastable state. In this technique, the optically metastable state is generated by the standard pulsed method and its emission is then monitored directly in real time. Examples of this method would include the study of O(2 $^1S_0$)[17]

$$[O(2\ ^1S_0)-O(2\ ^3D_2)] \quad \text{at} \quad \lambda=557.1\ nm$$

and I(5 $^2P_{1/2}$)[18]

$$[I(5\ ^2P_{1/2})-I(5\ ^2P_{3/2})] \quad \text{at} \quad \lambda=1315\ nm$$

It must be emphasised that the excited state is monitored in such measurements by means of electric dipole forbidden transitions where A_{nm} is very small. For O(2 $^1D_2$), $A_{nm}=1.28\ sec^{-1}$ (ref 4). This may be contrasted with an allowed transition for an atomic emission where A_{nm} is of the order of $10^8\ sec^{-1}$. Hence, the weak emission does not contribute significantly to the kinetic decay but is simply used as a spectroscopic marker of concentration. It further means that signal averaging generally has to be employed to extract the signal from the noise. An especially striking example of this is the study of O(2 $^1D_2$) generated by the laser pulsed irradiation of ozone[18] which employs the emission;

$$O[(2\ ^1D_2)-O(2\ ^3P_2)] \quad A_{nm}=6.9 \times 10^{-3}\ sec^{-1}$$

Such extremely weak emission involves extensive signal averaging as the number of quanta detected in any experiment is very small. On the other hand, in special cases such as I(5 $^2P_{1/2}$)[19], where very high concentrations of the 2 $P_{1/2}$ state can be generated, leading to a laser in chosen cases[20], single-shot experiments may be used to monitor the ($^2P_{1/2}-^2P_{3/2}$) emission and so obtain collisional data as well as data on diffusion and the Einstein coefficient itself[21].

As with these previous studies on various atomic states, this dissertion is concerned with the optically metastable states of Mg, Ca and Sr in the nsnp(^3P) levels. In terms of electronic structure, these states of the Group IIA elements do not arise from Rydberg excitation, namely, the principal quantum number is unchanged. On the other hand, the states are optically metastable (see later) involving mean radiative lifetime (τ_e) of the order of 10^{-3} sec (i.e. $A_{nm}=10^3\ sec^{-1}$) and similar considerations will apply to the experimental study of these Group IIA elements as has

been given in the methods referred to. Indeed, it will be seen that these similarities are strong (see later). It will also be seen that there are differences in the generation of the excited states of the Group IIA elements in that these are optically pumped directly from the ground state using atomic vapours by means of a pulsed dye laser, suitably tuned. However, once generated, similar considerations to monitoring will apply within the constraints of the repetition technique for the laser itself.

This dissertation does not deal with all techniques for monitoring electronically excited atoms. Reference may be made to the reviews cited as examples of atomic resonance methods[2-8]. We are primarly concerned here with examples of atomic resonance methods in order to place the dye laser excitation investigation in this work in the context of other work on optically metastable atomic states.

2. POTENTIAL ENERGY SURFACES

The largest body of unified rate data for the collisional behaviour of electronically excited states has been generated in recent years for the elements in Groups IV-VII.

$$C, Si, Ge, Sn, Pb(np^2)(^3P_{0,1,2} \ ^1D_2 \ ^1S_0)$$
$$N, P, As, Sb, Bi \ (np^3)(^4S_{3/2} \ ^2D_{3/2,5/2} \ ^2P_{1/2,2/3})$$
$$O, S, Se, Te \ (np^4)(^3P_{2,1,0} \ ^1D_2 \ ^1S_0)$$
$$Fl, \ Cl, Br, I \ (np^5)(^2P_{3/2,1/2})$$
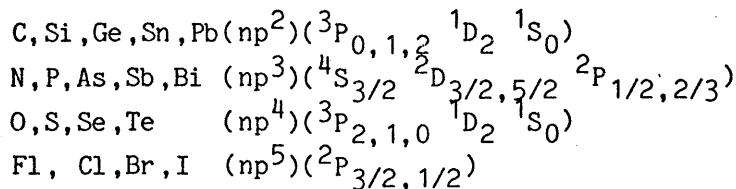
The rate data for these atomic states have been extensively reviewed as indicated hitherto[2-8]. Further, Golde[22] has reviewed rate data for the collisional behaviour of electronically excited noble gas atoms. The fundamental structure for considering rate data of atom-molecule collisions is governed by the magnitude and scope of the rate data available. In principal, a given rate constant is ideally considered in terms of the detailed construction of a potencial energy surface and the dynamics on that surface[23]. However it can readily be seen that the massive body of rate data for all these electronically excited atoms, many of which are heavy, and the large range of collision partners, requires some simplied approach in order to consider the data as a whole. The approach used in recent years by Donovan and Husain is to employ the symmetry of the potential surfaces involved on collision, through the agency of correlation diagrams. For light atom-molecule collisions, correlations diagrams are constructed on the basis of a weak spin-orbit coupling approximation[2,6,24] and have been used to discuss the difference in the collisional behaviour of a given atom or molecule in different electronic states. This approach is now, in fact, being used in bibliographic compilations of rate data[25]. For the heavy elements, Husain[6], has described the method of J, Ω coupling for atom-molecule collisions. This is a far more complex approach and the available pathways, given the loss of the spin selection rule, are less restrictive and more numerous. The various considerations of the potential energy surfaces for atom-molecule collisions will have practical applications in particular

systems. Its reference here is to provide the overall framework against which the data derived for the Group IIA elements will eventually be considered.

3. MAGNESIUM, CALCIUM AND STRONTIUM

It is proposed in the present investigation to study the collisional behaviour of the ^3P_J states of Mg, Ca and Sr using a somewhat more sophisticated method than employed hitherto for these particular states in the presence of a wide range of collision partners. The practical objective of such a study is to assist our understanding of quenching, including chemical reaction and energy transfer, and this may also include, for example, the use of an efficient energy store such as high densities of optically metastable $O_2(^1\Delta_g)$, hopefully leading eventually to the design of chemical lasers. This is, however, a limited aspect of such work. The studies will include the collisional behaviour of these ^3P states in the presence of species such as N_2O where highly vibrationally excited and electronically excited metal oxide diatomic molecules may be formed on collision, even with ground state atoms. The presence of other atoms such as Na and K, where collisions with the metastable ^3P_J atoms of Mg, Ca and Sr may lead to excimer formation, may also be investigated.

The further fundamental objective, is to investigate the general relationship between electronic structure and reactivity.

The ^3P_J levels constitute the lowest lying electronically excited states of these atoms above the $ns^2(^1S_0)$ ground states, namely (cm^{-1}) [26].

	Mg[3s3p(^3P_J)]	Ca[4s4p(^3P_J)]	Sr[5s5p(^3P_J)]
J=0	21,851	15,158	14,318
J=1	21,870	15,210	14,504
J=2	21,911	15,316	14,899

$$1\ cm^{-1} = 1.2398 \times 10^{-4}\ eV$$

The experiments envisaged in this work for these particular atomic states have in common the following aspects;

1) The production of metal atoms in a flow system using a heat pipe; the flow system would be equivalent to a static system for the purpose of the

atomic decay, in other words, the residence time of the flowing gas in the reaction vessel would be much greater than the atomic decay.

2) Repetitive dye laser excitation to the ^3P_J levels from the ground states ($^1S_0$) by firing the laser at a frequency of ca. 10 Hz and tuning to the wavelength corresponding to the transition to be excited state, i.e.:

Mg at λ= 457.1 nm   Ca at λ= 657.3 nm   Sr at λ= 689.3 nm

3) Averaging the particular signal used to monitor the ^3P_J state generated following dye laser excitation.

After dye laser excitation into the ^3P_J states, the following types of measurements on these optically metastable atoms can, in principle, be envisaged;

(i) <u>Time-resolved resonance fluorescence</u> by current measurements of electric dipole allowed fluorescence signals following further excitation with a resonance source. The resonance fluorescence signal, after passing either through a monochromator or an interference filter may be transformed into an electric current·by mean of a photomultiplier tube. The voltage drop caused by this current in a resistor (current-to-voltage converter) may be coupled to a boxcar integrator and the decay curve displayed on an XY-chart recorder. Inspection of standard compilations[27] indicate conveniently placed strong atomic resonance transitions for the $^3P_{0,1,2}$ levels of Mg and Sr in various parts of the spectrum. For Ca, by contrast, conveniently situated and relatively strong resonance transitions are those for the $^3P_1$ and $^3P_2$ levels, respectivelly;

$Ca[5s(^3S_1)-4s4p(^3P_1)]$ at λ= 612.2 nm
$Ca[5s(^3S_1)-4s4p(^3P_2)]$ at λ= 616.2 nm

This type of measurement may prove to be convenient if forbidden emission measurements for the ($^3P-^1S$) studies that are being undertaken are complicated excessively by scattered light from the laser source at the same wavelength. The forbidden emission measurements are resonance measurements in that the laser excitation and emission used to detect the decay of the atomic states are at the same wavelength and, of course, both

connect with the ground state. Time-resolved resonance fluorescence (and time-resolved resonance absorption), as conventionally described, are resonance measurements entirely with respect to the spectroscopic source. Of course, scattered light from the laser will be greater than scattered light from a spectroscopic source. However, it is hoped that interference from the former can be overcome and, indeed, the first measurements are being undertaken in such a basis (see later).
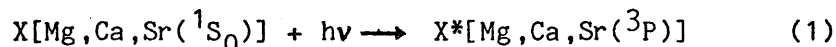
(ii) <u>Time-resolved resonance line absorption.</u> In this case, the resonance spectroscopic lamp would be used to further excite atoms previously excited by the laser. The use of a spectroscopic lamp in both cases implies some modification to the reaction vessel since a further optical window would be needed. The furnace containing the reaction vessel in this case should have an opening to allow light from the spectroscopic lamp to be shone on to the reaction vessel.

