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 (ایقبال)

Hew out a way of your own with your own axe
 It is downright damnation to tread the beaten track.
 If you do something really unique, it becomes a virtue
 even if it is a sin.

IQBAL

SPECTROSCOPIC STUDIES OF ATOMS AND MOLECULES

USING SYNCHROTRON RADIATION

by

MOHAMMAD ASLAM BAIG
M.Sc., M.Phil.

A Thesis submitted for the degree of
Doctor of Philosophy
in the
University of London

Department of Physics
Blackett Laboratory
Imperial College of Science and Technology
London S.W.7.

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ABSTRACT

The absorption spectra of several atoms and molecules have been investigated in the region 700-2000 Å in the first order of a 1m normal incidence vacuum spectrograph equipped with a 1200 $\text{\AA}/\text{mm}$ grating, using synchrotron radiation as the background continuum source. In atoms, the spectra of Mg I, Ca I and Sr I due to simultaneous excitation of both the valence electrons have been recorded. Rydberg series converging on the $3p\ ^2P_{1/2,3/2}$ in Mg I, $4p\ ^2P_{1/2,3/2}$ in Ca I and $5p\ ^2P_{1/2,3/2}$ limits in Sr I have been observed. Single excitation spectra above the first ionization potential, 3d-subshell excitation in Mn I, 4d-subshell excitation in Ag I and 5d-subshell excitation of Au I have been observed for the first time and the experimental results are compared with ab initio Hartree-Fock calculations.

The molecular spectra of Si O, Ge O, Al F, P₂ and PN have been observed. In the spectrum of Si O, Rydberg series converging on the ground state of the ion have been found yielding a more accurate value of the first ionization potential. Another Rydberg series has been detected, above the first ionization threshold converging on the $B^2\ \Sigma^+$ state of Si O⁺. In the spectrum of the Ge O molecule we have identified Rydberg series converging on the $X^2\ \Sigma^+$ state of Ge O⁺ which gives a more reliable value for the first ionization potential of Ge O. The spectra of Al F have been generated using different techniques than employed by previous investigators and numerous new bands have been found. There is a clear evidence of the existence of the Rydberg series but a detailed analysis was not performed because of the low resolution available to us. The spectra of the PN and P₂ molecule have been recorded by the thermal decomposition of P₃N₅ and weak features arrangeable into Rydberg series are attributed to the PN molecule. It is suggested that such observations could be extended into the X-ray region in order to observe inner shell excitation, if absorption columns of adequate vapour density can be produced.

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CHAPTER I

GENERAL INTRODUCTION

1.1 Introduction

Currently, vacuum ultraviolet spectroscopy of atoms and molecules is attracting much interest because significant departures from the Independent Particle model have been found. In addition, certain phenomena occur in this part of the spectrum which can be understood within the broad framework of the Independent Particle model but which, nevertheless, reveal the importance of electron-electron correlations, viz. autoionization, predissociation and simultaneous excitation and/or ionization of two or more electrons.

With a photon of energy 10-100 eV, one breaks into the sub-valence shells of the atom. The excitation of the valence electron, in the visible ultraviolet region, and the excitation of the inner shell electrons, in the X-ray region, can be very well represented by the independent/quasi particle model. It has been realised that new models are needed to describe photoexcitation at wavelengths which correspond to the binding energies of the inner valence shell.

Beutler (1933) carried out pioneer work on the vacuum ultraviolet absorption spectra of many elements and noble gases in the region 600-1200 Å, observing many well developed Rydberg series belonging to the normal arc spectrum converging on the ground state of the ion together with Rydberg series converging on the excited states of the ion. Beutler (1935) discovered several autoionizing Rydberg series between the levels of the $2P^0$ ground state of the ion in the noble gases. The spectra of noble gases have been extensively studied by Madden and Codling (1965) using synchrotron radiation as the background continuum. Madden and Codling (1965) observed not only the single excitation from the inner shell but also the double

excitation involving one electron from the inner shell and one from the outer shell, or both electrons from the same shell. The absorption spectrum of a neutral atom contains numerous Rydberg series of lines whose convergence limits correspond to the various excited states of the residual positive ion. All the lines of these series lie above the lowest ionization limit, therefore they correspond to transitions of the atom from its ground state to discrete excited states which are stationary only in an independent electron approximation. The configuration mixing or interchannel interaction cause these discrete states to autoionize into the continuum. Some of these excited states differ from the ground state of the ion by having a vacancy in an inner shell or subshell rather than in the outer subshell; they represent the thresholds for photoionization of an inner electron.

1.2 Independent Particle Model

To describe the electron states in an atom, one proceeds from the assumption, (central field approximation) that each of the atomic electrons moves in a spherically symmetric potential energy $U(r)$ that is produced by the nucleus and all the other electrons. The potential energy, $U(r)$ for a neutral atom has the Coulomb form $-e^2/r$ at a greater distance r from the nucleus, since the removal of the electron whose potential is being measured leaves a singly charged positive ion. The Schrödinger equation for an electron in an arbitrary centrally symmetric field $U(r)$ has the form

$$\nabla^2 \Psi + \frac{2m}{\hbar^2} [E - U(r)] \Psi = 0$$

This equation differs from the Schrödinger equation for the hydrogen atom only in that the arbitrary potential $U(r)$ appears here instead of the Coulomb potential $-e^2/r$. The angular momentum is conserved during motion in an arbitrary centrally symmetric field, therefore

each stationary state can be characterized by the assignment of the quantum numbers ℓ and m . The wavefunctions for stationary states have the form

$$\Psi = R(r) Y_{\ell m}(\theta \phi)$$

where $Y_{\ell m}(\theta \phi)$ are spherical functions and the radial part of the function $R(r)$ is defined by the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{\ell(\ell+1)}{r^2} R + \frac{2m}{\hbar^2} [E - U(r)] R = 0$$

This equation has finite and continuous solution only for definite values of E . The set of these values determines those possible energy values which a particle may have for motion in the given field

The effective potential energy in the above equation:

$$U_{\ell}(r) = U(r) + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2}$$

contains ℓ , but does not depend on m . Thus the levels are degenerate with respect to m . The character of the motion of a particle in a centrally symmetric field is completely determined by the values of E , ℓ and m . There do not exist two different wavefunctions Ψ corresponding to one and the same set of numbers E , ℓ and m . (excluding spin).

In the independent particle model, it is assumed that the photon is absorbed by one electron in the $n\ell$ th subshell of the atom. This electron is then excited into the discrete state (photoabsorption) and into the continuum state (photoionization). The relaxation of the remaining electrons is neglected and consequently the photoionization process reduces to a one electron problem. This model has been extensively used by Manson and Cooper (1963), Combet Farnoux (1967), McGuire (1967) who chose Herman and Skillman (1963) potential as $U(r)$. Their calculations allowed them to point out the existence of important features in the spectra over a large scale of elements and a relatively

broad energy range: (i) existence of a Cooper minimum in the cross section when an electron is ionized from a subshell with at least one node, (ii) the cross section relative to an np subshell often shows a decreasing behaviour from the threshold up to the Cooper minimum because of a potential barrier which keeps far out the low energy continuum states.

Hartree (1957) developed the self-consistent field method and it was assumed that each electron in a multi-electron atom is described by its own single electron wavefunction. The potential experienced by a particular electron is due to the nucleus and the remaining $(n-1)$ electrons. The part of the potential due to the remaining electrons is expressed in terms of their radial wavefunctions. Similar equations can be set up for each of the n -electrons. The radial wavefunctions generated by the solutions of these equations are used to produce a better approximation to the potential, which in turn is used to produce better wavefunctions. This process is continued until self-consistency is obtained.

This simple one electron model is expected to breakdown in the soft X-ray region for the following reason. It assumes that electrons in the various subshells of an atom can be adequately described as moving in a screened Coulomb field. This assumption is expected to be valid only for the innermost subshell. At photon energies large compared to the binding energy of a single electron in the subshell, two electron processes make a contribution to the total absorption which suggests that electron-electron correlation should also be considered.

1.3 Delayed Onset Effect

It was discovered that the continuous absorption cross section, which had always been thought of as decreasing uniformly with increasing

photon energy after the initial rise just above the threshold, can exhibit peaks many eV higher than threshold, while the absorption just above the threshold is very small. This effect was described as the 'delayed onset' of continuous absorption. An explanation, in terms of the independent particle model, was provided by Cooper (1964) who pointed out the importance of the angular momentum potential barrier for the outgoing ($\ell = 3$) electron. The effect of the $\ell(\ell+1)\hbar^2/2m_e r^2$ term in the Schrodinger equation, which is the analogue of the centrifugal potential in classical mechanics, tends to keep electrons away from the core. At threshold, the continuum function hardly penetrates the core, and the spatial overlap between the initial and final state function is very small. As the kinetic energy of the outgoing electron increases, its ability to penetrate the barrier increases also and the overlap becomes larger. This continues until the negative part of the continuum function overlaps the core function, when phase cancellation sets in and the overlap integral falls off. Since the photoionization cross section is proportional to the square of the overlap integral, we have a simple explanation of the delayed onset effect within the independent particle model.

In the case of heavy elements, two absorption maxima can occur, Combet Farnoux (1969), Connerade et al. (1973,1975,1976) owing to superposition of the $4f \rightarrow d$ and $4f \rightarrow g$ channels, both of which exhibit delayed onset, peaking at different energies above threshold.

1.4 Wavefunction Collapse

Wavefunction collapse is a term used to describe the sudden transfer of a wavefunction from the outer valley to the inner valley of a double valley potential when a relatively small change in the potential occurs.

The effective potential

$$V_{\text{eff}}(r) = V_{\text{coulomb}}(r) + \frac{\ell(\ell+1)\hbar^2}{2m_e r^2}$$

for a given atom must be established by a calculation and it may differ significantly for different configurations of the same atom. Supposing that $V_{\text{eff}}(r)$ has a double valley, we may interpret this as follows. Starting from large r and moving inwards towards the nucleus, the outer valley, where the potential is dominated by the Coulomb term for the $(z-1)$ electrons in the field of which an outer electron moves. As we proceed further inwards, the repulsive centrifugal term $\ell(\ell+1)\hbar^2/2m_e r^2$ takes over and V_{eff} rises quite steeply. We then begin to penetrate the atom and screening drops sharply, so that the electron is exposed to a much stronger nuclear field. However, because of the fast increase of the $1/r^2$ dependence at small r , the repulsive term takes over again and dominates $V_{\text{eff}}(r)$.

If we now produce a core hole inside the atom, the situation becomes even more interesting, because the atom tends to resemble the next adjacent element in the periodic table. Wavefunction collapse may not occur in the groundstate but it may occur in the core excited state because the radial potential is different.

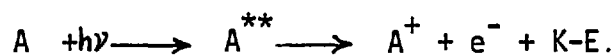
1.5 Configuration Mixing

According to the independent particle approximation, the electronic states of atoms and molecules are usually classified as belonging to various configurations. The energy levels of the same parity and J -value arising from two (or more) close or overlapping configurations appear to exert influences on each other. These influences are generally termed perturbations and are usually revealed by energy level shifts from the expected positions and line intensity and shape anomalies. An explanation of these effects may be

formulated in terms of configuration mixing: the wavefunction of an atomic state is considered as a linear combination of the wavefunctions of states of idealised configurations. The apparent breakdown of the simple selection rules and the asymmetric broadening of certain absorption lines may be attributed to the mixing of different configurations. Garton and Codling (1960) reported the absorption spectra of alkaline earths, observing Rydberg series due to simultaneous excitation of both valence electrons, which are due to the configuration mixing in the ground state.

1.6 Autoionization

The interaction of a photon having energy greater than the first ionization potential of an atom or molecule causes photoionization. When the energy of the incoming photon is sufficient to excite a high lying discrete state (due either to the excitation of an inner electron or to the simultaneous excitation of two electrons), the atom or molecule is promoted into a quasi-stable state lying above the first ionization threshold and this excited state undergoes radiationless decay into the adjacent continuum leaving a free electron and a positive ion. This phenomenon is termed autoionization and the excitation process can be represented as



where A is the target atom in the ground state, $h\nu$ is the incident photon energy, A^{**} is the excited state of the ion, A^{+} is the resultant ion in the ground state, e^{-} is the ejected electron and $K-E$ is the kinetic energy of the electron.

Autoionization may occur when the wavefunction of a discrete energy level mixes with that of a continuum of states arising from a configuration of the same parity and J-value and of equal energy. Absorption transitions to this mixed state exhibit properties of

both the discrete level and the continuum in that resulting broadened absorption lines are found. A detailed consideration of the interaction of a discrete level with a continuum has been given by Fano (1961) who was able to explain why such absorption lines are often asymmetric. It was pointed out that autoionized levels manifest themselves in continuous absorption spectra as very asymmetric peaks because, in the mixing of configurations to form a stationary state of energy E , the coefficients vary sharply when E passes through an autoionized level. This remark accounted qualitatively for the character of rare gas spectra in the range between the two ionization thresholds corresponding to the doubled $^2P_{1/2}$ and $^2P_{3/2}$ ground state of rare gas ions.

When an atom is in an autoionizing state it is energetically possible for it to decay spontaneously into an ion plus a free electron. The probability of this process depends on the strength of the interaction between the configurations involved. Autoionizing levels usually have much shorter lifetimes than other levels of comparable excitations. As a result of this short lifetime, typically 10^{-13} - 10^{-14} , the intensity of emission lines arising from the autoionizing level become so low as to become practically unobservable. This weakening does not arise in observing optical absorption spectra since the absorption intensity depends only on the population of the lower level and the oscillator strength. Autoionizing resonances occur in absorption measurements as discrete structure superimposed on the direct photoionization continuum. In the autoionization region, the absorption lines have a sharp 'edge' in the centre, and degrade slowly on both sides. Fano's theory (1961) indicates that in the case of an absorption line having an upper level which can find only one continuum for autoionization, the absorption cross section should actually vanish locally on one or other side of the line.

In the simplest of the configuration interactions involving a discrete state and a single continuum, the absorption cross section in the region of a resonance varies according to the relationship; Fano and Cooper (1965)

$$\sigma = \sigma_A \frac{(q + \epsilon)^2}{1 - \epsilon^2} + \sigma_B$$

where

$$\epsilon = \frac{E - E_r}{\frac{1}{2} \Gamma}$$

E_r is the resonance energy, Γ is the resonance width, q is the line profile index and defines the line shape and σ_A and σ_B represent two portions of the cross section corresponding to transitions to states of the continuum that do and do not interact with the discrete autoionizing state. Fano and Cooper (1965) introduced another parameter ' ρ ', the so-called autoionization to dipole correlation coefficient or overlap integral, relating to σ_A and σ_B in the relationship

$$\rho^2 = \frac{\sigma_A}{\sigma_A + \sigma_B}$$

The overlap involved is that between the final state continuum wavefunction reached via the autoionization process and that reached by the direct photoionization process. An alternative parametrization has been given by Shore (1967). Further extensions to the analysis have been made by Mies (1968) in which interaction between adjacent discrete terms via their underlying continua have added to the understanding of the cross section variation through complex autoionization features. The example of resonances are found in the pioneering work of Madden and Codling (1963) on He where the Rydberg resonance series converging onto the $n=2$ He^+ threshold were found.

1.7 Double Excitation Process

The simultaneous excitation or ionization of two or more electrons is a direct consequence of electron correlation. The effects which

made the main contribution to double excitation/ionization are: core relaxation, ground state correlation and virtual Auger processes.

In a simple model, when a high energy photon interacts with an atom, all the energy is converted into ejection of a single electron. After the removal of this single electron from one of the shells of the atom, there is a change in the effective charge experienced by all the other electrons which can lead to the simultaneous excitation or ejection of another electron. On this basis the two electron process can be decomposed into two sequential one-electron steps: first, ionization of one electron, followed by either excitation (shake-up) or ionization (shake-off) of another. It has been argued that the 'shake-up' and 'shake-off' picture is entirely equivalent to configuration mixing in the ground and excited states. The shake-up and shake-off model is more commonly used in connection with X-ray and photoelectron spectroscopy, while the configuration mixing approach is more familiar to optical spectroscopists. The shake theory is based on the sudden approximation which assumes that if there is an instantaneous change in the Hamiltonian of the atom from the initial state to the final state, the time dependent wavefunction describing the electron in the atom is made up of the overlap integral of wavefunction for the initial state and wavefunction for the various possible final stationary states.