(iii) <u>Time-resolved forbidden emission:</u> $nsnp(^3P_J)-ns^2(^1S_0)$. The forbidden transitions $(^3P_J-^1S_0)$ for Mg, Ca and Sr are sufficiently strong to permit detection of the ^3P_J states by direct emission, which is quite convenient for the proposed experiments, given that the effect of scattered light from the laser can be overcome. The literature indicates the following values for the mean radiative lifetimes for the transitions to be monitored.

Atom	τ_e for $(^3P_J-^1S_0)$	A_{nm}	Reference
Ca	1.4×10^{-4} sec	7.2×10^3 sec^{-1}	27
Sr	1.5×10^{-5} sec	6.7×10^4 sec^{-1}	27
Mg	2.2×10^{-3} sec	4.5×10^2 sec^{-1}	28

Thus, the forbidden emission would be monitored as a function of time following dye laser excitation using a boxcar integrator, a chart recorder and a monochromator adjusted to the appropriate wavelength.

The kinetic scheme for this type of experiment may be writen;

$$X[Mg,Ca,Sr(^1S_0)] + h\nu \longrightarrow X^*[Mg,Ca,Sr(^3P)] \qquad (1)$$

$$X^* \longrightarrow X + h\nu \qquad A_{nm} \qquad (2)$$

$$X^* + R \longrightarrow products \qquad k_R \qquad (3)$$

$$X^* \longrightarrow walls \qquad diffusion(\beta) \qquad (4)$$

13

The laser pulse is of the order of 20 nsec(see later) and this excitation may be considered effectively instantaneous in the time scale of this experiments. Thus, following laser excitation, the decay of X* may be described by the first order kinetic equation;

$$- d(X^*)/dt = [A_{nm} + \beta + k_R(R)](X^*) \qquad (i)$$
$$= k'(X^*) \qquad (ii)$$

where $k' = A_{nm} + \beta + k_R(R)$ is the first-order decay coefficient in a given experiment. We assume that β (sec^{-1}) may be considered as arising from the long-time solution of the diffusion equation. However, this requires the boundary conditions of an uncertain geometry, not the physical magnitude of the reaction vessel but the effective geometry of the combination of the excitation area for the laser and the light-gathering power of the optical detection system. In these experiments β will be allowed for empirically at a given fixed pressure of buffer gas in the presence of varying quantities of the added reactant gas R. R will include species that give rise to collisional quenching, including chemical reaction and energy transfer.

Hence equations (i) and (ii) yield on integration;

$$(X^*)_t = (X^*)_{t=0} \exp^{(-k't)}$$

and the resonance fluorescence emission is then given by;

$$I_F = \phi A_{nm}(X^*)_F \qquad (iii)$$

where ϕ represents a factor which involves the light gathering power of the optical detection system plus the sensitivity of the electronics. Hence

$$I_F = \phi A_{nm}(X^*)_{t=0} \exp^{(-k't)} \qquad (iv)$$

Thus, the semi-logarithmic decay of $I_F(^3P-^1S)$ with time yields k'. The variation of k' with (R) at a fixed total pressure yields k_R, the second-order rate-constant for collisional removal.

These methods will yield absolute data for the removal of the ^3P_J states of Mg, Ca and Sr by a wide range of collision partners. Where possible, measurements on individual spin-orbit states will also be carried out to investigate any effects of the spin orbit relaxation within

14

the $^3P_{0,1,2}$ levels. For Mg and Ca, it is highly probable that the spin orbit system will be in Boltzmann equilibrium throughout the kinetic decay in view of the small energy splittings involved. This would be reflected in equality in the first-order decay coefficients for all the $^3P_{0,1,2}$ states in a given experiment. On the other hand, the larger splittings in $Sr(^3P_{0,1,2})$ may give rise to an observable, time-dependent spin-orbit relaxation at short times following the dye laser excitation. As has been emphasised, the measurements now in hand on this system involve the time-resolved forbidden emission. However, the alternative spectroscopic resonance techniques may clearly be held as alternatives in the event of excessive difficulties being encountered with scattered light and these methods are also of interest in themselves.

It is not intended that the brief review presented here on the collisional behaviour of the Group IIA elements be exhaustive but recent work on the ^3P_J levels of Mg, Ca and Sr is described in order to place the proposed work in context.

The collisional behaviour of electronically excited atoms has been reviewed in recent years by Husain[6] including reference to the Group II elements where there was an emphasis on the reactivity of the heavier ground state species. For both fundamental and practical reasons, this is, of course, an area undergoing continual change. However, detailed studies on the ^3P_J levels of these atoms in particular, leading to absolute collisional rate data have been both very limited in scope and in the experiments employed themselves.

Among the three elements to be studied, Mg is the one which has received most attention, what is justified by the astrophysical interest for the emission lines from the metastable $^3P_{0,1,2}$ states of Mg. States in the triplet manifold of Group IIA atoms have sufficiently long radiative lifetimes and sufficiently slow quenching rates in Ar that they can be studied by the flow technique.

Taieb et al[29] have studied the quenching of $Mg(^3P_1)$ by several gases, measuring the decrease of the afterglow emission $(^3P-^1S)$ at $\lambda = 457.1$ nm. The $Mg(^3P_1)$ atoms were produced by a gas discharge in a flow system in He at pressures near 1 Torr.

Benard et al[30] have used flames containing Mg, Ca and Sr with reactions catalysed by N_2O and CO, to study the formation of the Mg, Ca and Sr metastable atoms at high temperature. They have shown that the addition of CO increases the prodution of these excited atoms, especially in the case of Mg. To account for this catalytic action a two step reaction mechanism was proposed;

$$Mg + N_2O \longrightarrow MgO^* + N_2$$
$$MgO^* + CO \longrightarrow CO_2 + Mg(^3P_J)$$
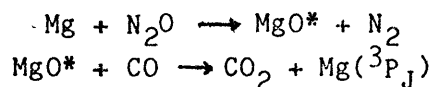
Retention of energy from the first step is required because the equilibrium reaction of MgO with CO would be endoergic for $Mg(^3P_2)$ formation. The additional energy most likely is provided by vibrational energy, indicated by the *, retained from the first step. Benard et al[31] have also added Ca and K to a flow containing $Mg(^3P_J)$ and observed excitation transfer to Ca and K and, for the first time, emission from the molecule KMg.

The molecular beam technique has been used by Kowalski and co-workers[32] and Brinkmann and co-workers[33-34] to study the reactions of the ^3P states of the Group IIA elements with halogens.

Kowalski[35] has measured the attenuation cross section for collisions of an excited atomic beam of Mg, Ca and Sr with a target of Cl_2 molecules. The experimental values obtained were compared with the theoretical values calculated assuming a harpoon mechanism. In a further experiment, Kowalski et al[32] have studied the reactions;

$$Mg^*(^3P) + (F_2, Cl_2) \longrightarrow MgF(Cl) + F(Cl)$$
$$Ca^*(^3P) + Cl_2 \longrightarrow CaCl + Cl$$
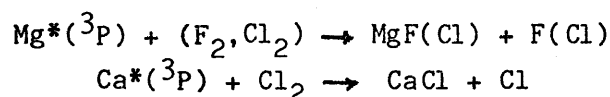
Absolute cross sections were measured for beam atenuation, chemiionization and chemiluminescence.

Brinkmann and co-workers[33-34] have studied the reactions;

$$Ca[4s3d(^1D_2)] + (HCl, Cl_2) \longrightarrow CaCl + (H, Cl)$$
$$Sr[5s4d(^1D_2)-5s5p(^3P)] + Cl_2 \longrightarrow SrCl + Cl$$
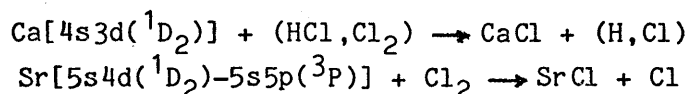
using the atomic beam technique, performing the analysis of the luminescence by high resolution spectroscopy. A model was proposed to explain the population of the different states.

Recently, the availability of tunable dye lasers, able to produce large number of photons in bandwidths comparable to the Doppler width of spectral transitions, has provided a new tool for the excitation of atoms such as Mg, Ca and Sr, to well defined electronic states, allowing their kinetic properties to be studied. Increasing numbers of studies have been

carried out using dye laser excitation of Group IIA elements.