When an inner shell electron is excited, the Auger process is also important: in Auger emission, the incident photon ejects an electron from the inner shell, an outer electron then fills this vacancy and a second electron is ejected to conserve energy. The kinetic energies of the two ejected electrons can be measured by photoelectron spectroscopy. It is important to distinguish between double ionization caused by the core-relaxation and Auger process, because

the final result of both processes is a doubly charged ion, in a particular state, and two free electrons. In core-relaxation, the excess energy following double ionization is distributed randomly between the two electrons. Therefore, even if the incoming photon energy and final ionic state are known, one cannot calculate the kinetic energy with which each electron will be ejected. However, in the case of Auger decay, the knowledge of the intermediate and final ionic states and the incoming photon energy allows exact calculation of the kinetic energy of each ejected electron.

Double excitations have been observed in the photoabsorption spectra of noble gases and of the alkaline earths. Most of the observations concern excitation of two valence electrons but some of them also involve inner shell electrons. These double excitations result from configuration mixing in the ground state. Ground state correlation is an important mechanism when the excitation involves electrons of the same shell and when that shell is a closed shell. Double excitation may occur due to configuration mixing in the excited state as has been described by Connerade (1978). Süzer et al. (1976) have observed the correlation satellites in atomic photoelectron spectra and have suggested that they could arise through initial state configuration interaction, final ionic state configuration interaction, continuum state configuration interaction or interchannel coupling. Connerade (1978) described two types of double excitations: Type 1 arises through mixing between parent ion configurations and the double excitations within these channels can be ordered into Rydberg series. Type 2, which arises through mixing after the Rydberg electron has been coupled to the ionic core. Since the excitation mechanism is not dependent on the mixing of a parent ion configuration, there can be two running electrons within a given

system. The ordering of double excitation into Rydberg series is therefore more complicated.

1.8 Aim of the Present Investigation

The purpose of the present work was to use the continuous radiation emitted by the 500 MeV electron accelerator in Bonn, to study double excitations in Mg I, Ca I and Sr I and inner shell excitations from the d-subshells in Ag I, Au I and Mn I and also to observe the spectra of simple diatomic molecules in the VUV region. These molecules, Si O, Ge O, Al F and PN have been observed in the ultraviolet but the most important region where Rydberg transitions were expected to occur was formerly unexploited. The Rydberg series yield an accurate and more reliable determination of the ionization potential.

CHAPTER II

EXPERIMENTAL PROCEDURE

2.1 Summary

The present investigation was carried out on the equipment installed at the 500 MeV electron accelerator at the Physikalisches Institut University of Bonn (F.R. Germany). This synchrotron radiation facility has been described by Connerade, Mansfield, Thimm and Tracy (1974) and, in this section, the various instruments and experimental techniques employed in photoabsorption studies are presented.

2.2 Historical Background

The absorption spectroscopy of atoms and molecules in the ultra-violet region was greatly stimulated by the development of emission continua of the rare gases, (Hopfield (1930), Tanaka et al. (1958), Huffmann et al. (1965)). All the rare gases emit continuous spectra with no structure except for a few emission lines which prove useful as internal wavelength standards. To excite the continua with useful intensity either a condensed or microwave discharge may be used. The main vacuum ultraviolet emission continua excited by condensed discharge are: the Hopfield emission continuum (Hopfield, 1930) extending from 600-1100 Å which is due to the transition from an upper stable molecular state of He_2 to the unstable ground state; Ne 744-1000 Å; Ar 1070-1650 Å; Kr 1250-1850 Å and Xe 1470-2250 Å which have a similar origin. When Argon, Krypton and Xenon are excited with a microwave discharge (2450 mc/sec) the continuum is more restricted in wavelength ranges: Ar 1060-1500 Å, Kr 1260-1700 Å and Xe 1500-2000 Å. One advantage of these microwave discharges is that they can be used in high orders of a long focal length concave grating spectrograph without any predisperser for order separation.

The molecular hydrogen continuum excited in a positive column

discharge extends from 1600 Å to 5000 Å. Below 1600 Å the "many line" molecular spectrum of hydrogen appears. The Lyman continuum (Lyman, 1924) is the only usable continuous emission which extends throughout the vacuum ultraviolet region with usable intensity in the region 900 Å to 7000 Å. The radiation is created by discharging a capacitor of about 0.5 uF through a low pressure gas enclosed in a glass capillary. This design had the disadvantages that the capillary was eroded rather rapidly and the continuous spectrum was overlaid by impurity emission lines. Garton (1954) eliminated these disadvantages by designing the so-called 'Garton flash tube' using wider bore tube to achieve the higher current density and reducing the duration of the flash to a microsecond by keeping the inductance of the circuit very low. A discharge of a few microfarads at 10 kV produces a continuum down to 300 Å. At still shorter wavelength the flash-tube continuum becomes a line spectrum which is very successfully used as a calibration source in the grazing incidence region (Radtke, 1979).

The most useful pulsed continuum source below 600 Å is the BRV source (Balloffet, Romand and Vodar, 1961) which covers the range from ultraviolet to soft X-rays. This source is designed with very low inductance to discharge the energy from a 0.1 uF capacitor charged to 25 kV in a very short time. The anode material is an element of high atomic number, the most successful being uranium or tungsten. Garton et al. (1969) modified this design and observed the absorption spectra of rare gases and metal vapours in the 100-600 Å wavelength range.

There are several disadvantages when the above mentioned continuum sources are used for photoabsorption experiments. Their spectral range is rather limited, emission lines can obscure weak features and reproducibility is poor, especially when they must be operated close to a furnace containing metal vapour.

The unique properties of synchrotron radiation are: continuous spectral distribution ranging from the radiowave up to the X-ray region, high intensity, superior to any other source in the vacuum ultraviolet and soft X-ray region i.e. from $\simeq 10$ eV to $\simeq 1000$ eV, high angular collimation confined to near the orbital plane and high degree of polarization.

2.3 Synchrotron Radiation

Electron synchrotron may be viewed as a human attempt to make an atom of very large size. According to classical theory of electromagnetism an electron on a circular orbit must radiate part of its energy and because of this radiated energy classical physics has failed in its description of the atom. The complete theory of orbital radiation was developed by Schott (1912) and Schwinger (1949) worked out the spectral distribution of the radiated power. The applications of synchrotron radiation have been reviewed by Codling (1973) and Marr (1976).

In the electron accelerator the electrons travel at relativistic velocities and the emitted radiation pattern is compressed into a narrow cone of half angle (formed by the axis tangent to the electron orbit and the side of the cone).

$$\theta_m \simeq \frac{1}{\gamma} = \frac{E_0}{E} = \frac{0.511}{E(\text{MeV})} \quad \sim \text{Typically milliradians.}$$

Here

$$\gamma = \frac{1}{[1 - v^2/c^2]^{1/2}} = \frac{E}{m_0 c^2}$$

where m_0 is the electron rest mass, v is the electron velocity and E is the electron energy.

From the above expression it is apparent that the angular divergence is a energy dependent parameter.

For an electron moving in a circular orbit the total energy lost to synchrotron radiation is

$$\delta E = \frac{4\pi}{3} \left(\frac{e^2}{R} \right) \gamma^4$$

thus $\delta E = 88.5 \frac{E^4(\text{GeV})}{R(\text{metres})}$ where $1 \text{ GeV} = 10^9 \text{ eV}$.

which implies that the radiation losses increase as the fourth power of the electron energy.

The instantaneous power radiated into all angles at a given wavelength is given by

$$\begin{aligned} I(\lambda) &= \left(\frac{3^{5/2}}{16\pi^2} \right) \left(\frac{e^2 c}{R^3} \right) \left(\frac{E}{m_0 c^2} \right)^7 G(\gamma) \\ &= 0.751 \frac{\{E(\text{GeV})\}^7}{\{R(\text{metres})\}^3} G(\gamma) \text{ erg sec}^{-1} \text{ \AA}^{-1} \end{aligned}$$

where $G(\gamma) = \gamma^3 \int_0^\infty K_{5/3}(\eta) d\eta$

and $K_{5/3}(\eta)$ is a modified Bessel function of order 5/3.

$$\gamma = \frac{4\pi R}{3\lambda} \left(\frac{m_0 c^2}{E} \right)^3 = \frac{\lambda_c}{\lambda}$$

Tomboulion and Hartman (1956) have shown that the critical wavelength is given by

$$\lambda_c = \frac{4\pi R}{3} \left(\frac{m_0 c^2}{E} \right)^3$$

λ_c is called the critical wavelength.

A more meaningful quantity is the wavelength at maximum intensity

(λ_m) which is related to λ_c by the formula $\lambda_m = 0.42 \lambda_c$.

A simple formula for λ_c and λ_m is given by:

$$\lambda_m(\text{\AA}) = \frac{2.35 R(\text{metres})}{\{E(\text{GeV})\}^3}$$

Synchrotron Radiation Spectral Intensity
Distribution of the 500 MeV Electron
Synchrotron

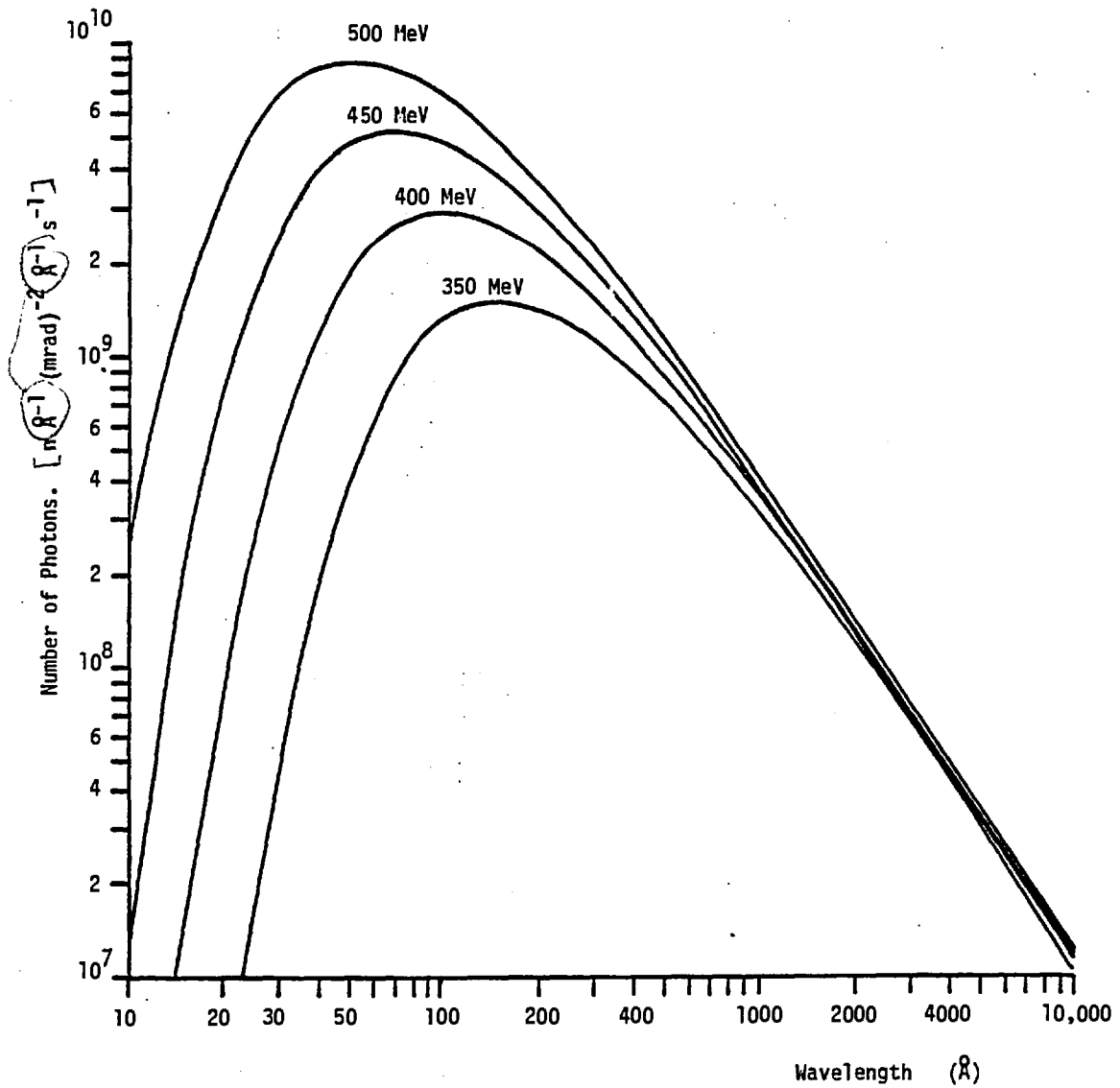


FIGURE 2.1 - Intensity distribution curve for the Bonn 500 MeV
 Electron Synchrotron.

$$\lambda_c(\text{\AA}) = \frac{5.59 R(\text{metres})}{\{E(\text{GeV})\}^3}$$

This wavelength is inversely proportional to the cube of the electron energy, the peak of the radiation shifts to shorter wavelength as E is increased.

2.4 Bonn Synchrotron Radiation Facility

In the Physikalisches Institut Der Universität Bonn, there are two electron accelerators:

- (i) 2.5 GeV having 7.65 m radius;
- (ii) 500 MeV having 1.7 m radius.

The calculated values for the peak intensity wavelength and critical wavelength are $\lambda_m = 1.15 \text{ \AA}$ and $\lambda_c = 2.7 \text{ \AA}$ for 2.5 GeV electron accelerator, which is a good soft X-ray source. The values for 500 MeV electron accelerator are: $\lambda_c = 76 \text{ \AA}$ and $\lambda_m = 32 \text{ \AA}$, which is a very good VUV source of radiation.

The present experiments were performed with the 500 MeV electron accelerator and Fig.(2.1) shows the intensity distribution curve at different energies. The peak intensity shifts towards shorter wavelength with increasing electron energies. This is most critical when working in the short wavelength region on the grazing incidence spectrograph, however it does not change much in the VUV region where our interest lies.