Wright et al[28] have carried out single-shot atomic resonance line absorption measurements on $Mg[3s3p(^3P_1)]$ following dye laser excitation of Mg vapour at $\lambda = 457.1$ nm in order to determine the mean radiative lifetime of $Mg[3s3p(^3P_1)-3s^2(^1S_0)]$. This was found to be $2.2 \pm 0.2 \times 10^{-3}$ sec when the collisional removal is extrapolated to zero pressure. A similar experiment was performed by Blickensderfer et al[36], again in the single-shot mode, in order to determine collisional rate constants for $Mg[3s3p(^3P_J)]$ quenched by a limited number of added gases. The excited state Mg atoms were observed by direct emission from $Mg(^3P_1-^1S_0)$ at $\lambda = 457.1$ nm and by atomic absorption $(^3P_2-^3S_1)$ at $\lambda = 518.5$ nm. The natural radiative lifetime of $Mg(^3P_1)$ is still uncertain, values being reported as ranging from 1.5 to 5.0 msec in this experiment when determinations were made in pure helium.

McIlrath[37] has photographically recorded at short time delay the absorption spectra of atomic calcium in what was effectivelly the single-shot mode following dye laser excitation of calcium vapour;

$$Ca[4s(^1S_0)] - Ca(4s4p(^3P)] \quad \text{at} \quad \lambda = 657.28 \text{ nm}$$
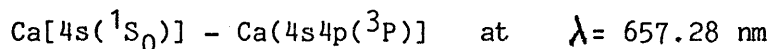
Mallins et al[38] have measured the rate constants for the quenching of $Ca(^3P)$ by the ground states of Ca and Mg and by inert gases. The excited atoms $Ca(^3P)$ were produced by cw ring dye laser excitation at $\lambda = 657.2$ nm from calcium metallic vapours produced in a heat pipe. The fluorescence signal was monitored via a phase sensitive detector.

Solarz et al[39] have studied the reaction

$$Sr[5s5p(^3P_1)] + HCl \longrightarrow SrCl^* + H$$
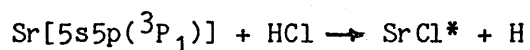
using laser excitation of the Sr atom and applying laser induced fluorescence to the product molecule in order to determine the vibrational distribution within the electronic ground state.

5. EXPERIMENTAL

The components to be used in the present experiment may be sumarised as follows:

1- The excitation system (tunable dye laser);
2- The gas handling system;
3- The reaction vessel and furnace;
4- The detection system;

A block diagram of the apparatus is shown in Fig.1. The scheme represents the experimental arrangement for the study of Mg atoms and does not exclude the possibility of modifications, should they become necessary, for the study of the ^3P_J levels of Ca, Sr or even Mg. The experimental system represents the initial arrangement for commencing the study of the ^3P_J levels of Mg Ca and Sr, following dye laser excitation.

It is convenient to consider some detailed aspects of each one of the components that constitute the complete apparatus.

5.1 Excitation System

In order to pump optically Mg, Ca and Sr atoms to the ^3P_J excited states, a tunable Nd-YAG pumped dye laser (JK Lasers) will be used. The Nd-YAG pumping laser has a wavelength of $\lambda = 1064$ nm. A second harmonic generator (DCDA crystal) allows a vertically polarised beam at $\lambda = 532$ nm to be generated. By using a third harmonic generator (KD*P crystal) the fundamental and the second harmonic beams combine to produce a horizontally polarised beam at $\lambda = 355$ nm. The possibility of choice of the pumping laser output wavelength enables a great number of dyes to be efficiently pumped and increases the tuneability of the dye laser. In our particular case, the following combinations of pumping beam and dyes could be used;

Atom	Pumping beam	Dye to be used	Required wavelength
Mg	355 nm	Coumarin 460	457 nm
Ca	532 nm	Cresyl Violet	657 nm
Sr	532 nm	Nile Blue	689 nm

5.2 Gas Handling System

The gas handling system, specially built for this experiment, is a conventional vacuum line able to produce a vacuum of 10^{-5} Torr. The vacuum line uses a rotary pump (Metrovac GDR1, Associated Electrical Ind. Ltd.) and an oil diffusion pump (Edwards 203B) for the vacuum itself and another rotary pump for the flow system (NGN model PD/2) The line was designed in such a way that experiments can be carried out either in a static or in a flow system. Needle valves, connected to the vacuum line, will enable the flow callibrations needed for the study of reactions of Mg, Ca and Sr with several collision partners in a flow system. The needle valve system was built in a way to allow up to three different calibrated flows to be set simultaneously. The gas pressure in the line can be measured at several points by means of a Pirani gauge (Genevac PGH3), a Penning gauge (Edwards model 6) and an MKS Baratron 221A. In addition to these gauges, two spirals and one Bourdon gauge have been built for use on the line. Figure 2 gives a general view of the apparatus including the vacuum system, the dye laser with the various units for its operation and the optical system. Figure 3 is a more detailed presentation of the main part of the vacuum system and includes standard apparatus for the preparation of mixtures, initially prepared with a bulb containing a magnetic stirrer, and pressure measuring devices. The main aspect of Figure 4, which is a back view of the vacuum system, is the arrangement for the flow system.

5.3 Reaction Vessel and Furnace

The reaction vessel to be used for the initial experiments has two quartz windows; one for entry of the laser beam and another, orthogonally placed, for the outlet of fluorescence signal. A Wood's horn is provided to avoid reflections from the laser beam, as shown in Figure 5. Two side arms

are designed as the gas inlet and outlet, respectively. In the inlet side arm, a bulge contains a small quantity of the metal to be studied, acting as a source of the metallic vapour. The whole vessel is placed in an electric furnace, shown in Figure 6, designed for temperatures up to T=1000 K. At this temperature the vapour pressure of Mg, Ca and Sr will be sufficiently high to allow metallic vapour to be carried into the reaction vessel by the flowing gas. The flowing gas is pre-heated before entering the furnace by mean of a heating tape wrapped around the side arm. A view of the full furnace housing is included in Figure 7. The gas flow is controled by means of two needle valves; the first one controls the pressure in the line, while the second one, placed before the rotary pump, controls the actual flow rate.

5.4 Detection System

The detection system comprises:

        1- A grating monochromator;
        2- A photomultiplier tube;
        3- A boxcar integrator;
        4- An XY chart recorder;

Figures 7 to 9 show photographs of the various components to be described and it is hoped that these are self-explanatory in indicating their employment in this system. The fluorescent signal of known wavelength, after passing through the monochromator, is transformed into an electric pulse by means of the photomultiplier tube. The photoelectric pulse is first amplified by means of a current-to-voltage converter and them analysed by a boxcar integrator and the resulting decay curve is displayed on an XY chart recorder.

5.4.1 Grating monochromator

A small, compact, limited resolution monochromator type Mini Chrom MC1-02 ptr Optics was coupled on to the entrance of the photomultiplier tube. The monochromator allows a wavelength setting with a precision of 0.2%. Three interchangeable slits are available; 0.15, 0.30 and 0.60 mm width by 4.0 mm in height. As the high resolution is not important in this

experiment, the widest slit was chosen as a starting point. The photomultiplier housing system was designed in such a way that the monochromator can be easily replaced by an interference filter whenever it should prove to be necessary.

5.4.2 Photomultiplier tube

A special photomultiplier tube is used for light detection. This is a relatively newly designed tube (E.M.I. type 9816 QB) specifically constructed for gating and incorporating a gating electrode which is defocussed when the gate is in operation. This is a 14-dynode device of high gain, of the order of 10^9 and characterised by a low dark current. The use of this gating facility, not employed in these initial experiments, may prove necessary should the effects of scattered light from the laser dominate the fluorescence signals from the excited atoms. The output from the laser, itself, may be used to initiate a gating system for the photomultiplier but the relevant circuits would require construction. Particularly sophisticated gating circuits have been published for use with this tube[40] but it is hoped that a simpler system, such as one involving a standard delay circuit as employed in flash photolysis could be modified in this particular application. The photomultiplier tube has been operated at 1300 V, since experiments showed that a maximum signal-to-noise ratio could be achieved at this voltage. The high tension supply for the photomultiplier tube is provided by a high voltage power supply (Brandemburg 415B). The signal from the photomultiplier tube is amplified, as described, by means of a current-to-voltage converter before being fed to the boxcar integrator.

5.4.3 Boxcar Integrator

The boxcar integrator system consists of a scan delay generator (Brookdeal 425A) and a linear gate (Brookdeal 415). The system can be used as a signal averager, giving an output suitable to be registered on an XY chart recorder. The experiment is performed in the repetitive mode, ca. 10 times a second. A signal from the laser system is used as a reference signal to trigger the boxcar integrator.

5.4.4 XY Chart Recorder

An XY chart recorder (Bryans 21001) has been used to record the signal from the boxcar integrator. The exponentially shaped curves can be used to calculate the first-order decay coefficient for the excited atom and hence the second-order rate constants for the reaction under consideration may be derived according to the kinetic scheme presented earlier.

FIGURE 1

Block diagram of the apparatus for the kinetic study of the ^3P states of Group IIA elements following excitation by pulsed dye laser and monitored by time-resolved fluorescence.

Oscilloscope

XY Chart
Recorder

Gas
Handling
System

Power Supply

Boxcar

Current-to
-Voltage
Converter

Monochromator
& P M Tube

Laser
Control Unit

To the
Pump

Nd- YAG Laser

Dye   Laser

45 degrees
Mirror
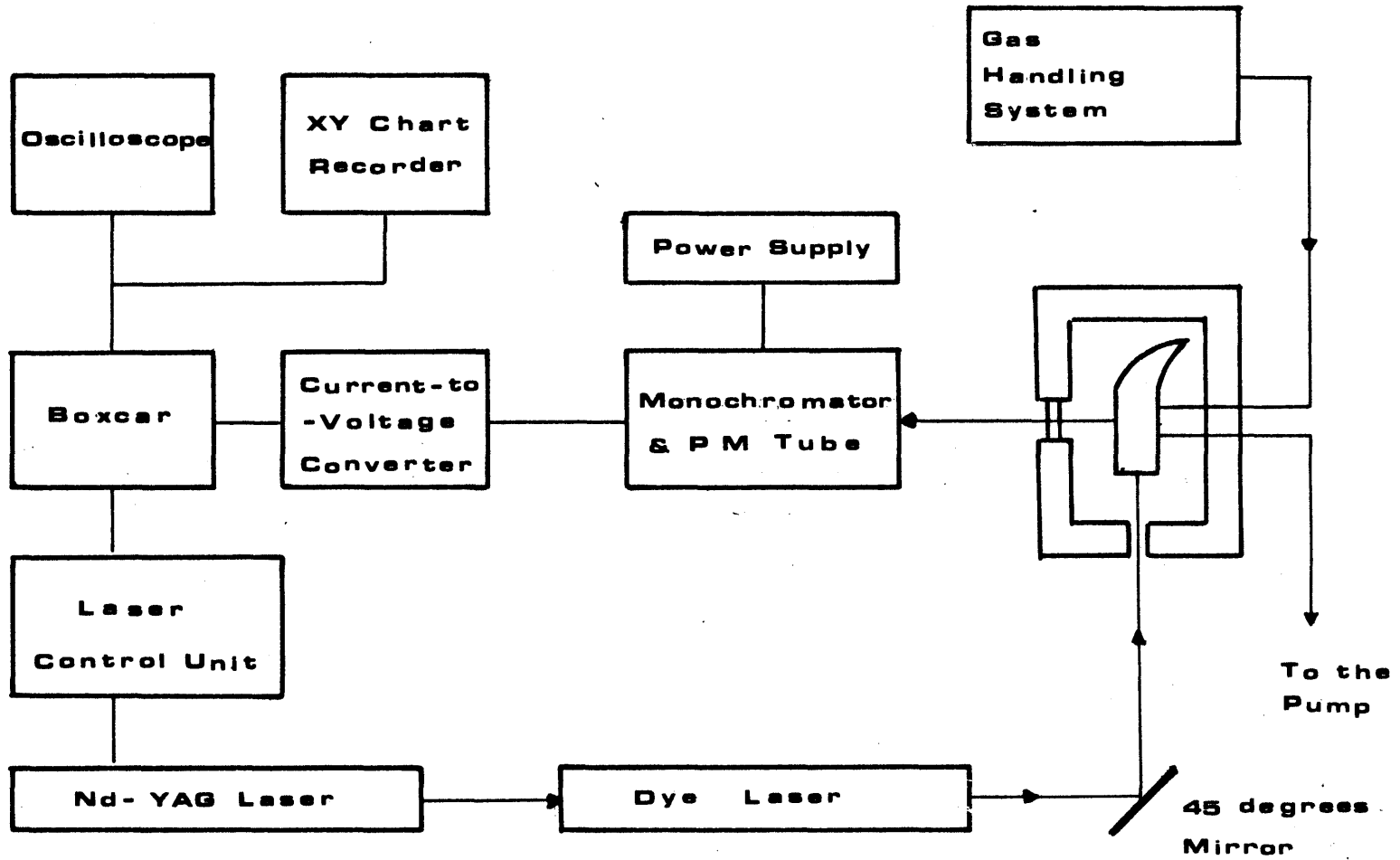
FIGURE 2

General view of the apparatus for the kinetic study of Group IIA elements in the ^3P states, generated by pulsed dye laser excitation and monitored by time-resolved forbidden emission, (^3P-^1S), using Boxcar integration.
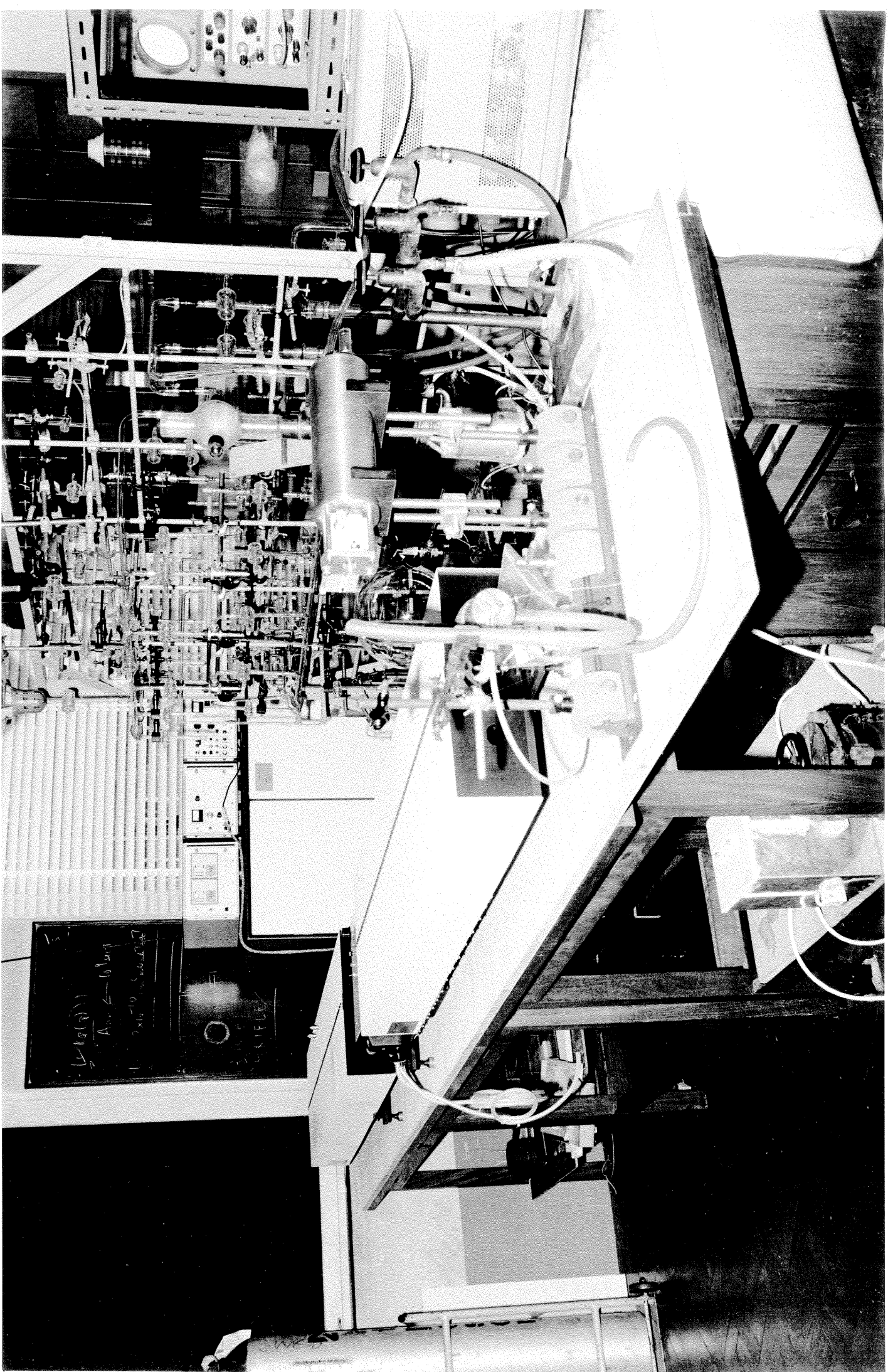
FIGURE 3