Fig.(2.2) shows a layout of the experiments designed for this facility. There are two main beams and one of them can be further used with the help of gold coated mirrors for three different beam lines I, II and III. On beam line I, a 1-m normal incidence spectrograph equipped with a 1200 ℓ/mm grating is installed, on beam line II a 2 m grazing incidence spectrograph, equipped with a 1200 ℓ/mm grating and on beam line III a 1 m Seya-Namioka spectrometer is installed,

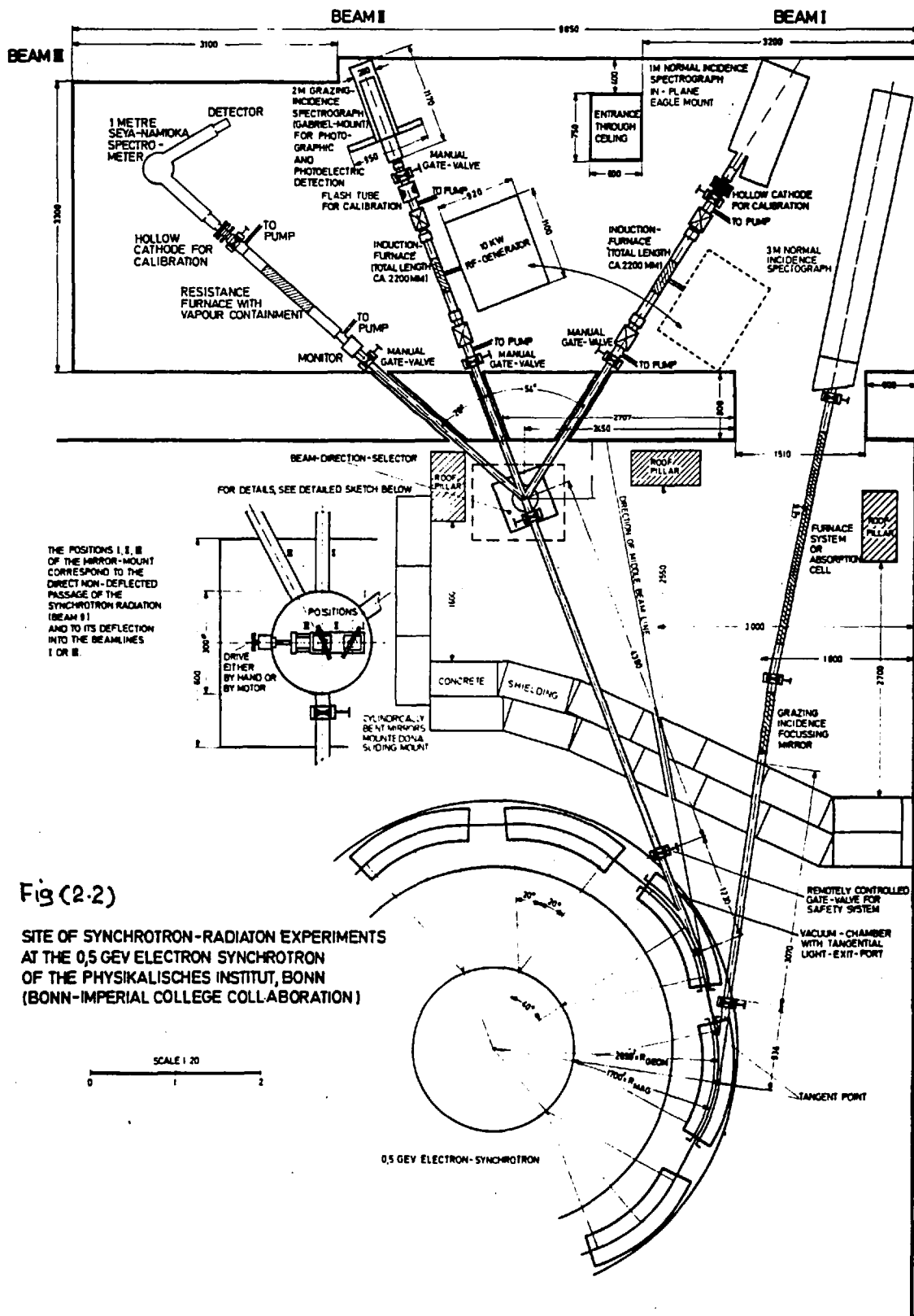


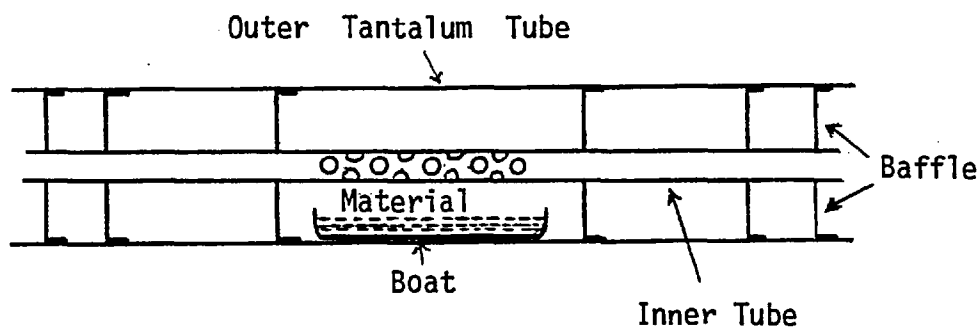
Fig (2-2)

SITE OF SYNCHROTRON-RADIATION EXPERIMENTS
AT THE 0.5 GEV ELECTRON SYNCHROTRON
OF THE PHYSIKALISCHES INSTITUT, BONN
(BONN-IMPERIAL COLLEGE COLLABORATION)

On the second beam line, a 3 m-normal incidence spectrograph, equipped with a 5000 ℓ/mm holographic grating has been installed which will be used to study the high resolution spectra of atoms and molecules.

2.5 Vapour Containment System

This system consists of two Tantalum tubes about 40 cm long. The outer tube is 0.3 mm thick and 15 mm inner diameter. The inner tube has 1 mm thickness and 4 mm inner diameter and contains holes in the middle which have a total area equal to the area of both ends of the tube. This tube is supported on six Tantalum baffles and the material is added in a small boat made of Tantalum or Tungsten which is kept in the middle of the tube. A typical layout of the system is shown below.

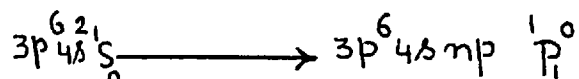


With this system a small amount of material is sufficient for several hours of experimentation. Before loading the material into the tube, the full system is inserted in the induction furnace and is heated to a temperature a little above the melting point of the material to be studied. This procedure served to remove practically all the impurities from the furnace tube.

This system has been very successfully used to study atomic photoabsorption spectra. We have also utilized this system to produce the column of molecular vapour. To study the Si O molecule, we mixed Si O₂ and Si O and heated it to a temperature of 1300°C. To check whether we were obtaining only Si O absorption we have photographed

the known band system of Si O in the u.v. region, Barrow and Rowlinson (1954). Secondly, heating Si O₂ to a higher temperature also gives the same band system which suggests that Si O₂ dissociates at higher temperatures and forms the Si O molecule.

To produce the vapour column of the Al F molecule, we have used a different method to that employed by previous investigators. We mixed Al + Mg F₂ and heated it to a temperature of 1200°C in the above mentioned vapour containment system. A chemical reaction takes place forming Al F + Mg. To check this reaction, we have rephotographed the well-known band systems of Al F and we have also found the principal series of the Mg atom



which suggests that the reaction indeed takes place as expected.

The spectra of the Ge O molecule was recorded by mixing Ge + Ge O₂ and heating it to a temperature of about 1100°C. In a similar way, we have detected some features of the PN molecule by the thermal decomposition of P₃N₅ into PN + P₂ + N₂.

The P₂ and N₂ molecular spectra are well known in this energy range and we have identified all the known band systems. The weak features are attributed to the PN molecule which has not been studied in this region before.

2.6 Clamshell Furnace

Two types of furnace were used to generate the atomic and molecular vapours. For low melting point elements a stainless steel tube was externally heated. The heating element was of Kantal wire mounted in a clamshell arrangement and insulated with ceramic and fibre glass wool. The maximum temperature achieved was up to 1000°C, which was estimated from the tube expansion (approximately 1mm for 100°C). The schematic drawing of the furnace is shown in Fig.(2.3).

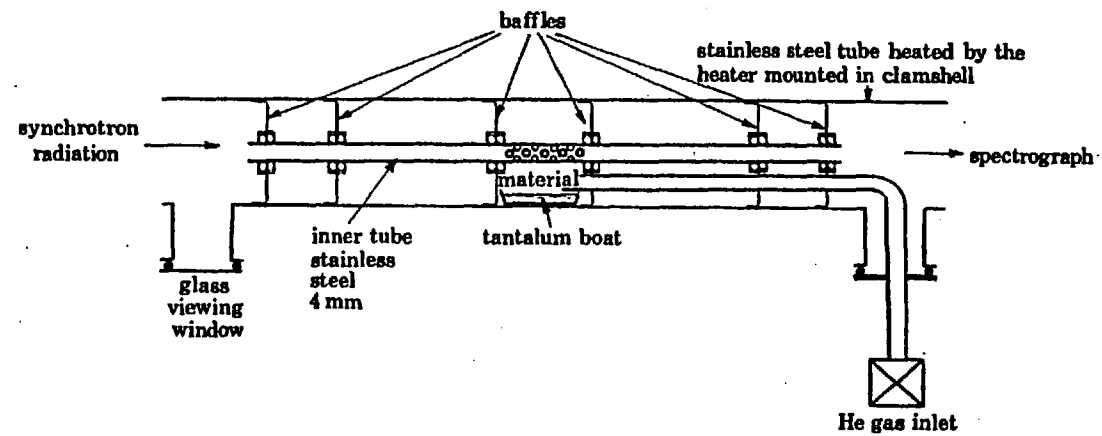


FIGURE (2.3) - Showing the schematic drawing of the clamshell furnace used in the present experiments.

The outer tube was 50 cm long with 2 mm wall thickness and 5 cm outer diameter. This furnace was equipped with the dynamic containment system described by Tracy (1975), and it was supported on six baffles. The inner tube was 40 cm long and 3 mm outer diameter with holes in the centre. About ten grams of spectroscopically pure sample, loaded in a boat, were sufficient for several hours of experimentation.

The furnace was heated using separate circuits for the centre and ends. The temperature at the ends of the furnace was kept higher than the middle to avoid the blockage of the inner tube. This windowless containment system was directly coupled to the vacuum of the accelerator. Water cooled baffles were used on both ends of the furnace with 8 mm inner diameter and 10 cm long fitted with NW40 Leybold flanges to couple with the furnace tube. The condensation of the metal vapour occurs on the outer portion of these water cooled baffles. A stable temperature was achieved by heating the furnace gradually over a period of one hour depending on the temperature desired.

2.7 Induction Furnace

For higher temperature elements, an induction furnace was used to record the spectra. The furnace design was based on the technique developed by Tomkins and Ercoli (1967) with slight modifications. Instead of only one current concentrator two aluminium water cooled current concentrators were employed with a single furnace tube 30 cm long. This arrangement, shown in Fig.(2.4), holds the centre of the furnace at an even temperature with two slightly hotter zones ≈ 5 cm from each end. The exact temperature profile is strongly dependent on the wall thickness of the Tantalum furnace tube. This furnace tube is supported on two Zirconia rings to isolate it from the radiation shields. Inside the furnace tube an inner liner Tantalum tube 30 cm long, 4 mm inner diameter supported on six Tantalum baffles was used.

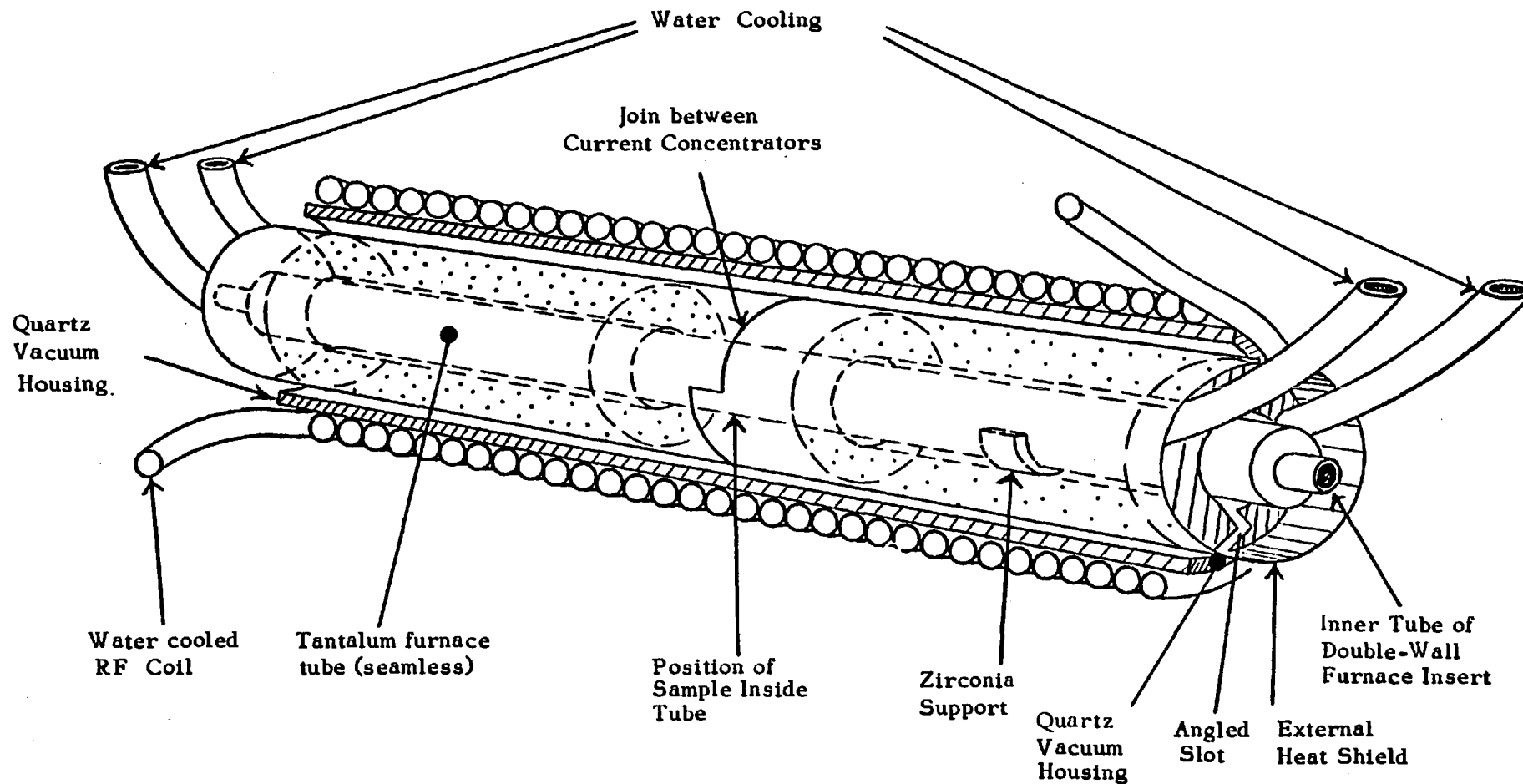


FIGURE (2.4) - Schematic drawing of the Induction Furnace assembly.

The sample material was loaded in a tantalum boat and was kept at the centre of the double wall furnace insert, and a slightly higher temperature was maintained on each side to improve the containment of the vapour.

Furnace tubes of tantalum or molybdenum of 0.1 and 0.3 mm wall thickness were used with a 500 kHz 10 kW oscillator (Radtke, 1975), and temperatures up to 2000°C were easily achieved.

The outer wall of the vacuum system is made of quartz and visible deposits of the material served as a useful indication that the central tube of the double wall containment system was filled with vapour.

An advantage of the R.F. induction heating is that the furnace tube is heated directly and has low thermal capacity. The temperature can be raised to the maximum value within one minute, and can also be lowered rapidly if the measurements are interrupted.

2.8 Spectrograph

The spectra were photographed in the first order of a 1 m normal incidence Eagle mounting vacuum spectrograph. The spectrograph was equipped with an Al F/Mg coated Bausch & Lomb grating with 1200 lines/mm blazed at 1500 Å.

The spectra were recorded using Ilford Q2 plates with exposure times ranging between 20-40 minutes. The plates were developed in D-19 developer for about 2 minutes.

2.9 Wavelength Standards

A hollow cathode type discharge tube 10 cm long and 8 mm inner diameter was used to calibrate the absorption spectra. The hollow cathode was placed on the axis between the synchrotron and the furnace system to avoid any line shift due to different illumination of the grating. After the hollow cathode another copper tube 10 cm long and 6 cm inner diameter was fixed in a stop in order to maintain a

relatively higher pressure in the hollow cathode section than the furnace system.

At a pressure of 300 microns of Ar/N₂ and 240 volts across the tube, the steady current was usually $\approx$ 300 mAmps yielding emission lines of Ar I, Ar II, N I, N II, C I, Ly α and Ly β . These are well known wavelength standards in the vacuum ultraviolet region (Elden, 1973). Typical exposure times required were about 2-3 minutes to superimpose the standards.

If the emission and absorption spectra illuminates different portions of the grating, one observes a small wavelength shift between these two spectra. To minimize this source of error, we have connected the hollow cathode discharge tube in front of the furnace system. Our furnace system has only 4 mm inner diameter. Light from the synchrotron must first pass through this hollow cathode (6 mm inner diameter), go through the furnace system and then fall on the slit of the spectrograph. This is possible only if the whole system is on the same axis and the light coming from the synchrotron and hollow cathode illuminates the same part of the grating.

A further check of the wavelength shift can be accomplished with our furnace system. Ly α at 1215 Å is always present in absorption spectra. It originates from atomic hydrogen produced when residual water vapour is reduced by the hot metal. As the intensity of this line is low, it is a very useful internal wavelength standard to check that emission and absorption spectra have been accurately superimposed.

CHAPTER III

DOUBLE EXCITATION IN Mg I, Ca I and Sr I

3.1 Summary

Absorption spectra of Mg I, Ca I and Sr I have been observed in the spectral region 700-2000 Å using synchrotron radiation as the background source. New data have been recorded due to simultaneous excitation of both the valence electrons: $3p\,ns,nd$ in Mg I, $4p\,ns,nd$ in Ca I and $5p\,ns,nd$ in Sr I. About 30 new levels in Mg I, 45 in Ca I and 60 in Sr I are reported.