Front view of the vacuum system for dye laser excitation studies indicating the main line, the gas handling systems, pressure measuring devices and bulb with magnetic stirrer for mixture preparation.
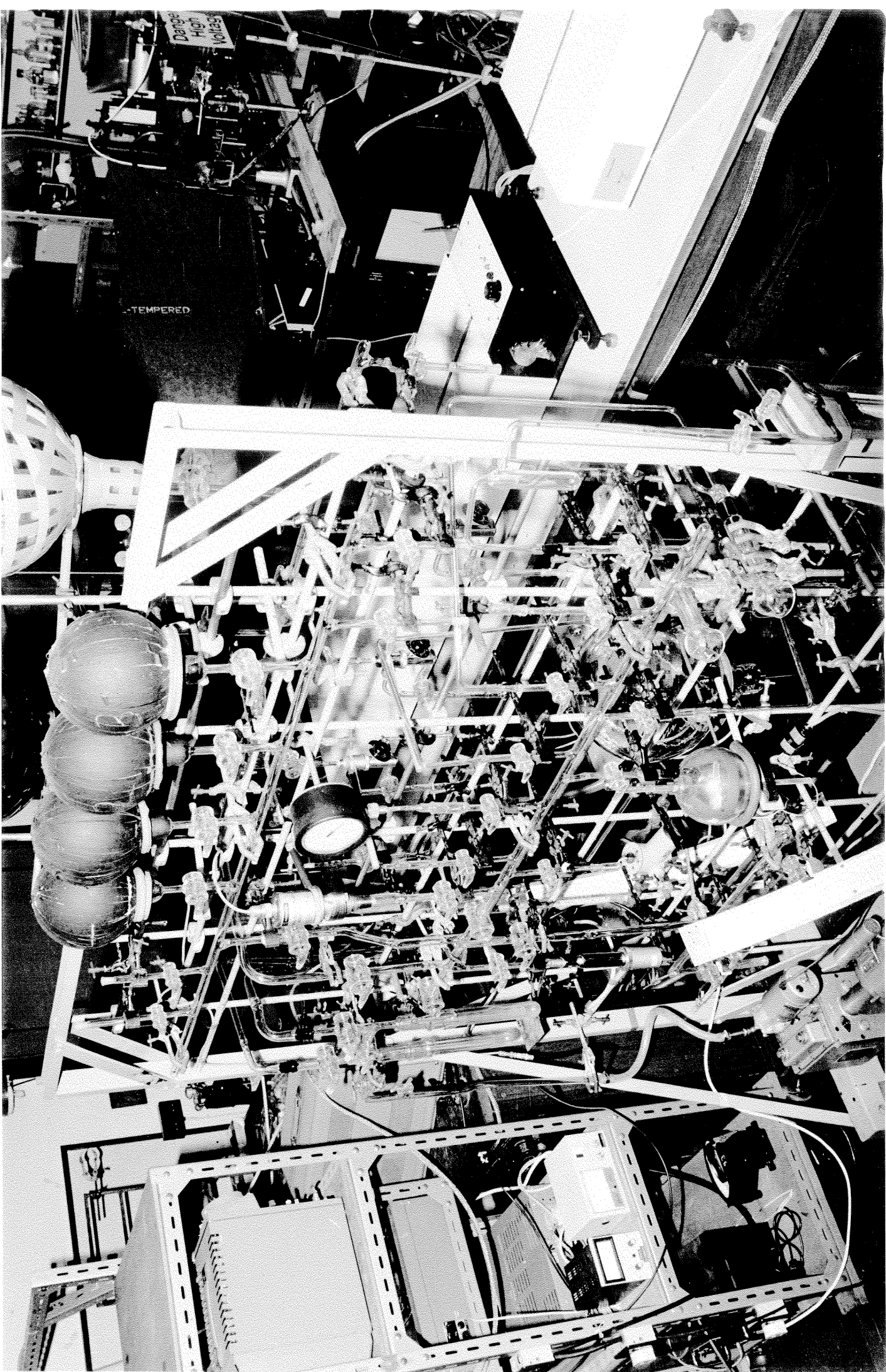
FIGURE 4

Back view of the vacuum system employed in the dye laser excitation
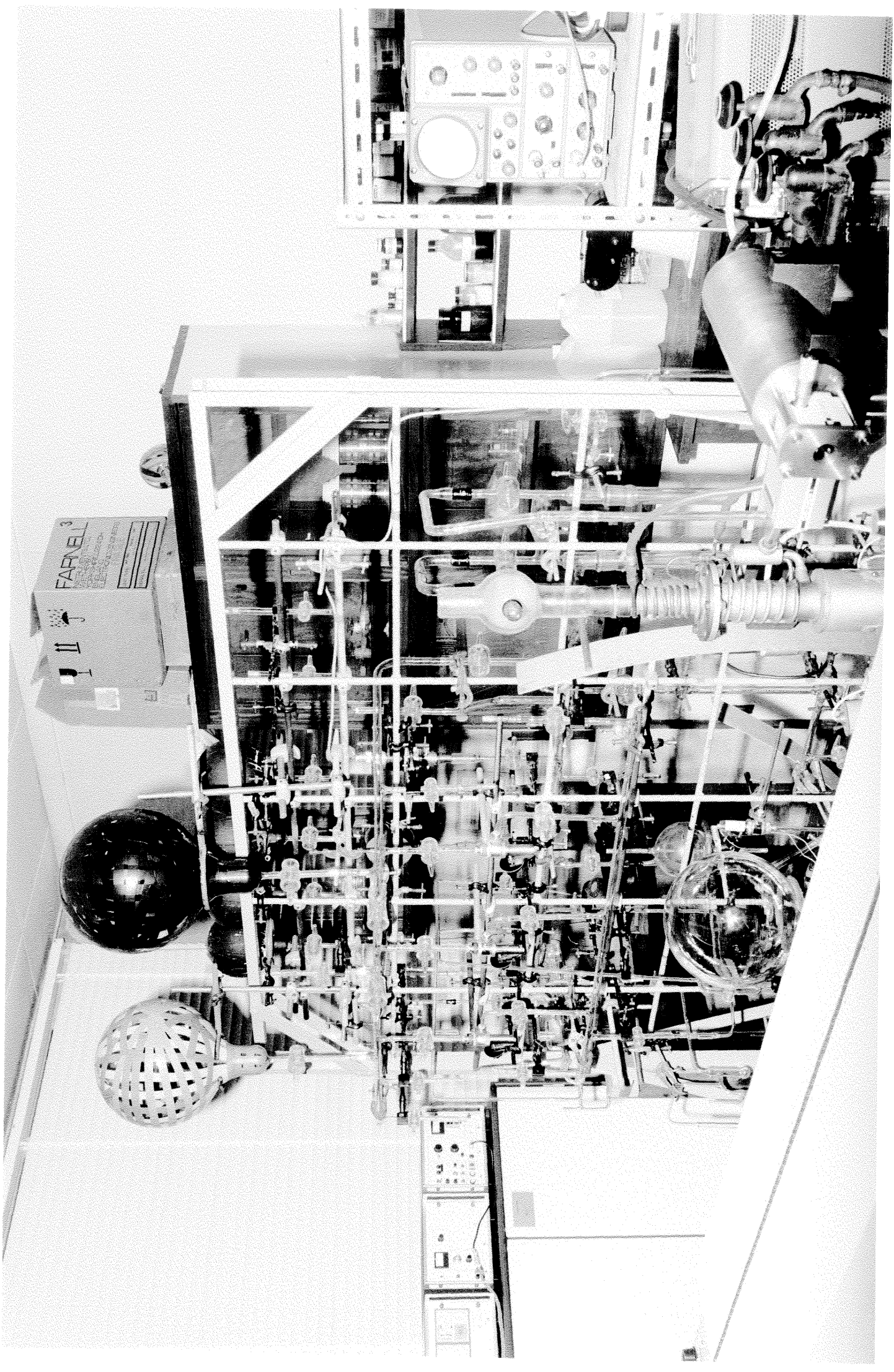studies of the Group IIA elements including the diffusion pump and flow
system.

FIGURE 5

Quartz reaction vessel indicating orthogonally placed optical windows and
a Wood's horn.

FIGURE 6

Photograph of the inside of the furnace indicating the heating coils and the port holes for entry of laser beam and exit of spectroscopic signal.
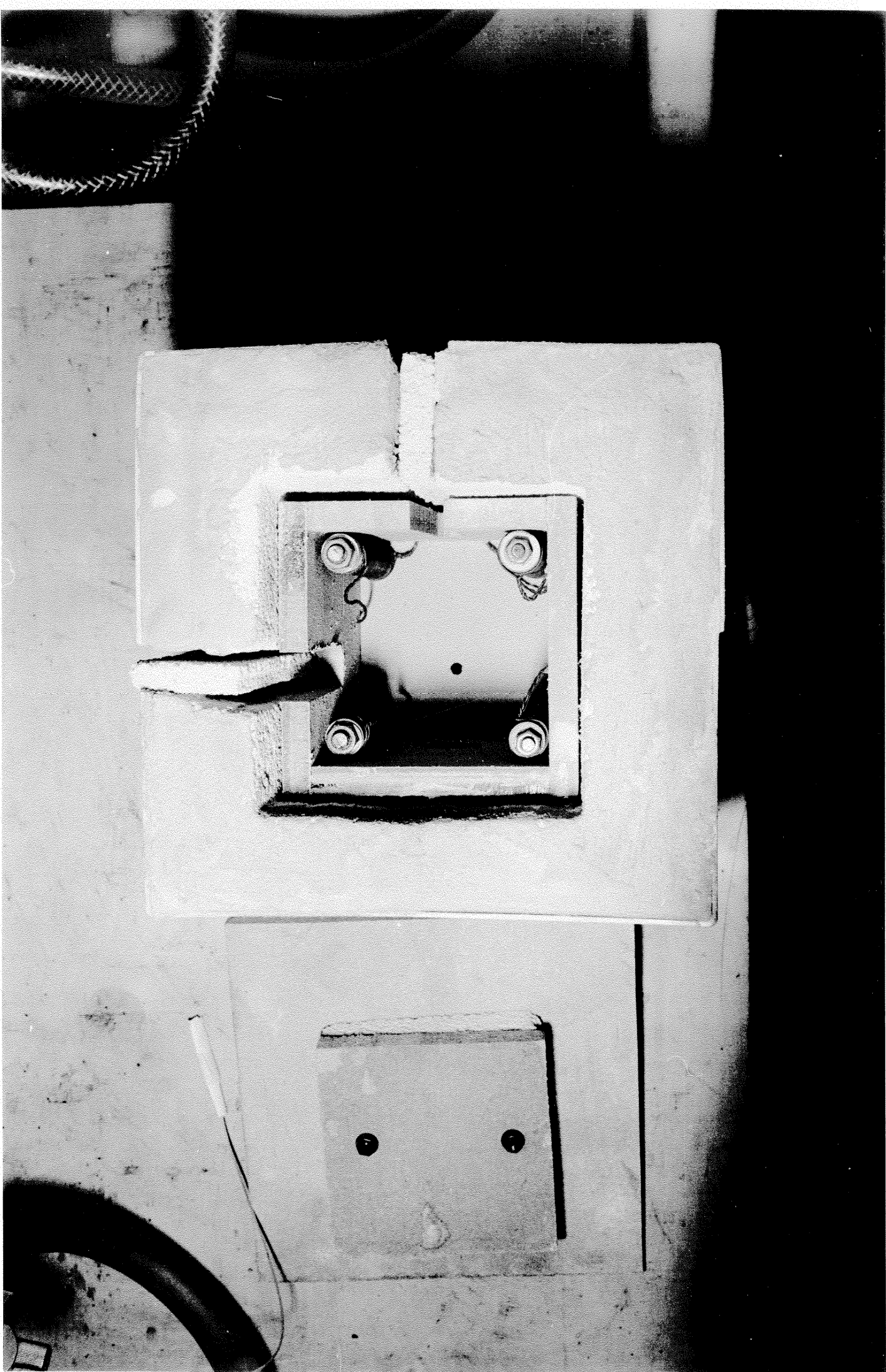
FIGURE 7