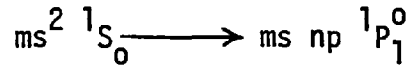
3.1.1 Introduction

The alkaline earths have ground state configurations $ms^2\,^1S_0$ with two valence electrons which move outside a closed shell surrounding the nucleus. The binding energy of these electrons is very low, therefore the ionization potentials are much lower than for the noble gases which have completely filled outer electronic shells. The ground state configuration ms^2 strongly mixes with the configuration mp^2 because the energy required for excitation within the same shell is very low. Therefore, a transition from the ground state to a state $mp\,ns$ or $mp\,nd$ may be regarded as single electron transition from the mp^2 component of the ground state. The configuration mixing with $(m-1)d^2$ is also very important. Therefore, double excitation in the alkaline earths can be attributed to a ground state interaction involving exchange of angular momentum between electrons.

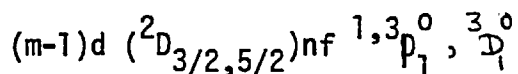
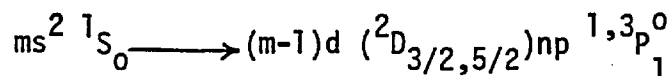
Due to the configuration interaction between singly excited states and states where both valence electrons are excited, the spectra of these atoms are very complex. The breakdown of Russell-Saunders coupling due to spin-orbit interaction further complicates the spectrum.

Considering first the excitation of a single electron from the

outer shell due to photoabsorption



one observes transitions to the odd parity $J=1$ levels from the even parity ground state. These transitions correspond to the principal series which converges on the ground level $^2S_{1/2}$ of the ion. These Rydberg series have been extensively studied, Brown et al. (1973), Garton and Codling (1960, 1965, 1968) and Esherick (1977). The spin forbidden transitions from the $ms^2 \ ^1S_0$ ground state even parity to $J=0$ and 2 levels have been studied by multiphoton ionization spectroscopy, Armstrong (1977, 1979) and Esherick (1977), which gave long Rydberg series converging on the $^2S_{1/2}$ limit. These series were strongly perturbed particularly in Ba I due to the interaction of $(m-1)d^2 \ np \ ^1,^3P_1^0$ doubly excited configurations. The double excitations in alkaline earths were revealed by the excitation of the outer electron of the ion from the ms orbital to the $(m-1)d$, which produce a second ionic core $(m-1)d \ ^2D_{3/2,5/2}$ above the $ms \ ^2S_{1/2}$ state. The transitions



are allowed by the $\Delta J = +1$ selection rule which permits six Rydberg series converging on the $^2D_{3/2,5/2}$ limits. All these levels lie above the first ionization threshold and exhibit autoionization effects. This autoionization results from the configuration interaction between the discrete levels and $ms \ \epsilon p \ ^1,^3P_1^0$ continua. These levels show asymmetric resonances with high absorption followed by low absorption in the direction of increasing energy. The profile may be due to interaction with several continua. The level $(m-1)d \ np \ ^3P_1^0$ interacts not only with the continua $ms \ \epsilon p \ ^1P_1^0$ but also with the

nearby levels $(m-1)d\ np\ ^1P_1^0$, however, among all the observed Rydberg series, the $(m-1)d\ np\ ^1P_1^0$ transition will be most diffuse and strong. This Rydberg series has been studied by Garton and Godling (1965,1968), Ditchburn and Hudson (1960), Kaiser (1960), Garton et al. (1968), Garton and Tomkins (1969) and Brown et al. (1977), and Brown and Ginter (1978).

Considering now the double excitation due to the ground state configuration ms^2 mixing with the mp^2 configuration, the absorption spectrum here consists of transitions

$$ms^2\ ^1S_0 \longrightarrow mp(^2P_{1/2,3/2})ns, nd\ ^1,^3P_1, ^3D_1$$

forming odd parity channels with $J=1$ which are based on the $mp\ ^2P_{1/2,3/2}$ term of the ion. There are five such channels with addition of an 's' or 'd' electron to the $mp\ ^2P$ core: two belonging to the $^2P_{1/2}$ lower ionic core level and three to the $^2P_{3/2}$ upper ionic core level.

The term 2P lies above the $ms\ ^2S$ and $(m-1)d\ ^2D$ terms of the ion, therefore continuum of all $J=1$ channels associated with 2S and 2D cores will be present in this energy region. There are eight such channels:

$$ms \in p(^1,^3P_1^0),\ (m-1)d \in p(^1,^3P_1^0, ^3D_1^0)\ \text{and}\ (m-1)d \in f(^1,^3P_1^0)$$

which will interact with the levels based on the $mp\ ^2P_{1/2,3/2}$ core to produce autoionization. Therefore all the features will autoionize strongly. Garton et al. (1974) observed these transitions in Ba I and Esteva et al. (1972) observed them in Mg. We have extended the observations in Mg I and report the analogous transitions in Ca I and Sr I for the first time. The detailed analysis of these spectra are presented in the next sections.

We have found that the $mp(^2P_{1/2,3/2})ns,nd$ configuration changes coupling from LS to jj with increasing n . Therefore, we present

below the coupling schemes.

The energy of an atom is determined by the assignment of the values of n and ℓ for all the electrons. The corresponding states of each electron configuration differ by the mutual orientation of the orbital angular momenta and spins of the electrons. For two electrons in LS coupling ℓ_1 and ℓ_2 form a vector resultant L about which they are considered to be precessing rapidly; similarly s_1 and s_2 precess rapidly about S . The precession of L and S about their resultant J is much slower, corresponding to the assumption that the spin-orbit energy splitting is much smaller than the splitting due to electrostatic interaction. For the ground and low excited configurations, the coupling of the four angular momentum vectors ℓ_1, s_1, ℓ_2, s_2 is usually described by LS coupling for elements of lower atomic number.

$$[(\ell_1 \ell_2)L, (s_1 s_2)S]J$$

If the residual electrostatic interaction between electrons is neglected, the electrons move quite independently of each other in a central field, each electron separately being subject to a spin-orbit interaction. Thus the vector model pictures a rapid precession of each ℓ_i and s_i about their resultant j_i . The residual electrostatic interaction applied afterwards as a small perturbation causes a much slower precession of the j_i about their resultant J which is a constant of the motion in both LS and jj-coupling schemes. Therefore for high- z elements it is the magnetic interaction between the spins of each electron and its own orbital motion which predominates.

$$[(\ell_1 s_1)j_1, (\ell_2 s_2)j_2]J$$

Racah (1942) described a new type of vector coupling in complex spectra. The jk coupling which takes place when the electrostatic interaction

is weak compared to the spin-orbit interaction of the parent ion, but is strong compared to the spin coupling of the external electron. In this case the total angular moment J of the parent ion and the orbital moment ℓ of the external electron are coupled together and have a resultant k ; then k is coupled with the spin of this electron, and their resultant is J .

$$[(\ell_1, s_1) j_1, \ell_2) k, s_2] J$$

Since the exchange forces act on the spins, it is not sufficient for this coupling that the spin-orbit interaction of the external electron is weak, but also the exchange integrals G_k must be small compared to F_2 . The general structure of a configuration in JK coupling is a pair structure. We present below the ps and pd terms built on the $2P_{1/2,3/2}^0$ limit in the three above mentioned coupling schemes.

(i) LS Coupling

<u>Ion state</u>		<u>Added Electron</u>	
		<u>s</u>	<u>d</u>
p	$2P_{1/2}$	$3P_0^0, 3P_1^0$	$3D_1^0, 1D_2^0, 3D_2^0, 3D_3^0$
	$2P_{3/2}$	$1P_1^0, 3P_2^0$	$3P_0^0, 1P_1^0, 3P_1^0, 3P_2^0, 3F_2^0, 3F_3^0, 1F_3^0, 3F_4^0$

(ii) Jk Coupling

		<u>s ($\ell=0$)</u>	<u>d ($\ell=2$)</u>	
p	1/2	$\left[\frac{1}{2}\right]_{01}^0$	$\left[\frac{3}{2}\right]_{12}^0$	$\left[\frac{5}{2}\right]_{23}^0$
	3/2	$\left[\frac{3}{2}\right]_{12}^0$	$\left[\frac{1}{2}\right]_{01}^0$	$\left[\frac{3}{2}\right]_{12}^0$
			$\left[\frac{5}{2}\right]_{23}^0$	$\left[\frac{7}{2}\right]_{34}^0$

(iii) jj Coupling

		<u>s ($J=1/2$)</u>	<u>d ($J=3/2, 5/2$)</u>	
p	1/2	$\left[\frac{1}{2} \frac{1}{2}\right]_{01}^0$	$\left[\frac{1}{2} \frac{3}{2}\right]_{12}^0$	$\left[\frac{1}{2} \frac{5}{2}\right]_{23}^0$
	3/2	$\left[\frac{3}{2} \frac{1}{2}\right]_{12}^0$	$\left[\frac{3}{2} \frac{3}{2}\right]_{0123}^0$	$\left[\frac{3}{2} \frac{5}{2}\right]_{1234}^0$

In absorption only $\Delta J=1$ upper states are accessible.

3.2 Magnesium

3.2.1 Summary

The absorption spectra of magnesium vapour have been reinvestigated in the region 700 to 2000 Å using synchrotron radiation as the background source. Extensions to the double excitation spectrum of the valence shell have resulted and are compared with recent data obtained by electron impact spectroscopy.

3.2.2 Introduction

The absorption spectrum of Mg I in the ultraviolet region due to the excitation of a single electron from the 3s shell was reported by Codling (1961). This principal series was extended to higher n values by Brown et al. (1973) who give a more accurate value of the first ionization potential of Mg I. Rydberg series due to the inner shell excitation of a single electron from 2p subshell were recorded by Newsom (1971) and more recently Ederer et al. (1979) extended these observations and found transitions due to simultaneous excitation of two electrons, one from the 2p and the other from the 3s shell, and also both electrons from the 2p-subshell, in the region 226-170 Å.

The spectra due to simultaneous excitation of two valence shell electrons were observed by Mehlmán and Esteva (1969), Esteva, Mehlmán and Romand (1972). The levels which were not accessible under optical selection rules have been reported by Trajmar and Williams (1976), Breuckman et al. (1976), Pejcev et al. (1977) and Rassi et al. (1977) using electron impact spectroscopy.

The ab initio calculations of inner shell and doubly excited states in Mg I have been reported by Mansfield and Connerade (1972), Hansen (1975), McGuire (1976), and for outer shell photoionization and double excitation by Burke and Moores (1968), Kulander and Dehler (1972), Laughlin and Victor (1972), Bates and Altick (1973), Dubau and Wells (1974) and Thompson et al. (1974).

The absolute photoionization cross section measurements have been reported by Bradley et al. (1973) and previously unobserved transitions, $3s3p\ ^1P_1 - 3p^2\ ^1S_0$, have been detected by Bradley et al. (1976) by the technique of selective excitation using tunable dye lasers.

Rassi et al. (1977) pointed out the uncertainties of classification among the doubly excited states because the analysis of electron impact spectra relies on comparisons with optical spectra in order to separate the dipole transitions from the "non-optical" excitations. It therefore seemed useful to repeat the experiment of Esteva et al. (1972) at higher spectral dispersion, using the windowless furnace technique and the clean continuum emitted by the 500 MeV Bonn Synchrotron. Extensions of the double excitation spectrum have resulted and transitions have been detected which were suspected by Rassi et al. (1977).

3.2.3 Results

The present investigation covered the wavelength range 700-2000 Å. Absorption spectra were obtained using a windowless clamshell furnace, equipped with a dynamic containment insert and heated to about 800°C temperature. Densitometer traces of the Mg I absorption spectrum in three regions where discrete structure occurs, are reproduced in Figures (3.2.1, 3.2.2, 3.2.3). The most striking feature of the spectrum is the onset of the continuous absorption above the first ionization threshold. Transitions due to excitation of a single electron from the 3s shell and simultaneous excitation of both valence electrons have been observed and a new Rydberg series converging on $3p\ ^2P$ limit has been detected in accordance with the electron impact studies.

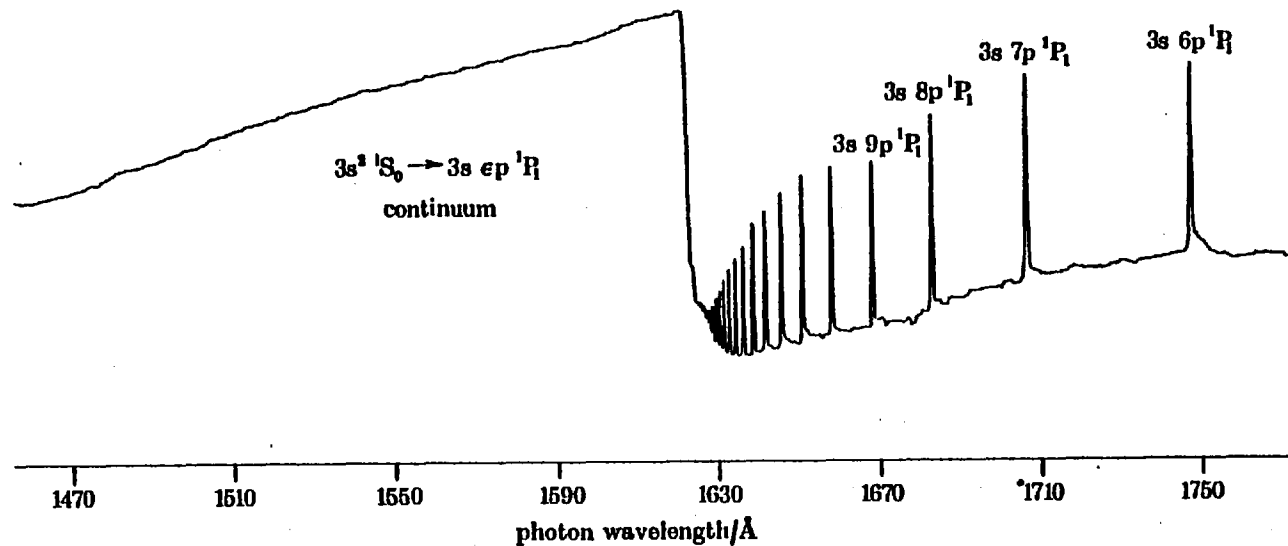
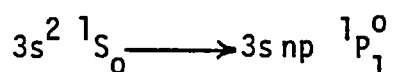


FIGURE (3.2.1) - The principal series due to excitation of $3s^2 \ ^1S_0 \rightarrow 3snp \ ^1P_1^0$ in Mg I, showing the sudden onset and uniform decrease of continuous absorption above the first ionization threshold.

3.2.4 Analysis

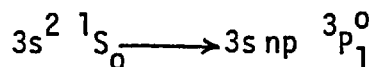
3.2.4a 3s np Configuration

The ground state configuration of Mg I is $2p^6 3s^2 {}^1S_0$ and excitation of a single electron from the 3s shell results in a Rydberg series converging on the ground state of the ion. The excitation scheme is



This configuration have been extensively studied by Codling (1961) and Brown et al. (1973). Neither of the previous authors give data on the onset of continuous absorption above the first ionization threshold. Our data confirm that the onset is fairly rapid, i.e. that the continuous absorption rises in a small wavelength interval until the double excitation spectrum is reached. This is the behaviour expected within a photoionization channel in which potential barrier effects are small and is in quite good agreement with early low resolution measurements of the variation in photoabsorption cross section with wavelength by Ditchburn and Marr (1953).

We have covered the spectral range to 2000 Å and did not detect lines due to the forbidden transitions



which were reported by Codling (1961). Likewise, Brown et al. (1973) observed the principal series with much higher path length than in either Codling's (1961) experiment or the present work and did not detect any forbidden transitions.

3.2.4b 3p ns,nd Configuration

The transitions correspond to the simultaneous excitation of both the valence electrons due to configuration mixing in the ground state. The ground state configuration $3s^2$ strongly mixes with $3p^2$

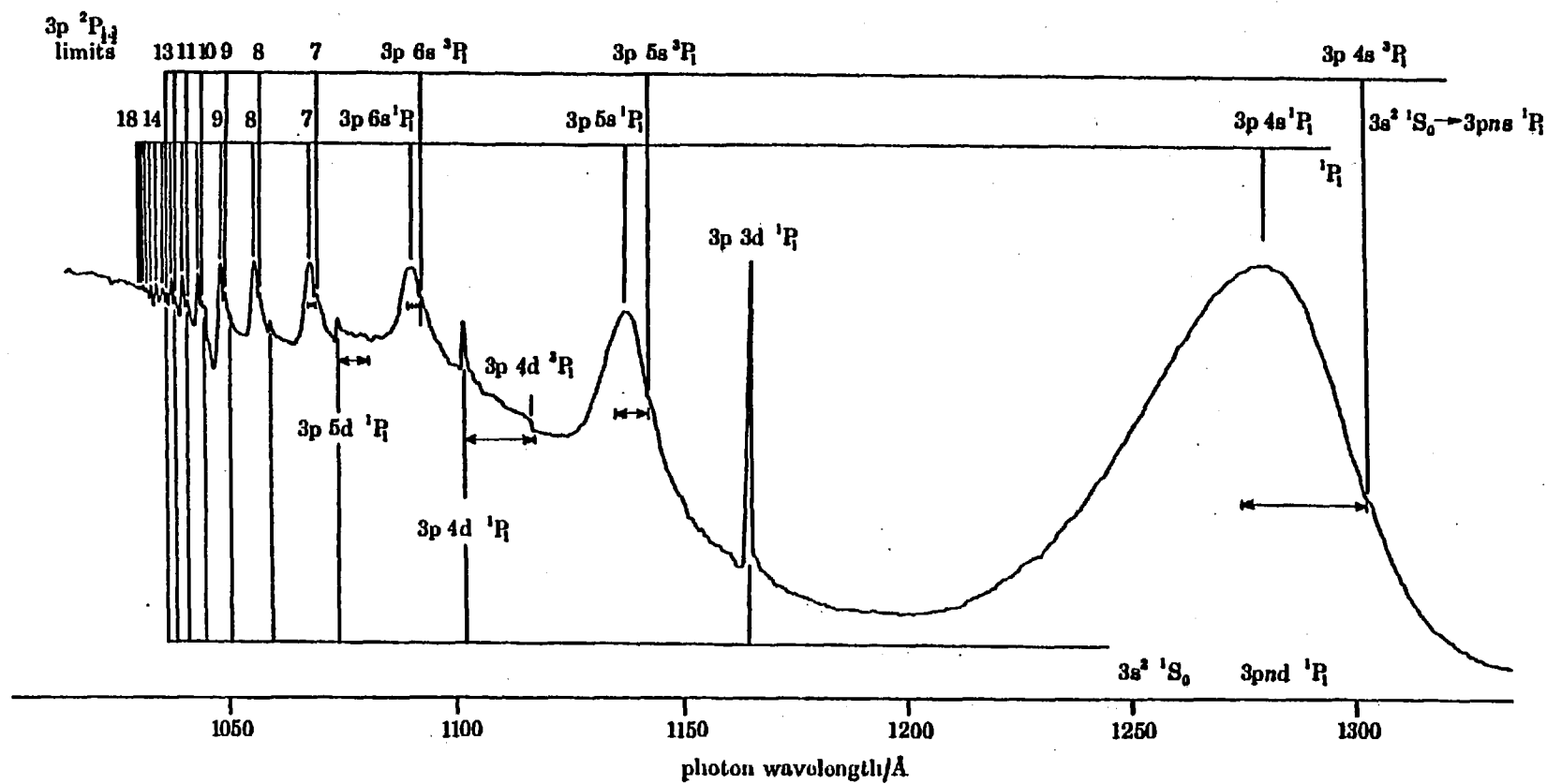
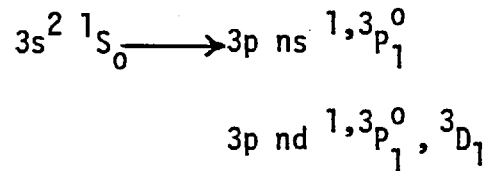


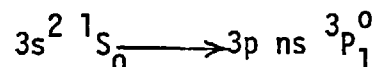
FIGURE (3.2.2) - The double excitation series : $3s^2\ ^1S_0 \rightarrow 3pns, nd\ ^1P_1, ^3P_1$ converging to the $3p$ limit of Mg I.

because of the small energy interval. The excitation scheme is



All the members of these series lie above the first ionization threshold and therefore autoionize due to mixing with the $3s \ \epsilon p \ ^1P_1^0$ continuum. The double excitation series converging on the 3p limit is reproduced in Fig.(3.2.2), which were previously observed by Esteva et al. (1972). We have extended both of the series they reported to higher n-values and the profiles reported here are more reliable than previous data. As a result of higher spectral dispersion and a more uniform continuum source in the present experiment, we detect a third series which is not listed by Esteva (1972). The lower member of this series is blended with the $3p \ ns \ ^1P_1^0$ profiles but it stands out more clearly around n=6 to n=10.

Rassi et al. (1977) have studied the doubly excited levels in Mg I in low energy electron impact experiments with excitation energy ranging from 27-500 eV. They observed five transitions which were arranged into series converging on the 3p limit. Rassi et al. (1977) suggested that these are non-optical transitions from $3p \ ns \ ^3P_1^0$ with n=4 to n=8 in rough agreement with the energies calculated by Burke and Moores (1968). The energies given by Rassi et al. (1977) agree within ± 0.01 eV with our measurements, therefore the series can be attributed to the double excitations



which violates the $\Delta s = 0$ selection rule of strict LS coupling.

We observe the series up to n=10 after which it merges with the $3p \ nd \ ^1P_1^0$ series.

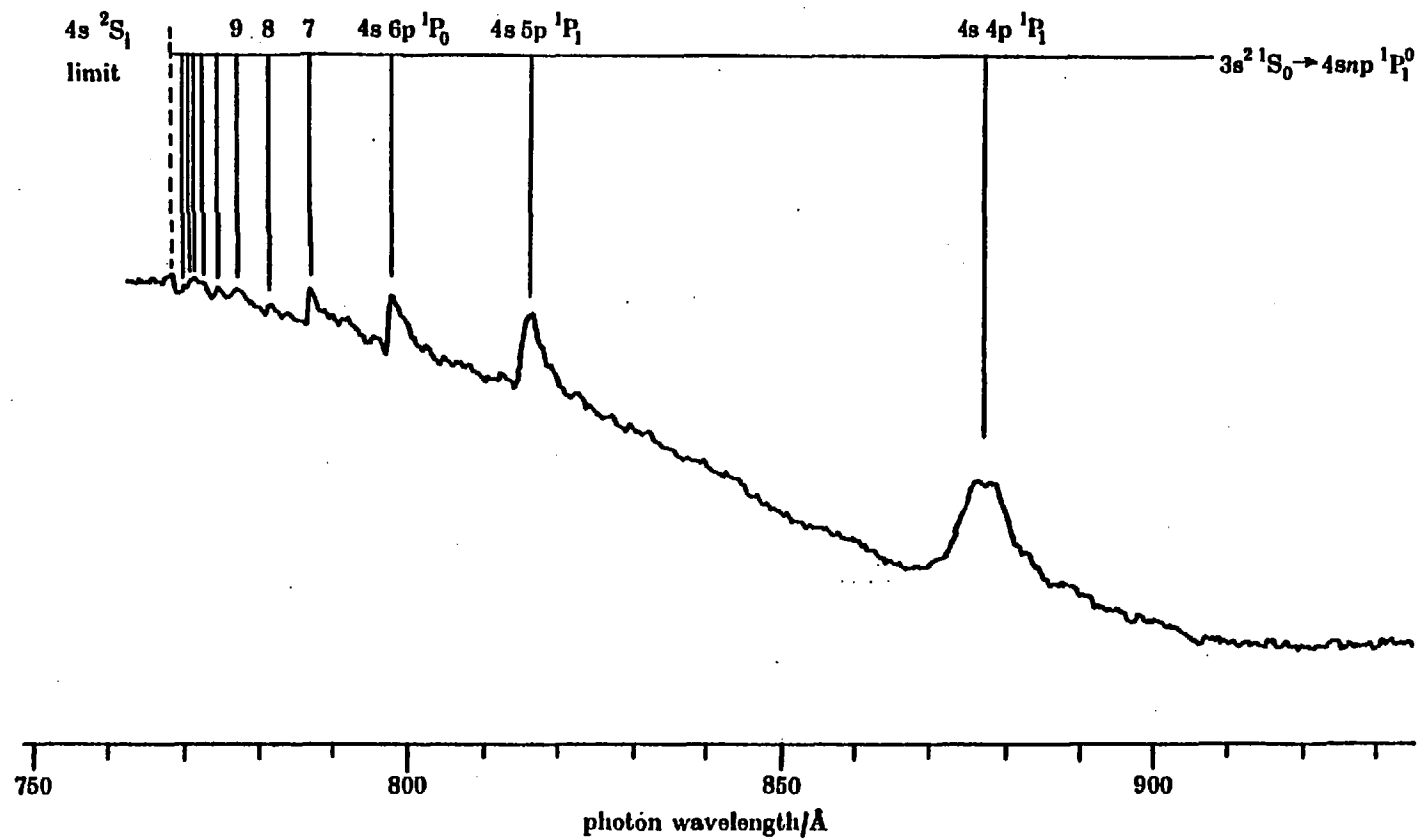


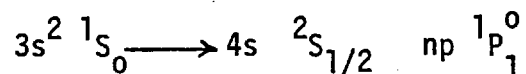
FIGURE (3.2.3)- Showing the series due to double excitation $3s^2\ 1S_0 \rightarrow 4s\ np\ 1P_1^0$ of Mg I.

To see the variation in coupling with increasing n in the $3p\ ns$ configuration, Connerade (private communication) recomputed the lowest doubly excited configurations and extended the ab initio treatment to all relevant configurations with $n \leq 10$ using the MCHF 72 Hartree-Fock code of Froese Fischer (1972, 74, 77) in single configuration unrestricted mode. The calculations show that the configurations $3p\ ns$ vary from near LS coupling ($\alpha = 0.0396$) at lower n to intermediate jj coupling ($\alpha = 2.5179$) at high n . The tendency towards jj coupling with increasing n , readily understood since the mean radius of the $3p$ wavefunction changes little as n increases, $\langle r \rangle_{3p}$ remains nearly constant, whereas $G^1(3p, ns)$ which depends on the overlap between the $3p$ and ns wavefunctions decreases from 2498 to $42\ \text{cm}^{-1}$ from $n=4$ to $n=10$.

The $3p\ ns\ ^3P_1^0$ levels are more stable under autoionization into the $3s\ \epsilon p\ ^1P_1^0$ continuum than $3p\ ns\ ^1P_1^0$, therefore the transitions to 3P_1 appear as sharp lines with the 1P_1 profiles which are reproduced in Fig.(3.2.2).

3.2.4c 4s np Configuration

Esteva et al. (1972) observed four members of this series which is again due to the simultaneous excitation of two valence electrons.

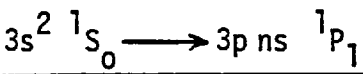


We have extended this series to $n=10$ and the densitometer trace is reproduced in Fig.(3.2.3). This series exhibits Beutler-Fano profiles very similar in appearance to those of the $3p\ ns\ ^1P_1$ series whereas the $4s\ np\ ^1P_1$ series is much weaker. The first member of the $3p\ ns\ ^1P_1$ series is $3p4s\ ^1P_1$, which is a very broad and intense transition. This can also be regarded as the first member of the $4s\ np\ ^1P_1$ series.

The wavelengths and identifications are given in Tables(1,2,3,4).

TABLE 3.2.1

Doubly Excited Series in Mg. I.



Present Experiments				Previous Experiments γ /eV		
		$\lambda/\text{\AA}$	γ /eV	M	E	R
n	n*	peak	peak	peak	edge	peak
4	2.42	1271.34	9.75	9.86	9.52	9.81
5	3.42	1135.58	10.92	10.93	10.86	10.97
6	4.43	1088.90	11.35	11.38	11.36	11.41
7	5.41	1067.44	11.61	11.62	11.60	11.64
8	6.43	1055.18	11.75	11.75	11.73	11.76
9	7.43	1047.77	11.83	11.82	11.82	11.84
10	8.46	1042.81	11.89	-	11.89	11.89
11	9.45	1039.50	11.93	-	11.92	11.93
12	10.51	1036.96	11.96	-	11.94	-
13	11.58	1035.09	11.98	-	11.97	-
14	12.48	1033.86	11.99	-	-	-
15	13.61	1032.66	12.01	-	-	-
16	14.72	1031.75	12.02	-	-	-
17	15.97	1030.94	12.03	-	-	-
18	16.82	1030.49	12.03	-	-	-

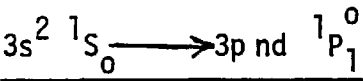
Series Limit = 97430.1 cm⁻¹

M - Mehlman and Esteva (1969).

E - Esteva et al. (1972).

R - Rassi et al. (1977).

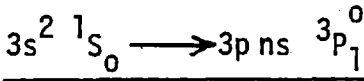
TABLE 3.2.2



Present Experiments				Previous Experiments ν /eV		
		$\lambda/\text{\AA}$	ν /eV	M	E	R
n	n*	peak	peak	peak	peak	peak
3	3.09	1163.80	10.65	10.65	10.65	10.64
4	4.08	1101.60	11.26	11.26	11.26	11.26
5	5.07	1073.51	11.55	11.55	11.55	-
6	6.04	1059.10	11.71	11.71	11.70	-
7	7.05	1050.17	11.80	-	11.80	-
8	8.05	1044.54	11.87	-	-	-
9	9.05	1040.70	11.91	-	-	-
10	10.07	1037.92	11.94	-	-	-
11	11.03	1035.97	11.97	-	-	-

The limit assumed is 97430.1 cm⁻¹

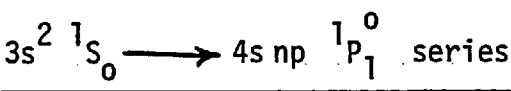
TABLE 3.2.3



Present Experiments				Rassi et al. (1977)
		$\lambda/\text{\AA}$	ν /eV	
n	n*	peak	peak	peak, ν /eV
4	2.31	1299.75	9.54	9.54
5	3.34	1141.85	10.86	10.85
6	4.34	1091.51	11.36	11.35
7	5.31	1069.11	11.60	11.60
8	6.28	1056.53	11.73	11.74
9	7.27	1048.74	11.82	-
10	8.20	1043.87	11.88	-
11	9.20	1040.25	11.92	-
12	10.30	1037.30	11.95	-

This series exhibit an anomalous intensity variation which corresponds to the fact that it arises by breakdown of LS characterization, which increases towards the high series members.

TABLE 3.2.4



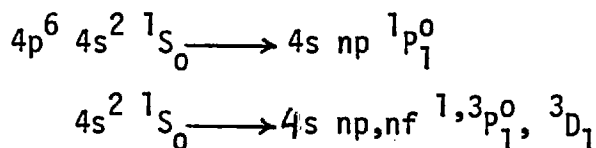
Present Experiments			Previous Experiments ν /eV		
$\lambda/\text{\AA}$					
n	n*	peak	ν /eV	M	E
3	1.44	1271.34	9.75	9.86	9.52
4	2.53	874.46	14.18	14.17	14.18
5	2.59	813.38	15.24	15.27	15.26
6	4.49	794.10	15.61	15.65	15.62
7	5.41	782.94	15.83	-	15.83
8	6.56	775.65	15.98	-	-
9	7.58	771.81	16.06	-	-
10	8.45	769.61	16.11	-	-
11	9.42	767.82	16.15	-	-
12	10.41	766.51	16.17	-	-

M. Mehlman and Esteva (1969); E. Esteva et al. (1972). The first member of this series is common to the series of Table (3.2.1).

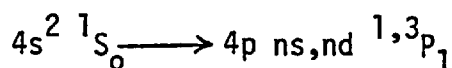
3.3 Calcium

3.3.1 Summary

Absorption spectra of Ca I have been recorded in the energy range 800-2000 Å. In addition to the known transitions



we have observed about 60 new transitions which are due to simultaneous excitation of both the valence electrons.