Photograph of a section of the apparatus for the dye laser studies of
Group IIA elements including the furnace, the nebuliser flame system and
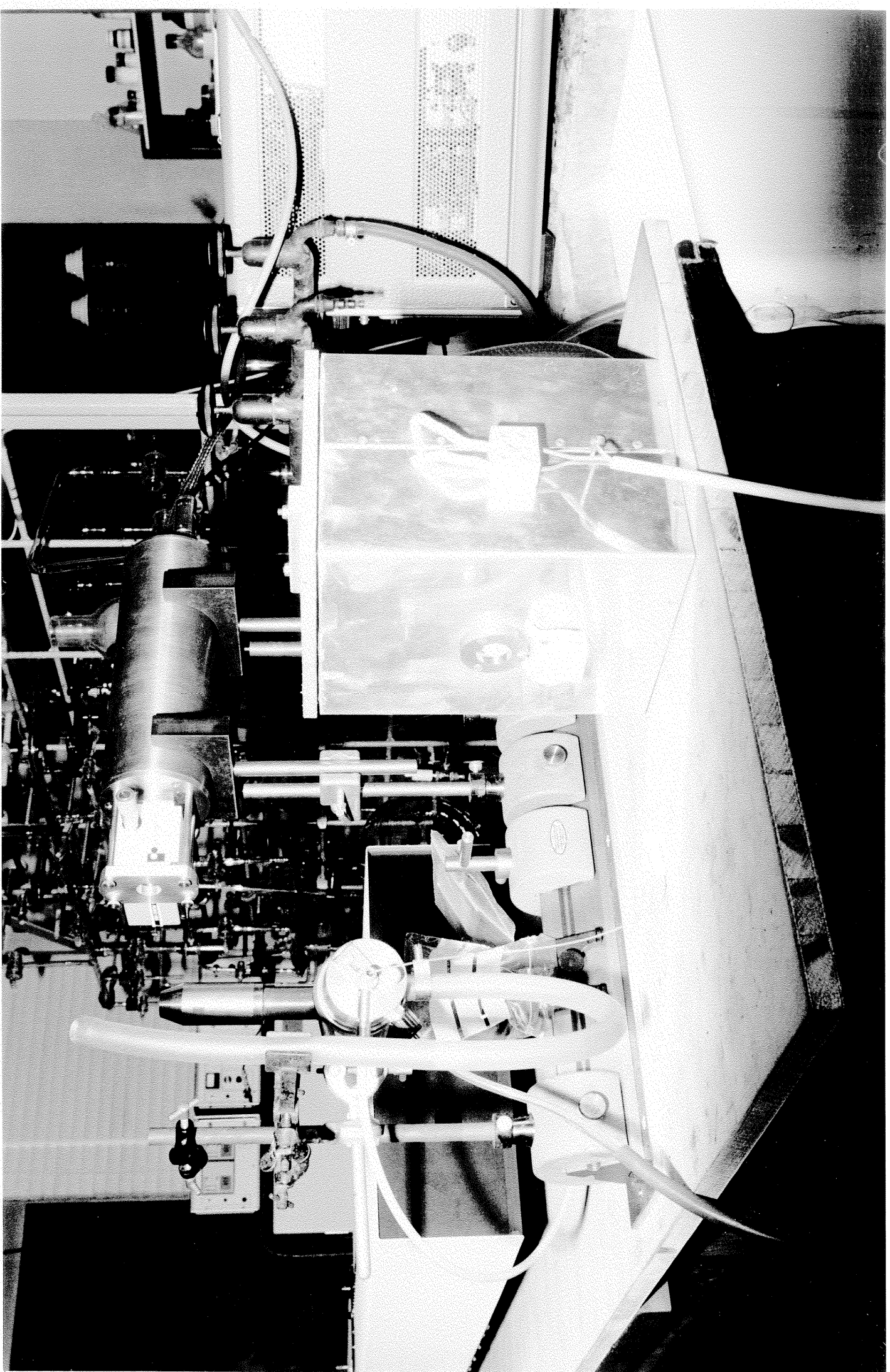the monochromator plus photomultiplier detection system.

FIGURE 8(a)

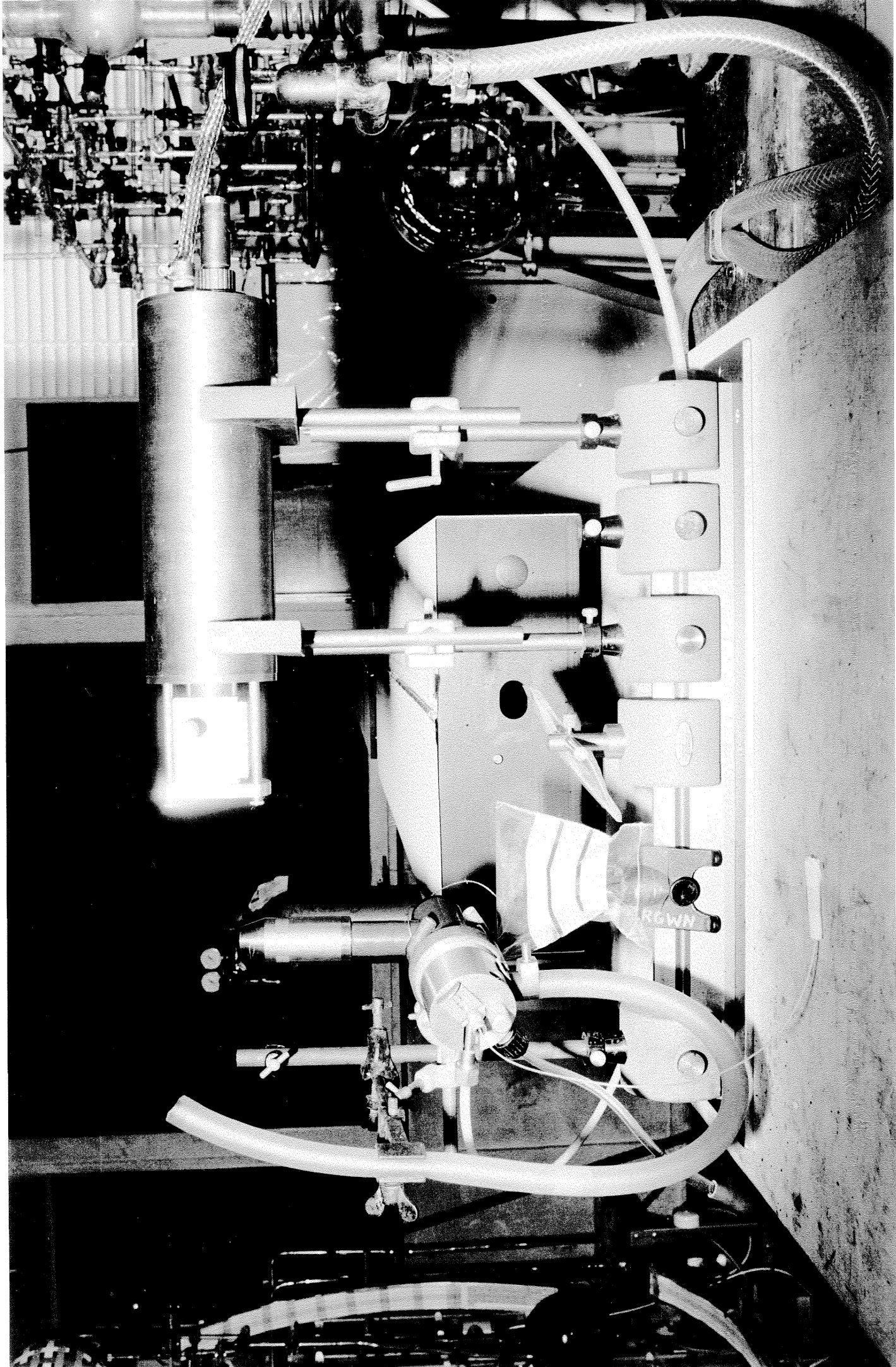View of nebuliser, monochromator and photomultiplier detection system.