These Rydberg series are converging onto the $4p {}^2P_{1/2, 3/2}$ level of Ca II.

3.3.2 Introduction

Calcium is an important element of the alkaline earth group, being the first member with an empty inner d shell. The ground state configuration $4s^2 {}^1S_0$ strongly mixes with the $4p^2$ and $3d^2$ configurations. Therefore, in addition to the spectra due to excitation of a single valence electron, one observes structure due to the simultaneous excitation of both valence electrons. The absorption spectra, corresponding to transitions from the even parity $4s^2 {}^1S_0$ ground state to odd-parity $J=1$ excited states, have been extensively studied, Kaiser (1960), Ditchburn and Hudson (1960), Garton and Codling (1965) and Brown and Ginter (1973). The even parity states $J=0$ and 2 were observed by Armstrong et al. (1977) using multiphoton ionization spectroscopy. The data was analysed by multi-channel quantum defect theory, Fano (1970, 77), and some of the previous assignments were revised. More recently, Armstrong et al. (1979) have observed the odd-parity $J=1$ spin forbidden transitions

from the $4s^2\ ^1S_0$ ground state to $4s\ np\ ^3P_1^0$ excited states yielding triplet Rydberg series.

The absorption cross section in the vacuum ultraviolet region has been measured by Ditchburn and Hudson (1960), Newsom (1966) and Carter et al. (1971). The oscillator strength and photoionization cross section, in the two channel approximation, have been calculated by Moores (1968), Burke and Moores (1968), applying multichannel quantum defect theory. The ejected electron spectra was reported by Schmitz (1976) and recently Pejcev et al. (1977) reported the high resolution ejected electron spectrum in the range 12 to 28 eV.

The inner shell excitation involving the 2p subshell (Mansfield (1976)) and the 3p subshell (Mansfield and Newsom (1977)) have been observed. Some features were attributed to simultaneous excitation of two electrons, one from the 3p subshell and one from the 4s shell and identification was supported by Hartree-Fock calculation. Wilson (1969) performed the H.F. (E_{av}) calculations for 3d 4s and $4p^2$ configurations and Hansen (1975) reported the multi-configuration H.F. calculations including $nd(n+1)s\ ^1D$ and $(n+1)p^2\ ^1D$ terms.

Rydberg series due to excitation of both valence electrons converging on $mp\ ^2P_{1/2,3/2}$ core level have been observed in Ba I and Mg I. The purpose of the present investigation was to record the analogous transitions in calcium.

3.3.3 Results

In the present investigation we have recorded the spectral region between 700 to 2000 Å using synchrotron radiation as the background source. The calcium vapour was obtained by heating the metal in an induction furnace at temperatures ranging from 700 to 1000°C. The spectra were recorded in the first order of a 1 metre normal incidence spectrograph equipped with a 1200 lines/mm grating. In addition to the known levels in the ultraviolet region, about 60 new

levels have been observed. All these levels are broad and diffuse due to autoionization and are arranged in Rydberg series converging on $2p_{1/2,3/2}$ levels of ion.

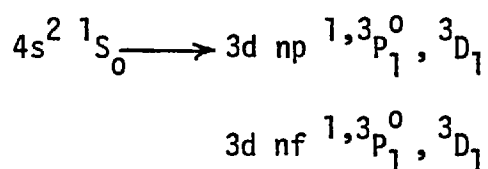
3.3.4 Analysis

3.3.4a 4s np Configuration

The principal series arise from the excitation of single valence electron $4s^2 1S_0 \rightarrow 4s np 1P_1^0$ $J=1$ and have been observed by Garton and Codling (1965), and Shahanova (1960) to $n=33$. Brown et al. (1973) have extended this series to $n=79$ yielding a more accurate value of the first ionization potential $49305.99 \pm 0.02 \text{ cm}^{-1}$. The higher members of this series are regular whereas some of the lower members are perturbed, which led to several differing assignments of the interlopers. Garton and Codling (1965) made the assignment for the perturber as $3d 4p 1P_1^0$ based on the extrapolation of the $3d np 1P_1^0$ series whereas revisions by Friedrich and Treffitz (1969) based on configuration mixing calculations.

3.3.4b 3d np,nf Configuration

The ground state configuration of Ca I $4s^2 1S_0$ simply mixes with the $3d^2$ configuration and results in strong double excitation in the absorption spectra. The excitation scheme is



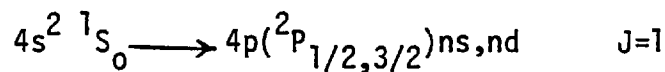
which form six Rydberg series converging on $3d^2 D_{3/2,5/2}$ level of Ca II. The series were observed by Garton and Codling (1965) and have been extended to high n values by Brown et al. (1973). All the transitions are optically allowed from the ground state with $\Delta J=+1$ selection rule and lie above the first ionization threshold.

Most of the lines are autoionized which may be explained by configuration interaction between the discrete levels and the continua $4s \epsilon p \ ^1P_1^0$. The leading member $3d 4p \ ^1P_1^0$ of the series lies below the first ionization limit and causes a perturbation in the principal series (Garton and Codling (1965)). A detailed analysis of this configuration is given by Brown et al. (1973). Perturbations in this configuration were also detected due to the $4p 5s$ levels at $1740 \text{ \AA}$. This conjecture is confirmed by the observation of this series up to $n=16$ in the present work.

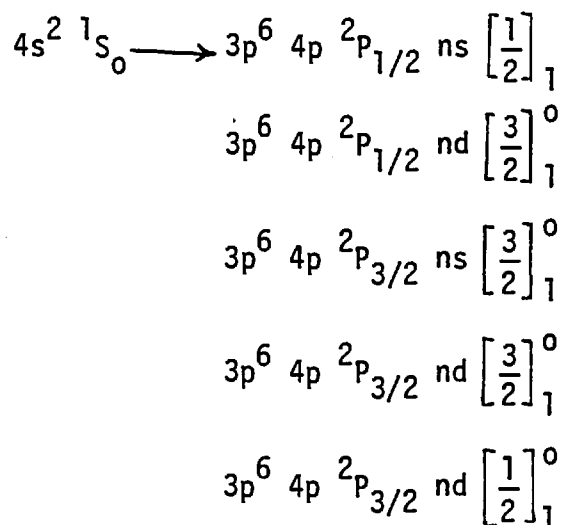
3.3.4c 4p ns,nd Configuration

The Rydberg series due to simultaneous excitation of both valence electrons are reproduced in Fig.(3.4). All these transitions are observed for the first time and are arranged into Rydberg series converging on the $4p \ ^2P_{1/2,3/2}$ level of the ion.

The excitation scheme is



Five Rydberg series of two electron transitions are expected, according to JK coupling (Racah (1942), Cowan and Andrew (1965))



We have used the JK symbolism, Racah (1942), Cowan and Andrew (1965), because the main contribution to the energies of the series levels is

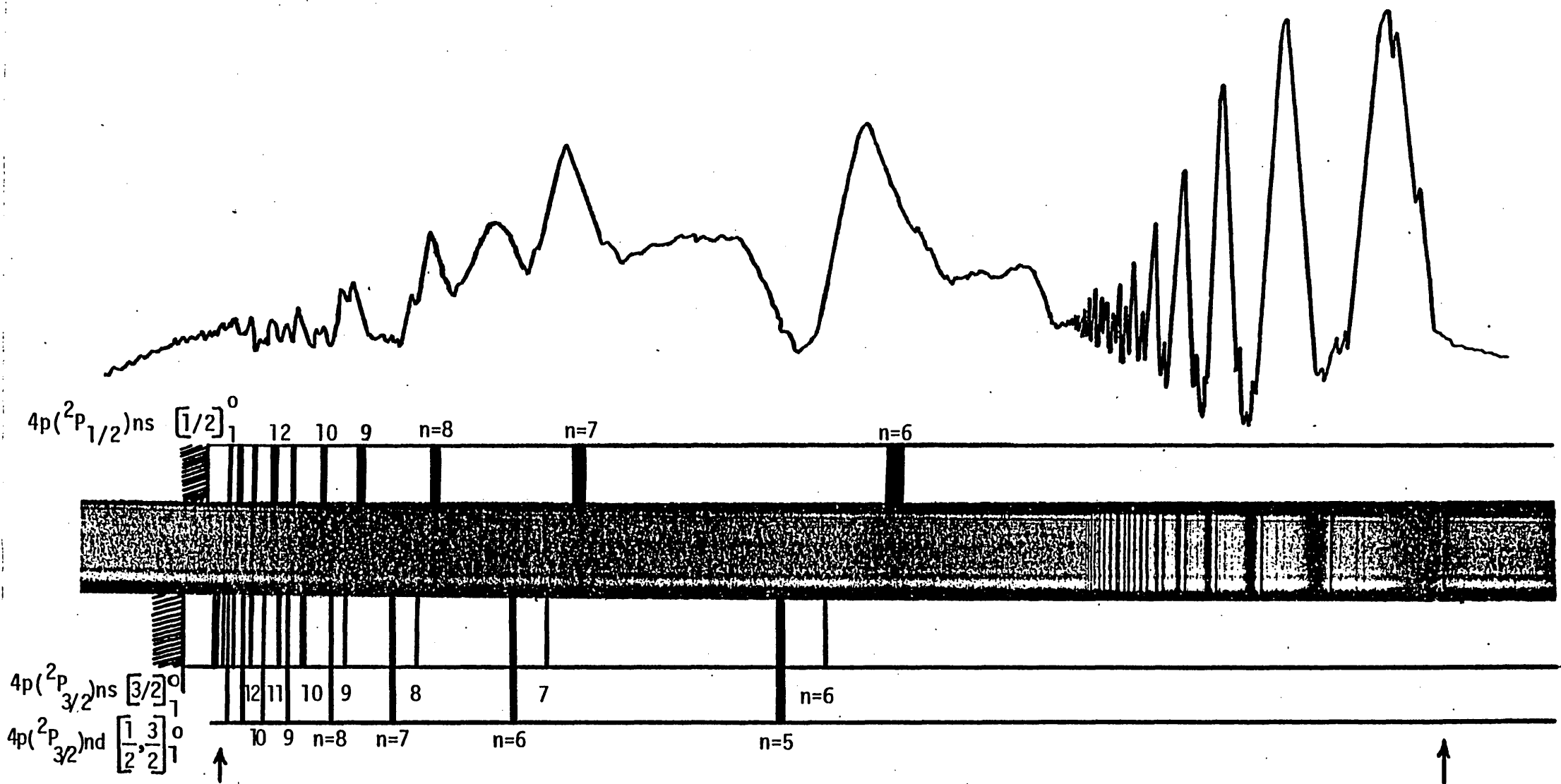


FIGURE 3.3.1 - Double excitation series converging on the $4p \ ^2P_{1/2,3/2}$ limit of Ca II.

due to the spin-orbit interaction in the 4p-core. The assignments to ns,nd have been made from consideration of the effective quantum numbers.

We have arranged all the observed lines into three Rydberg series, one converging on the lower $^2P_{1/2}$ level of the core and two on the higher $^2P_{3/2}$ level of the core. All the lines are very broad and are very different in appearance from the corresponding transitions in Mg I, particularly 3p nd $^1P_1^0$ series. In Mg I all the lines appear very sharp (see Fig.3.2) and all the members of this series lie above the first ionization threshold, whereas the situation in Ca I and Sr I is quite different. This difference may be attributed to the influence of the centrifugal barrier on the properties of the nd-wavefunction. The nd-wavefunctions are well behaved in Mg I, whereas for Ca I and Sr I the 3d and 4d wavefunctions collapse, Connerade et al. (1979), due to the influence of the centrifugal term.

The most prominent series are $^1P_1^0$, whereas the $^3P_1^0$ series has an anomalous course of intensity which is due to transition from LS to jj coupling with increasing n. The value of n^* for the 4pns series also agrees with those of Mg I as one would expect since there is no potential barrier in the ns channel.

We have measured the wavelengths at maximum absorption, which is satisfactory for the 4pnd series because the line profiles are fairly sharp and symmetric. For the 4pns series we have determined the wavelength from the densitometer traces because the profiles were broad and overlapped. All the observed levels with wavelengths and identifications are collected in tables.

Considering now all the series separately.

4p($^2P_{1/2}$)ns $\left[\frac{1}{2}\right]_1^0$ series

This series consists of broad resonances and in pure LS coupling may be assigned as $^3P_1^0$ which converge at a series limit 74494.34 cm^{-1} .

The level at 1740 Å is assigned as 4p 5s by Brown et al. (1973) and the singly excited level 4s 4p $^3P_1^0$ at 15210 cm⁻¹ can also be regarded as the first member of this series yielding $n^* = 1.36$. This series has been observed up to n=16 for the first time and wavelengths and wavenumbers are collected in Table (3.3.1).

$$\underline{4p(^2P_{3/2})ns \left[\frac{3}{2} \right]_1^0 \text{ series}}$$

In LS coupling this series may be assigned $^1P_1^0$ and the singly excited level 4s 4p $^1P_1^0$ at 23652 cm⁻¹ may be regarded as the first member yielding $n^* = 1.47$. The n=5 member of the series is responsible for perturbation in the 3d np,nf series. Ditchburn and Hudson (1960) identified the perturber as 4p 4d but Garton and Codling (1965) reassigned it as 5s 4p. Borwn et al. (1973) also support this assignment and thus we have adopted it in the table. This series has been observed up to n=15 and wavelength and wavenumbers are listed in Table (3.3.2).

$$\underline{4p(^2P_{3/2})nd \left[\frac{1}{2}, \frac{3}{2} \right]_1^0 \text{ series}}$$

In LS coupling this is a $^1P_1^0$ series and the leading member of this series is 3d 4p at 36732 cm⁻¹, which is outside our spectral range. This value is taken from AEL (1958) yielding $n^* = 1.70$. The n=4 level is missing. However, Borwn et al. (1973) identified three weak lines and attributed them to this configuration. Connerade et al. (1979) performed single configuration Hartree-Fock calculations and obtained the splitting between the three terms 3D_1 , 3P_1 , 1P_1 . Connerade (1979) argued that the calculated splitting obtained from quasi-LS coupling formula is much larger than observed by Brown et al. (1973) and, secondly, that the lines observed by Brown et al. (1973) are comparatively sharp although they occur above the first ionization threshold whereas the higher members of this series are broad, which casts doubt on the assignment given by Brown et al. (1973).

TABLE 3.3.1

Spectrum of Ca I

$$4s^2\ ^1S_0 \longrightarrow 4p(^2P_{1/2})ns\ [1/2]_1^0$$

$$\text{Series limit} = 74494.341\ \text{cm}^{-1}$$

n	$\lambda\ \text{\AA}$	$\nu\ \text{cm}^{-1}$	n^*
5 †	1740	57462	2.54
6	1539	64977	3.40
7	1551.1	68913	4.43
8	1412.69	70787	5.44
9	1391.44	71868	6.46
10	1381.01	72411	7.25
11	1372.29	72871	8.22
12	1365.22	73248	9.38
13	1361.58	73444	10.21
14	1358.29	73622	11.20
15	1356.08	73742	12.06
16	1354.06	73852	13.05

In LS coupling, this is a $^3P_1^0$ series.

The singly excited level $4s4p\ ^3P_1$ at $15210\ \text{cm}^{-1}$ can also be regarded as the first member of this series, yielding $n^* = 1.36$.

† Value reported by Brown et al. (1973).

TABLE 3.3.2

Spectrum of Ca I

$$4s^2 \, ^1S_0 \longrightarrow 4p(^2P_{3/2})ns \left[\frac{3}{2} \right]_1^0$$

$$\text{Series limit} = 74719.23 \, \text{cm}^{-1}$$

n	$\lambda \, \text{\AA}$	$\nu \, \text{cm}^{-1}$	n^*
5	1740	57461	2.52
6	1528	65445	3.44
7	1444.1	69247	4.48
8	1308.43	71001	5.43
9	1388.75	72007	6.36
10	1376.36	72655	7.29
11	1367.79	73111	8.26
12	1361.58	73444	9.28
13	1356.99	73693	10.34
14	1354.06	73852	11.25
15	1351.92	73969	12.09

In LS coupling, this is a $^1P_1^0$ series.

The singly excited level $4s4p \, ^1P_1^0$ at $23652 \, \text{cm}^{-1}$ can also be regarded as the first member of this series, yielding $n^* = 1.47$.

The $n=5$ member of the series is probably responsible for a series perturbation discussed by Ditchburn & Hudson (1960) who identified the perturber as $4p4d$, but the perturbing level was reassigned by Garton & Codling (1965) as $5s4p$, and is thus included in the present table.

TABLE 3.3.3

Spectrum of Ca I

$$4s^2\ ^1S_0 \longrightarrow 4p(^2P_{3/2})nd\ \left[\begin{smallmatrix} 1/2, 3/2 \\ 1 \end{smallmatrix} \right]_1^0$$

Series limit = 74719.23 cm⁻¹

n	λ (Å)	ν _{cm⁻¹}	n [*]
3	2722	36732	1.70
*			
5	1502	66578	3.67
6	1435.9	69643	4.65
7	1403.76	71237	5.61
8	1383.34	72289	6.72
9	1372.29	72871	7.71
10	1365.22	73248	8.64
11	1360.23	73517	9.56
12	1356.08	73742	10.60

In LS coupling, this is a $1P_1^0$ series.

* The n=4 member has been tentatively identified by Brown et al. (1973) and is discussed in the text.

This series has been followed up to $n=12$ yielding consistent quantum defect. Wavelengths and wavenumbers of the observed lines are collected in Table (3.3.3).

3.4 Strontium

3.4.1 Introduction

The absorption spectrum of strontium vapour in the ultraviolet region due to the excitation of a single electron from the outer shell and simultaneous excitation of both valence electrons was observed by Garton and Codling (1968) and Esterick (1977). The double excitation series shows autoionization features and Garton et al. (1968) derived the line shape parameters according to the theory developed by Fano (1961) and Fano and Cooper (1965).

A two-channel quantum defect model, describing the interaction between the principal channel $5s \in p \ ^1P_1^0$ and the doubly excited channel $4d np \ ^1P_1^0$, was applied by Lu (1977) to analyse the strongly perturbed principal series. Armstrong et al. (1977) observed the even parity $J=0$ and 2 levels using multiphoton ionization techniques and the data was analysed by applying multichannel quantum defect theory developed by Fano (1970, 1977). More recently, Armstrong et al. (1979) have observed the odd parity $J=1$ spin forbidden transitions using the technique of multiphoton ionization via intermediate selective excitation. Long triplet Rydberg series were found which suggest some revision of the previous assignments.

Photoionization cross section measurements in the autoionization region was reported by Hudson et al. (1969) and recently Newsom (1973) has re-examined the spectrum just above the first ionization threshold.

High lying autoionizing states of strontium due to inner shell excitation from $3p$ and $3d$ subshells have been reported by Mansfield

and Connerade (1975). The absorption spectrum due to 4p subshell excitation has also been observed by Mansfield and Newsom (1979) and interpretation is supported by Hartree-Fock calculations.

Schmitz et al. (1976) studied the electron impact excitation at incident electron energy of 2 KeV and observed 34 lines in the ejected electron spectrum. In order to excite both dipole allowed and dipole forbidden transitions White et al. (1979) recorded the ejected electron spectrum in the range 10-22 eV at much lower incident electron energies.

We report new observations in the absorption spectrum of Sr I which are arranged into Rydberg series converging on the $5p\ ^2P_{(1/2,3/2)}$ levels of the ion.

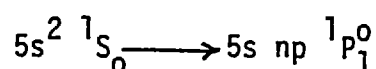
4.3.2 Results

The absorption spectrum of strontium vapour has been observed in the range 700-2100 Å using synchrotron radiation as the background source. Rydberg series due to single valence electron excitation and due also to simultaneous excitation of both valence electrons have been observed converging on $^2S_{1/2}$, $4d\ ^2D_{3/2,5/2}$ and $5p\ ^2P_{1/2,3/2}$ levels of the ion. About 60 new levels have been observed for the first time which are classified into Rydberg series converging to the $5p\ ^2P_{1/2,3/2}$ level of the ion.

4.3.3 Analysis

4.3.3a $5s\ np\ ^1P_1^0$ Configuration

The transitions correspond to the principal series of Sr I according to the excitation scheme

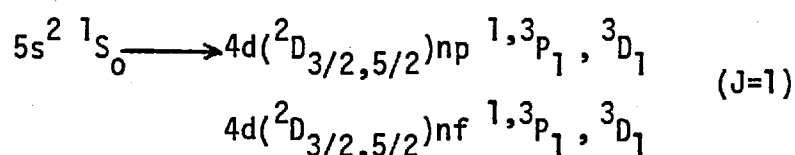


converging on the $^2S_{1/2}$ level of Sr II. Garton and Codling (1968) observed this series using a 3 m normal incidence spectrograph equipped

with 1200 lines/mm grating and a hydrogen continuum discharge tube as the background source. Garton and Codling (1968) reported this series up to $n=33$ and calculated the accurate value of the first ionization potential of Sr I $45932.0 \pm 0.2 \text{ cm}^{-1}$. Esherick (1977) extended this series up to $n=60$ while he observed even parity states using multiphoton ionization spectroscopy. A perturbation was also detected in this series at $n=8$ and was attributed due to the existence of a level $4d5p \ ^1P_1^0$ originating due to double excitation of both the valence electrons. This assignment was consistent with the higher members of this series observed by Garton and Codling (1968).

4.3.4b $4d(^2D_{3/2,5/2})np,nf$ Configurations

The absorption spectrum of Sr I consists of strong and broad features above the first ionization threshold. These transitions are attributed to simultaneous excitation of both the valence electrons according to the excitation scheme



which form six Rydberg series converging on the $4d \ ^2D_{3/2,5/2}$ term of Sr II. Garton and Codling observed 94 absorption lines and 88 of them were classified into six series. The extrapolated $4dnp \ ^1P_1^0$ series also confirm the assignment of the perturber in the principal series yielding consistent quantum defect. The first member of the series $4dnp \ ^1P_1^0$ above the first ionization potential i.e. $4d6p \ ^1P_1^0$ has a very large width and the next two members exhibit pronounced intensity and width perturbations. Garton and Codling (1968) attributed this perturbation to the presence of a diffuse feature and a Fano-resonance which was assigned as $6s5p \ ^{1,3}P_1^0$. We confirm this assignment by observing the higher members of the series, which is discussed overleaf.

4.3.4c 5p($^2P_{1/2,3/2}$)ns,nd Configuration

Rydberg series due to simultaneous excitation of both valence electrons have been observed converging on the second excited state of the ion $5p\ ^2P_{1/2,3/2}$.

Strontium is a heavier atom than calcium and shows stronger spin-orbit interaction, therefore jk coupling is a more realistic coupling scheme to describe this excitation which gives five Rydberg series.

$$\begin{aligned}
 4p^6\ 5s^2\ ^1S_0 &\longrightarrow 4p^6\ 5p\ ^2P_{1/2}\ ns\ \left[\frac{1}{2}\right]_1^0 \\
 &\qquad\qquad\qquad 4p^6\ 5p\ ^2P_{1/2}\ nd\ \left[\frac{3}{2}\right]_1^0 \\
 &\qquad\qquad\qquad 4p^6\ 5p\ ^2P_{3/2}\ ns\ \left[\frac{3}{2}\right]_1^0 \\
 &\qquad\qquad\qquad 4p^6\ 5p\ ^2P_{3/2}\ nd\ \left[\frac{1}{2}\right]_1^0 \\
 &\qquad\qquad\qquad 4p^6\ 5p\ ^2P_{3/2}\ nd\ \left[\frac{3}{2}\right]_1^0
 \end{aligned}$$

Two of the series will converge on $5p\ ^2P_{1/2}$ core level and three on the $^2P_{3/2}$ core level. We have arranged all the observed transitions into three Rydberg series, one converging on the $^2P_{1/2}$ level and two converging on the $^2P_{3/2}$ level. All the transitions are very broad and diffuse, which is due to the interaction with eight available continua, namely

$$5s\ \epsilon p(^1,^3P_1^0),\ 4d\ \epsilon p(^1,^3P_1^0, ^3D_1^0)\ \text{and}\ 4d\ \epsilon f(^1,^3P_1^0, ^3D_1^0)$$

The appearance of the levels is very similar to that of calcium, with slightly better developed structure, but remarkably different from that of Mg I, particularly for $5pnd\ ^1P_1^0$ series. The same explanation also applies here as has been given in Ca (Section 4.2) i.e. it is due to the influence of the centrifugal term $\frac{\ell(\ell+1)\hbar^2}{2m r^2}$

DOUBLE EXCITATION IN STRONTIUM

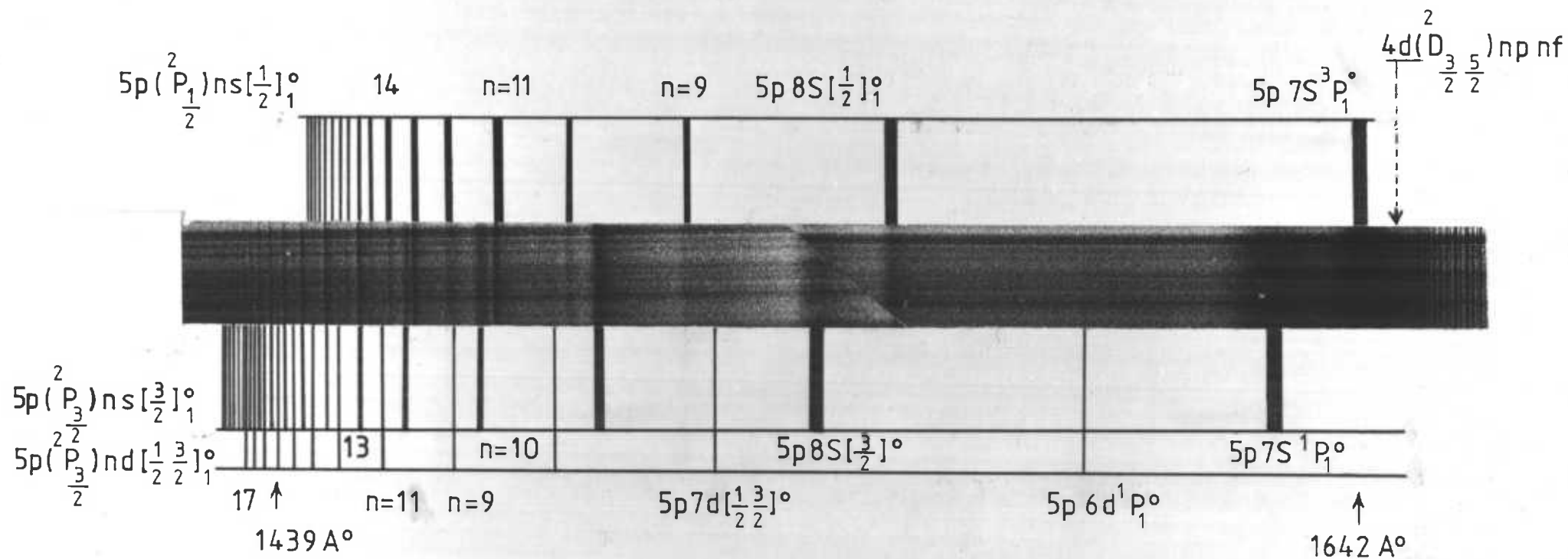


Fig. 3.4.1.

on the nd wavefunction. This phenomena has been discussed in detail by Connerade et al. (1979). We will consider all the series separately.

$$\underline{5p(^2P_{1/2})ns \left[\frac{1}{2} \right]_1^0 \text{ Series}}$$

This series is the strongest among the observed new transitions and has been detected up to $n=26$. In LS-coupling this is a $^3P_1^0$ series and a singly excited level $5s5p \ ^3P_1^0$ at 14504 cm^{-1} can also be regarded as the first member yielding $n^* = 1.41$, which is consistent with the higher members.

Garton and Codling (1968) reported a level at $1891 \text{ \AA}$ which is a perturber of the $4dnp, nf$ configuration and was assigned as $5p6s \ ^3P_1^0$. We confirm this assignment by extrapolating the higher members of this series. The wavelengths, wavenumbers and identifications are presented in Table (4.3.1) whereas the spectrum arranged into Rydberg series is reproduced in Fig.(4.3.1).

$$\underline{5p(^2P_{3/2})ns \left[\frac{3}{2} \right]_1^0 \text{ Series}}$$

This is also a strong and broad series. This series has been observed up to $n=27$ converging on the 70442.25 cm^{-1} limit. In LS-coupling this series can be designated $^1P_1^0$, and the singly excited level $5s5p \ ^1P_1^0$ at 21698 cm^{-1} can also be regarded as the first member yielding $n^*=1.50$. Garton and Codling (1968) assigned a perturber of the $4dnp, nf$ configuration at $1862 \text{ \AA}$ as $5p6s \ ^1P_1^0$, which fits very well with our present interpretation. The wavelengths and identifications are presented in Table (4.3.2).

$$\underline{5p(^2P_{3/2}) \text{ nd } \left[\frac{1}{2}, \frac{3}{2} \right]_1^0 \text{ Series}}$$

This is a very diffuse series and has been observed up to $n=18$ after which it merges with the $5p(^2P_{3/2})ns \left[\frac{3}{2} \right]_1^0$ series. The leading member of this series is $4d5p \ ^1P_1^0$, given by Garton and

TABLE 3.4.1

Spectrum of Sr I

$5s^2\,^1S_0 \rightarrow 5p(^2P_{1/2})ns\, [1/2]_1^0$

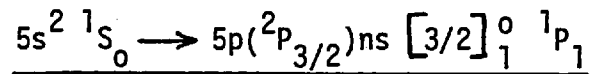
Series limit = 69640.79 cm⁻¹

n	λ(Å)	ν(cm ⁻¹)	n [*]
6 ≠	1891	52882	2.56
7	1642	60899	3.54
8	1552.08	64430	4.59
9	1512.84	66101	5.57
10	1490.36	67098	6.57
11	1476.61	67723	7.56
12	1468.80	68083	8.39
13	1461.10	68442	9.57
14	1457.07	68631	10.42
15	1453.07	68820	11.56
16	1450.72	68931	12.44
17	1448.50	69037	13.48
18	1446.81	69118	14.49
19	1445.38	69186	15.53
20	1444.42	69232	16.39
21	1443.47	69278	17.38
22	1442.71	69314	18.32
23	1442.05	69346	19.28
24	1441.50	69372	20.21
25	-	-	-
26	1440.59	69416	22.09

≠ Value reported by Garton and Codling (1968).

In LS coupling, this is a $^3P_1^0$ series. The singly excited level

$5s\,5p\,^3P_1^0$ at 14504 cm⁻¹ can also be regarded as the first member, yielding $n^* = 1.41$.

Spectrum of Sr I

Series limit = 70442.25 cm⁻¹

n	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	n [*]
6 [*]	1862	53706	2.56
7	1626	61486	3.50
8	1537.16	65055	4.51
9	1495.89	66850	5.53
10	1473.78	67853	6.51
11	1459.86	68500	7.52
12	1450.72	68931	8.52
13	1442.42	69328	9.52
14	1439.92	69448	10.51
15	1436.51	69613	11.50
16	1433.87	69741	12.51
17	1431.88	69838	13.48
18	1430.23	69919	14.48
19	1428.89	69984	15.48
20	1427.83	70036	16.45
21	1426.88	70083	17.47
22	1426.10	70121	18.49
23	1425.51	70150	19.39
24	1424.91	70180	20.45
25	1424.39	70205	21.53
26	1424.07	70221	22.29
27	1423.80	70235	22.99

* Value reported by Garton and Codling (1968). In LS coupling, this is a ${}^1P_1^0$ series. The singly excited level $5s5p \, {}^1P_1^0$ at 21698 cm⁻¹ can also be regarded as the first member, yielding n^{*} = 1.50.

Codling (1968) as the perturber of the principal series. This assignment was proposed as long ago as 1932 by Shenstone. The second member is missing due to the collapse of the 5d-wavefunction as discussed by Connerade et al. (1979). Assignments to ns, and nd series have been made by considering the residual part of the effective quantum numbers. Wavelengths, wavenumbers and identifications given below.