FIGURE 8(b)

View of nebuliser and air-acetylene flame system, monochromator and photomultiplier detection system.
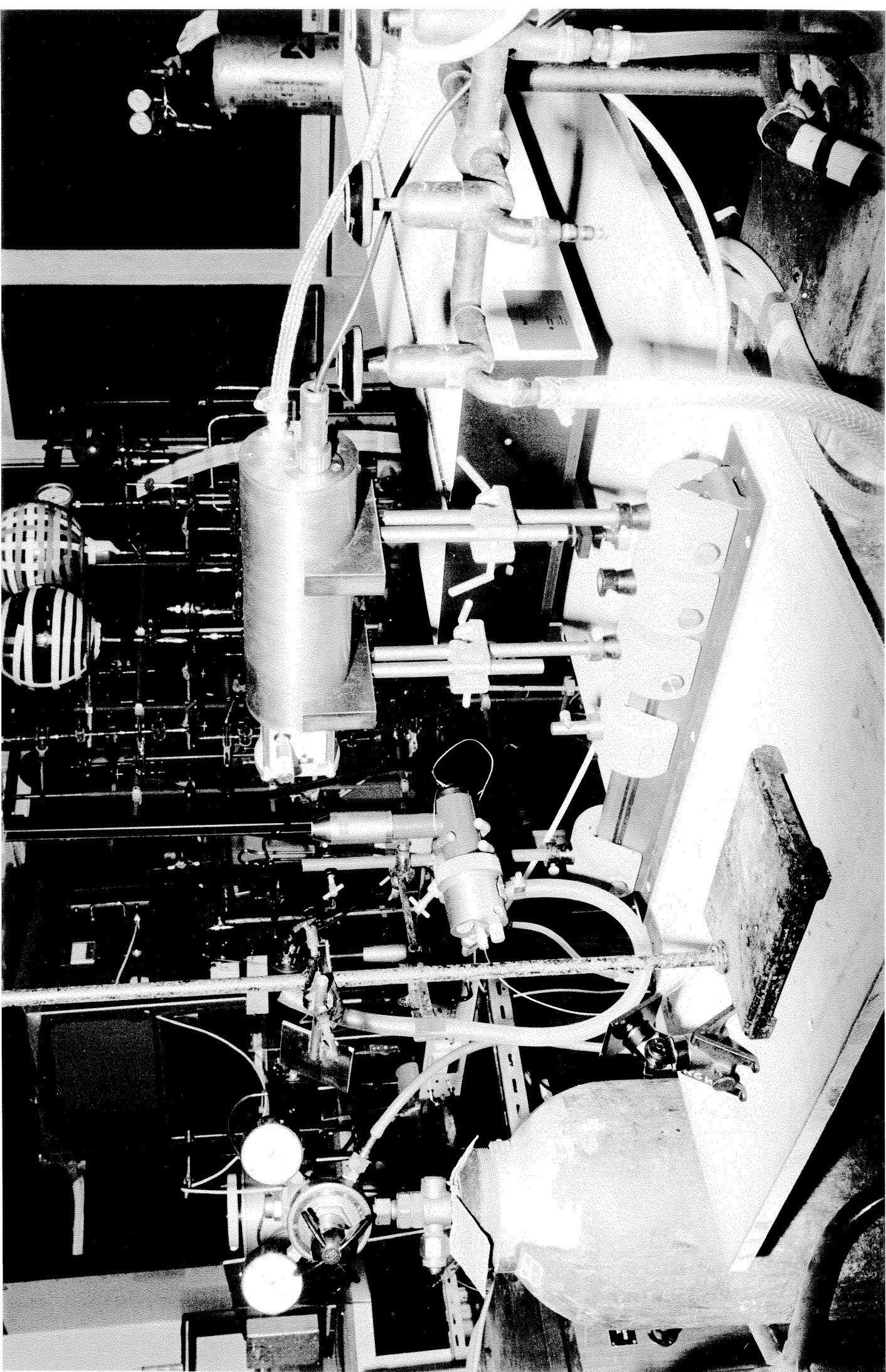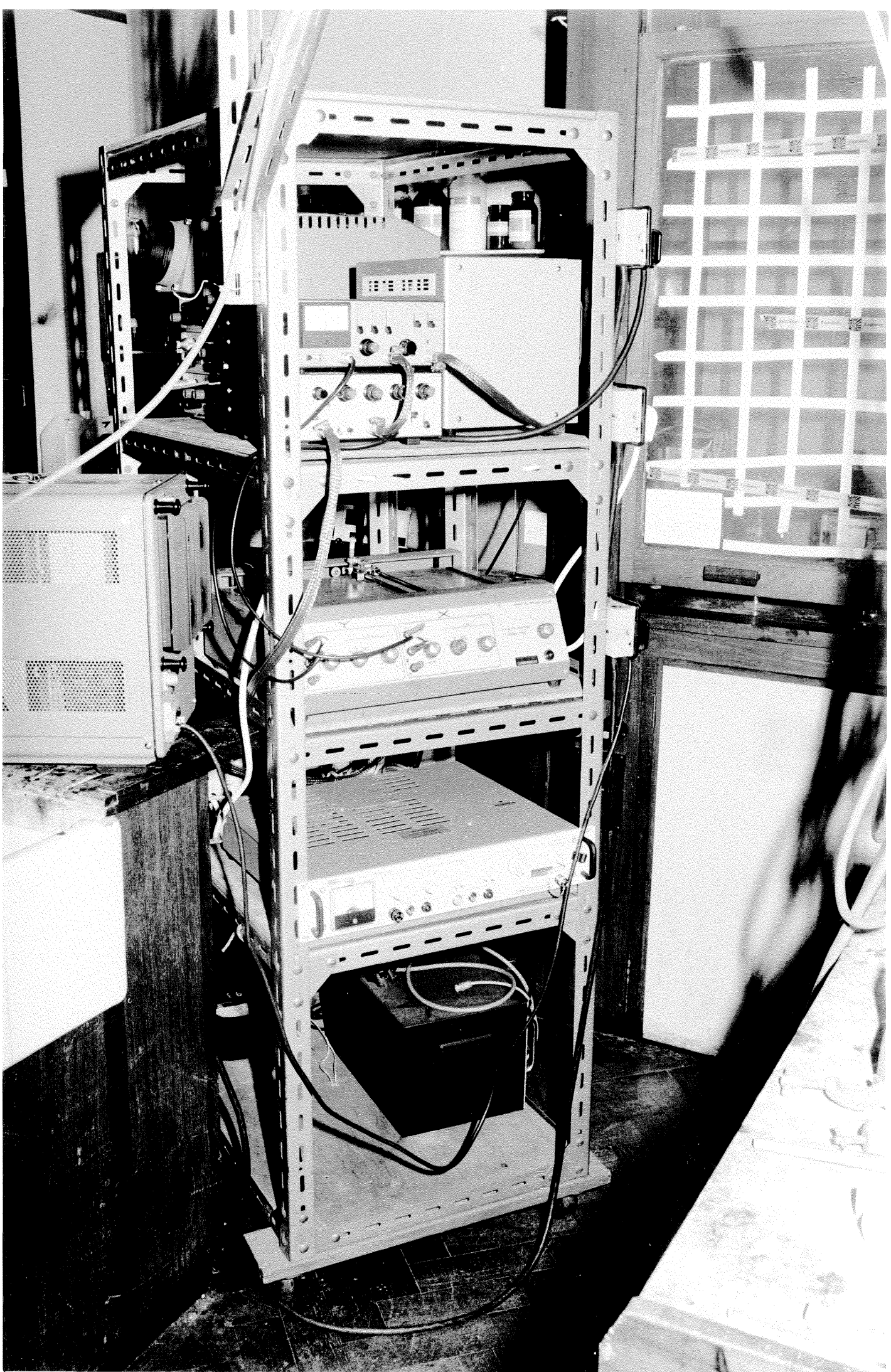
FIGURE 9

Electronic units employed in the dye laser studies including the current-to-voltage-converter, the Boxcar integrator, the XY-recorder and the osciloscopes for visual display.

6. PRESENT STAGE OF THE EXPERIMENTS

This brief chapter is to indicate the stage of experimental development achieved so far and to outline the nature of the measurements to be carried out in the near future. Clearly, it will be necessary to modify any plans in the light of the future results arising from the initial measurements, in particular the magnitude of the signals and the effect of scattered light, especially for the experiments involving the detection of $(^3P-^1S_0)$ forbidden emission referred to previously.

During this first year, the apparatus described earlier was built, assembled and tested. The complexity of the system is evident from the Figures and several parts of the equipment had to be designed and specially constructed to meet specific requirements (e.g., the reaction vessel, furnace, gas handling system). Once completed and tested, the first step was the tuning of the dye laser, in order to start the kinetic study of Mg atoms. Whilst the order of study of these atoms is not critical, it was decided to start with the least reactive of the three elements whose kinetic properties are to be investigated. Following this, the kinetic behaviour of the ^3P states of Ca and then Sr will be investigated.

The initial tuning of the laser was made with the help of an air-acetylene burner coupled to a nebuliser (PYE Unicam). The experimental arrangements are shown in the photographs presented earlier. An aqueous solution of $MgCl_2$ was used in the nebuliser in order to generate free Mg atoms in the flame. The presence of Mg in the flame was initially detected by observing the light emission signal due to the transition $(^1P_1-^1S_0)$ at $\lambda = 285.2$ nm. The Mg in the flame was excited by the laser allowing a fine tuning to be made. The fluorescence signal from the transition $(^3P-^1S_0)$ at $\lambda = 457.1$ nm was isolated using the monochromator whose wavelength readings on the drum had been previously calibrated by means of known atomic lines from a spectroscopic lamp.

The initial laser tuning procedure with the nebuliser system indicates that the system may be applied to the study of Mg atoms, generated from a flow over the heated metal. Inspection from vapour pressure data and, indeed, from previous published work, indicates that suitably high pressures for optical pumping to the ^{3}P state can be achieved using temperatures in the region of T= 800 K. The initial experiments will involve helium buffer gas in the flow as this species would be expected to be characterised by a very low collisional deactivation cross section. The principal function of this buffer gas is to prevent significant diffusional rate of the ^{3}P atoms generated out of the optical collection volume. Sensible total pressures of helium that will be used can readily be seen from rough inspection of the "long-time" solution of the diffusion equation, using a reasonable estimate for the diffusion coeficient for the atom.

Tables 1 and 2 constitutes a summary of present collisional rate data for the ^{3}P atomic states of Mg, Ca and Sr. Clearly, the majority of data concerns the magnesium atoms.

TABLE 1

Rate constants for the collisional quenching of
$Mg(^3P_J)$ by various gases (k, $cm^3molecule^{-1}sec^{-1}$)

Quenching gas	Blickensderfer et al[36]	Taieb et al[29]
H_2	9.13×10^{-13}	1.05×10^{-13}
N_2	4.15×10^{-13}	7.14×10^{-13}
O_2		2.99×10^{-11}
He	$<6.64 \times 10^{-17}$	
N_2O		2.45×10^{-11}
CO	9.96×10^{-13}	1.99×10^{-12}
CO_2		1.20×10^{-11}
CH_4	2.76×10^{-14}	
C_2H_2		2.99×10^{-11}
C_2H_4	3.44×10^{-11}	
C_6H_6	1.13×10^{-10}	

TABLE 2

Total collision cross sections (in Å^2) for the removal of $Mg(^3P)$, $Ca(^3P)$ and $Sr(^3P)$ by halogen molecules

Reaction	$\sigma_T(\text{Å}^2)$	Reference
$Mg(^3P) + F_2$	56	Kowalski et al[32]
	84	Engelke[42]
$Mg(^3P) + Cl_2$	77	Kowalski et al[32]
$Ca(^3P) + Cl_2$	96	Kowalski et al[32]
	124	Telle et al[41]
$Sr(^3P) + Cl_2$	180	Kowalski[35]

The first studies will be concerned with the collisional quenching of $Mg(^3P)$ with non-reactive gases indicated in Table 1 in order to test the system as a kinetic tool. Clearly, one may extend the range of gases to other species such as the noble gases, spherical molecules such as CF_4 and SF_6 and also reactant gases such as halogens. A limited body of data with the halogens have been reported hitherto, as seen in Table 2 and it is proposed to extend these measurements to cover the range of the ^3P states of the Group IIA elements with all the halogens. Apart from collisional quenching of $Mg(^3P)$, given that some of the noble gases, especially He, will not be expected to be characterised by efficient quenching processes, in the absence of a curve crossing mechanism for such species, it is hoped that the decays will yield data on diffusion coefficients themselves. Of course, ideally, this would require a detailed knowledge of the geometry of the system. At least, it could be possible to establish a diffusional component from a first-order kinetic contribution to decay with the reciprocal of the total pressure. Clearly, it will always be necessary to account for the component due to spontaneous emission as indicated in the rate equations presented earlier in this dissertation. In overall terms, the use of the monochromator enables studies to be made on electronically excited product states, of which MgO, which has been mentioned, would be an obvious first example.

Having extended the measurements on $Mg(^3P)$ as indicated and compared data with those derived previously, it is proposed that extensive investigations be applied to Ca and $Sr(^3P)$. Similar considerations to

those presented for $Mg(^3P)$ will apply. Thus, having derived absolute collisional rate data for these atomic states with a range of collisional partners, the result will be considered within the context of the symmetry of potential surfaces described generally, earlier in this dissertation.

7. REFERENCES

1 - J.G. Calvert, J.N. Pitts, Photochemistry, Wiley, New York, 1966

2 - R.J. Donovan, D. Husain, Chem. Rev., 70(1970)489

3 - D. Husain, R.J. Donovan, Advances in Photochemistry, 8(1971)1

4 - R.J. Donovan, D. Husain, Ann. Reports(A), 68(1971)123

5 - R.J. Donovan, D. Husain, L.J. Kirsch, Ann. Reports(A), 69(1972)19

6 - D. Husain, Ber. Bunsen. Ges., 81(1977)168

7 - J.H. Kolts, D.W. Setser, Reactive Intermediates in the Gas Phase, Ed. D.W. Setser, Chap. 3, pg.190, Academic Press, 1979

8 - R.J. Donovan, H.M. Gillespie, Specialist Periodical Reports, Reaction Kinetics, 1(1975)14

9 - D. Husain, J.G.F. Littler, Int. J. Chem. Kinetics, 6(1974)61

10 - R.F. Heidner III, D. Husain, J.R. Wiesenfield, J. Chem. Soc. Faraday II, 69(1973)927

11 - D. Husain, N.K.H. Slater, J. Chem. Soc. Faraday II, 76(1980)606

12 - D. Husain, N.K.H. Slater, J. Chem. Soc. Faraday II, 74(1978)1627

13 - D. Husain, N.K.H. Slater, J. Chem. Soc. Faraday II, 74(1978)1222

14 - D. Husain, L. Krause, N.K.H. Slater, J. Chem. Soc. Faraday II, 73(1977)1706

15 - D. Husain, L. Krause, N.K.H. Slater, J. Chem. Soc. Faraday II, 73(1977)1678

16 - R.H. Strain, J. McLean, R.J. Donovan, Chem. Phys. Letters, 20(1973)504

17 - R.A. Young, G. Black, T.G. Slanger, J. Chem. Physics, 48(1968)2067 ; 49(1969)4769

18 - J.A. Davidson, C.M. Sadowski, H.I. Schiff, G.E. Street, C.J. Howard D.A. Jennings, A.L. Schmeltekopf, J. Chem. Phys., 64(1976)57

19 - E.W. Abrahanson, L.J. Andrews, D. Husain, J.R. Wiesenfield, J. Chem. Soc. Faraday II, 68(1972)48

20 - G.C. Pimentel, Sci. Amer., 214(1966)32

21 - D. Husain, J.R. Wiesenfield, Trans. Faraday Soc., 63(1967)1349

22 - M.F. Golde, Gas Kinetics and Energy Transfer - Specialist Periodical Reports, Ed. P.G. Ashmore and R.J. Donovan, 2(1977)123

23 - I.W.M. Smith, Physical Chemistry of Fast Reactions, Vol2, Plenum, New York, 1980

24 - K.E. Shuler, J. Chem. Phys., 21(1953)624

25 - K. Schoefield, J. Phys. Chem. Ref. Data, 8(1979)723

26 - Nat. Bur. Stand. Circular 467, "Atomic Energy Levels",
   (U.S. Department of Commerce), Ed. C.E. Moore (1958)

27 - C.H. Corliss and W.R. Bozman, "Experimental transition
   probabilities of spectral lines of seventy elements",
   Nat. Bur. Stand. (U.S. Department of Commerce), Monograph 53(1962)

28 - J.J. Wright, J.F. Dawson, L.C. Balling, Phys. Rev., A9(1974)83

29 - G. Taieb, H.P. Broida, J. Chem. Phys., 65(1976)2914

30 - D.J. Benard, W.D. Slafer, P.H. Lee,
   Chem. Phys Letters, 43(1976)69

31 - D.J. Benard, P.J. Love, W.D. Slafer,
   Chem. Phys. Letters, 48(1977)321

32 - A. Kowalski, M. Menzinger, Chem. Phys. Letters, 78(1981)461

33 - U. Brinkmann, H. Telle, J. Phys., B10(1977)133

34 - U. Brinkmann, V.H. Schmidt, H. Telle
   Chem. Phys. Letters, 73(1980)530

35 - A. Kowalski, Z. Naturforsch., 34a(1979)459

36 - R.P. Blickensderfer, W.H. Breckenridge, D.S. Moore,
   J. Chem. Phys., 63(1975)3681

37 - T.J. McIlrath, Appl. Phys. Letters, 15(1969)41

38 - R.J. Mallins, D.J. Benard, Chem. Phys. Letters, 74(1980)321

39 - R.W. Solarz, S.A. Johnson, R.K. Preston,
   Chem. Phys. Letters, 57(1978)514

40 - D. Husain, P.E. Norris, J. Chem. Soc. Faraday II, 73(1977)415

41 - H. Telle, U. Brinkmann, Mol. Phys., 39(1980)361

42 - F. Engelke, Chem. Phys., 44(1979)213