TABLE 3.4.3

Spectrum of Sr I

$$5s^2\,^1S_0 \rightarrow 5p(^2P_{3/2})nd\, [1/2,3/2]_1^0$$

$$\text{Series limit} = 70442.25\text{ cm}^{-1}$$

n	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	n^*
4	2429	41172	1.94
5	-	-	-
6	1587	63012	3.84
7	1516	65963	4.95
8	1486	67294	5.90
9	1468.8	68083	6.82
10	1455.25	68717	7.97
11	1448.50	69037	8.84
12	1443.47	69278	9.71
13	1438.89	69498	10.78
14	1435.66	69654	11.80
15	1433.19	69774	12.82
16	1431.04	69879	13.96
17	1429.52	69954	14.99
18	1428.30	70013	15.99

In LS coupling, this would be the $1P^0$ series.

CHAPTER IV

INNER SHELL EXCITATION IN Ag I, Au I and Mn I

4.1 Introduction

The simplest inner shell excitation spectra are those of elements which have closed subshells in the ground state. In noble gases, with ground state configurations $ms^2 mp^6 {}^1S_0$, optically allowed transitions are due to the promotion of the s-subshell electron to the p-orbitals:

$$ms^2 mp^6 {}^1S_0 \longrightarrow ms({}^2S_{1/2})mp^6 np {}^1P_1^o$$

which give Rydberg series converging on the $ms {}^2S_{1/2}$ level of the ion. These states lie above the first ionization threshold and therefore autoionize due to the interaction with the continua $mp^5 {}^2P \in s$ or $\in d$, and these resonances exhibit characteristic Beutler-Fano profiles.

At higher energy, another one electron transition is possible due to the promotion of an inner d-shell electron to the outer p and f orbitals, e.g.

$$(m-1)d^{10} ms^2 mp^6 {}^1S_0 \longrightarrow (m-1)d^9 ({}^2D_{3/2,5/2})ms^2 mp^6 np {}^1P_1^o$$

In this case there are many continua available for interaction with the high lying discrete state and the resultant spectrum becomes more complicated.

The complexity of atomic spectra further increases for elements with single outermost 's' electrons in the ground state, such as alkali, $mp^6 ms {}^2S_{1/2}$. The excitation of a single electron from the mp-subshell gives a mixture of overlapping $p \rightarrow s$ and $p \rightarrow d$ transitions. Connerade (1970) pointed out that the configurations $3p^5 3d, 3p^5 4s$ of K II; $4p^5 4d, 4p^5 5s$ of Rb II and $5p^5 5d, 5p^5 6s$

of Cs II tend to overlap in energy, so that strong mixing between the configurations with $(m+1)s$ and md electrons takes place. The Rydberg electron is incapable of distinguishing between the two configurations of the core so that instead of observing the single electron excitations

$$mp^6(m+1)s^2s_{1/2} \longrightarrow mp^5(m+1)s(1,3p)ns,nd$$

which obey the $\Delta\ell = \pm 1$ selection rules of the Rydberg electron, one observes a much more complex structure which can be described as

$$mp^6(m+1)s^2s_{1/2} \longrightarrow mp^5(m+1)sx(md)ns,nd$$

where $\{(m+1)s \times md\}$ is taken to signify all the $mp^5(m+1)s$ and mp^5md levels which contain any $mp^5(m+1)s$ character.

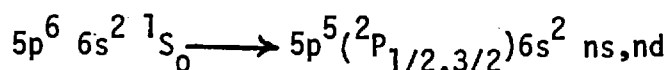
The complexity arises from the transitions obeying the usual $\Delta\ell = \pm 1$ selection rule for the Rydberg electron but with the additional possibility of $\Delta\ell = +2$ for a core electron. In inner shell excitation, these transitions may be regarded as double excitations, as have been for alkali metals. Connerade (1978) has discussed two types of double excitations, namely,

Type 1 - Double excitation which arises through mixing between two configurations of the same parity in the parent ion. This mixing is independent of the Rydberg electron and therefore gives rise to complete supernumerary Rydberg series.

Type 2 - Double excitation which arises through mixing after the Rydberg electron has been coupled to the ionic core. Since the mixing depends very much on what other configurations may occur close to the energy of a specific Rydberg state, double excitations produced in this way are strongly affected by the proximity in energy of single excitations. This process which may be described as the final excited state configuration interaction can perturb Rydberg series.

The best example was found in the absorption spectrum of Zn I by Mansfield and Connerade (1978) where a Rydberg series due to double excitation overlapped with terms of innershell excitation.

Excitations of type 2 are also observed in the inner shell spectra of the alkaline-earths and in particular Ba I. Instead of series converging on just two series limits, according to one electron excitation scheme



The 5p spectrum of Ba I is found to consist of 14 Rydberg series converging on 12 limits, Connerade et al. (1979). The complexity of the resulting structure is attributed to strong sd mixing, Connerade (1978).

The Spectra of Noble Metals

The d-subshell excitation spectra of the noble metals are of considerable interest from the standpoint of atomic spectroscopy because they are among the simplest alkali-type subvalence excitation spectra in the Periodic Table. Complexities may arise due to s-d mixing as was observed in alkali metals which result in final ionic state configuration interaction but are likely to be less pronounced in the noble metals, where the 'd' subshell has a much higher binding energy than the outermost 's' electron, so that s-d mixing becomes unlikely.

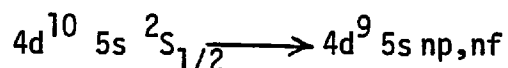
The absorption spectra due to excitation of a single electron from the 3d subshell in Cu I, 4d subshell in Ag I and the 5d subshell in Au I enable one to study the coupling of a single s electron to configurations with a single vacancy in the d-subshell. The spectra of 3d-excitation in Cu I has been reported by Tondello (1973) and in the present investigation we have observed the absorption due to

4d-excitation in Ag I and 5d-excitation in Au I, which completes this interesting family of spectra.

4.2 4d-excitation in Ag I

4.2.1 Summary

The absorption spectrum of Ag I in the range 700-2000 Å has been investigated. More than 60 new transitions have been found which are attributed to excitation of a single electron from the 4d-subshell.



A detailed identification of $4d^9 5s 5p$ configuration is compared with ab initio Hartree-Fock calculations.

4.2.2 Introduction

The silver atom has a single 's' electron outside the completely filled d shell in the ground state; therefore it is easily excited due to its lower binding energy. The spectrum is therefore expected to be very simple, as for alkali elements. The emission spectra were first studied by Blair (1930) and Rasmussen (1940) who classify most of the intense lines down to 2000 Å. Shenstone (1940) made a detailed investigation of the arc spectra of Ag I down to 1500 Å and identified all the lines. The absorption studies were initiated by Paul (1937) in the region 800 to 1430 Å using a resistively heated tungsten furnace and the Lyman continuum as the background source. Paul (1937) observed three very intense lines at 1507 Å, 1515 Å and 1550 Å and also proposed a series due to the $^2S-^2P$ transition. Shenstone (1940) pointed out that Paul's observations include impurity lines and the proposed Rydberg series is also not real. Recently, high resolution absorption spectra of Ag I in the u-v region have been obtained by Brown and Ginter (1977) on a 6.6m spectrograph in the 3rd and 4th order using microwave excited Ar I as background

continuum and extended the principal series to $n=71$ yielding a more accurate value of the first ionization potential.

The relative photoionization cross section in the region 1600-1200 Å has been measured by Tegeder and Lincke (1971). The photoelectron spectroscopy and angle resolved u.v. photoemission spectroscopy of Ag I, in which excitation from the 4d bands is involved, have been studied by Norris and Williams (1976), Batlye and Huffner (1977) and Hansson and Foldstrom (1977). Semi-empirical calculations have also been reported by Martin and Sugar (1969) who analysed the $4d^9 5s5p$ configuration using Shenstone's (1940) data.

Johansen and Lincke (1975) re-examined the arc spectrum of Ag I and remarked that the $4d^9 5s5p$ configuration is now fully analysed.

The purpose of the present work was to extend the absorption spectra of Ag I above the first ionization threshold where numerous Rydberg series were expected, due to excitation of a single electron from the 4d subshell and also to compare our results with ab initio calculations by Connerade and Mansfield (1978, private communication).

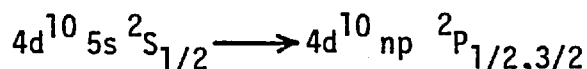
4.2.3 Results

In the present studies we have covered the region 750-1800 Å using synchrotron radiation as the background continuum. A windowless containment system was used as the absorption cell. About 5 grams of spectroscopically pure silver wire was loaded into a tantalum boat and a molybdenum tube 0.3 m thick and 40 cm long was used to contain the vapour. The sample was heated with induction furnace at a temperature of about 1400°C corresponding to an Ag vapour pressure around 2 Torr. Spectra were recorded in the first order of a 1 m normal incidence spectrograph equipped with a 1200 lines/mm grating.

4.2.4 Analysis

The absorption spectrum of Ag I between 900-1700 Å is shown in Figure (4.2.3) densitometer traces of this region are also reproduced in Figure(4.2.1) which shows the variation of line profiles with changing vapour pressures. We have recorded the low vapour pressure spectra to get the profiles of the broad features which tends to saturate at higher vapour pressures. The advantage of higher vapour pressure spectra is to get more series members near the series limit.

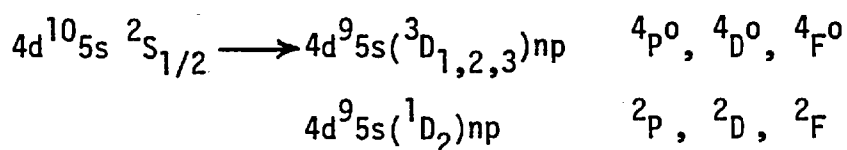
The ground state of silver is $4d^{10}5s^2S_{1/2}$. Excitation of a 5s electron to 'p' orbitals



This is the principal series which converge on the ground level of Ag II. Brown and Ginter (1977) have extended this series up to $n=71$ and determined a more accurate value of the first ionization potential of silver $61106.56 \pm 0.06 \text{ cm}^{-1}$. In the present investigation, we do observe these transitions but they are very weak (see Fig.4.2.1) and our measurements are in quite good agreement with those of Brown and Ginter (1977).

4.2.4a $4d^9 5snp, nf$ Configurations

The excitation of a single electron from the d-subshell corresponds to the transition which lies above the first ionization threshold. All the levels are autoionized due to the interaction with the $4d^{10}\epsilon p$ continuum. Thus, the configurations arising from the excitation of the inner 4d electron to a 'p' orbital in Ag I is



Similar configurations will arise when an electron from the

4d SUBSHELL EXCITATION SPECTRUM OF AgI

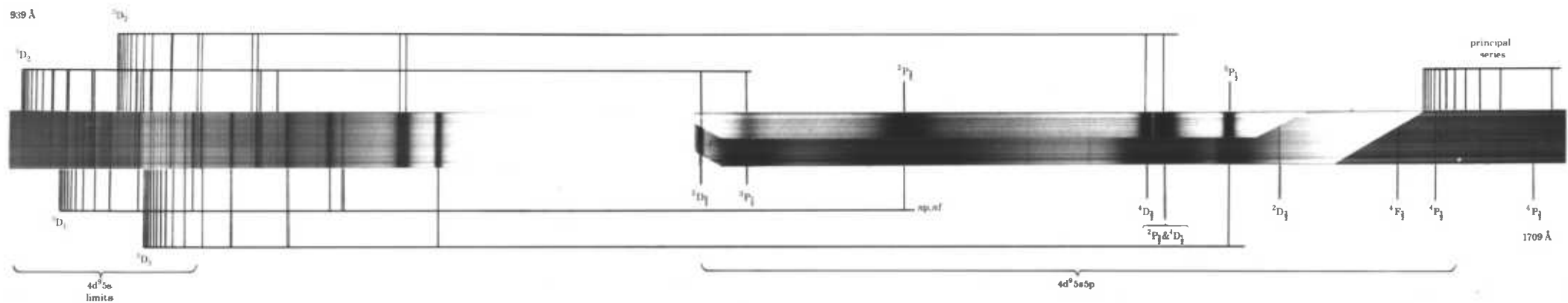


Fig. 4.2.1

4d shell is promoted to the 'f' orbitals. These configurations converge on the excited states $4d^9 5s(^3D)$ and $4d^9 5s(^1D)$ of Ag II. The 3D_3 is at $100270.46 \text{ cm}^{-1}$, 3D_2 at 101847.56 , 3D_1 at 104845.26 and 1D_2 at $107152.26 \text{ cm}^{-1}$ above the ground state $^2S_{1/2}$ of Ag I. Various transitions are expected from the ground state $4d^{10} 5s^2 S_{1/2}$ to the final bound states according to the dipole selection rules.

The $4d^9 5s np$ configuration gives rise to terms

$$4d^9 5s \left[^3D \right] + p \left[^4P, ^4F, ^4D, ^2D, ^2P \right] \quad J = \frac{1}{2} \text{ or } \frac{3}{2}$$

$$4d^9 5s \left[^1D \right] + p \left[^2P, ^2D \right]$$

We have written all the terms in order of increasing energy. We list only $J=1/2$ or $3/2$ levels omitting $(^3D)^2F$ and $4d^9 5s(^1D)^2F$.

All the states from the configurations $4d^9 5s n l$ fall above the first ionization limit and can interact with the adjacent continuum. As a result, lines will appear broadened by autoionization and the broadening will be larger the nearer the upper states are to the first ionization limit.

4.2.4b $4d^9 5s 5p$ Configuration

Considering first only the $4d^9 5s 5p$ configuration, this will give terms $^4P_{1/2,3/2}^o$, $^4F_{3/2}$, $^4D_{1/2,3/2}$, $^2D_{3/2}$ and $^2P_{1/2,3/2}$ built on the $4d^9 5s(^3D)$ core and $^2P_{1/2,3/2}$ and $^2D_{3/2}$ built on the $4d^9 5s(^1D_2)$ core. All the levels of this configuration lie above the first ionization limit except $4d^9 5s(^3D_3)^4P_{1/2,3/2,5/2}$. We have observed all the levels corresponding to this configuration which are marked in Fig.(4.2.1) which shows the overall spectrum due to 5d-subshell excitation (930-1720 Å). The principal series, which is very weak, has also been marked.

Calculations of level structure in intermediate coupling for the $4d^9 5s 5p$ configuration were reported by Martin and Sugar (1969),

who used a semi-empirical average of configuration approach. In such an approach the magnitude of the Slater-Condon integrals are treated as adjustable parameters and are obtained by comparison with experiment. Discrepancies were found among the $(5s5p\ ^1P)$ based levels and were attributed to perturbation by the configuration $4d^8 5s^2 5p$.

Connerade and Mansfield (1978) performed ab initio calculations of the $4d^9 5s5p$ configuration in both average of configuration and LS-dependent Hartree-Fock schemes using the MCHF-72 code of Froese-Fischer (1972), without including configuration mixing with double d-vacancy configurations. The Slater-Condon parameters were then used to diagonalise the $d^9 sp$ energy matrix in intermediate coupling. Connerade and Mansfield (1978) discovered that to obtain the realistic estimates of the Slater-Condon integrals, the $5s5p\ ^1P$ based terms must be calculated independently in the Hartree-Fock routine.

Every allowed transition to $4d^9 5s5p$ has been found in the present investigation and is here compared with intermediate coupling level structure calculations, Connerade and Mansfield (1978), using unscaled LS-dependent Hartree-Fock estimates of the Slater-Condon integrals. In Fig(4.2.3) we reproduce the low magnification densitometer trace of Ag I absorption spectrum showing the broad structure attributed to 4d-5p excitation and comparison with calculations by Connerade and Mansfield (1978).

The intensities of the transitions were estimated by Connerade and Mansfield (1978) from the 2P content of the upper levels in intermediate coupling and are also in quite good agreement with observations.

The energy spanned by the $4d^9 5s5p$ configuration is smaller than calculated even on the basis of LS-dependent Hartree-Fock parameters (Fig. 4.2.3). This discrepancy is not large but suggests a systematic depression of the $(5s5p\ ^1P)$ based levels.

4d SUBSHELL EXCITATION SPECTRUM OF AgI

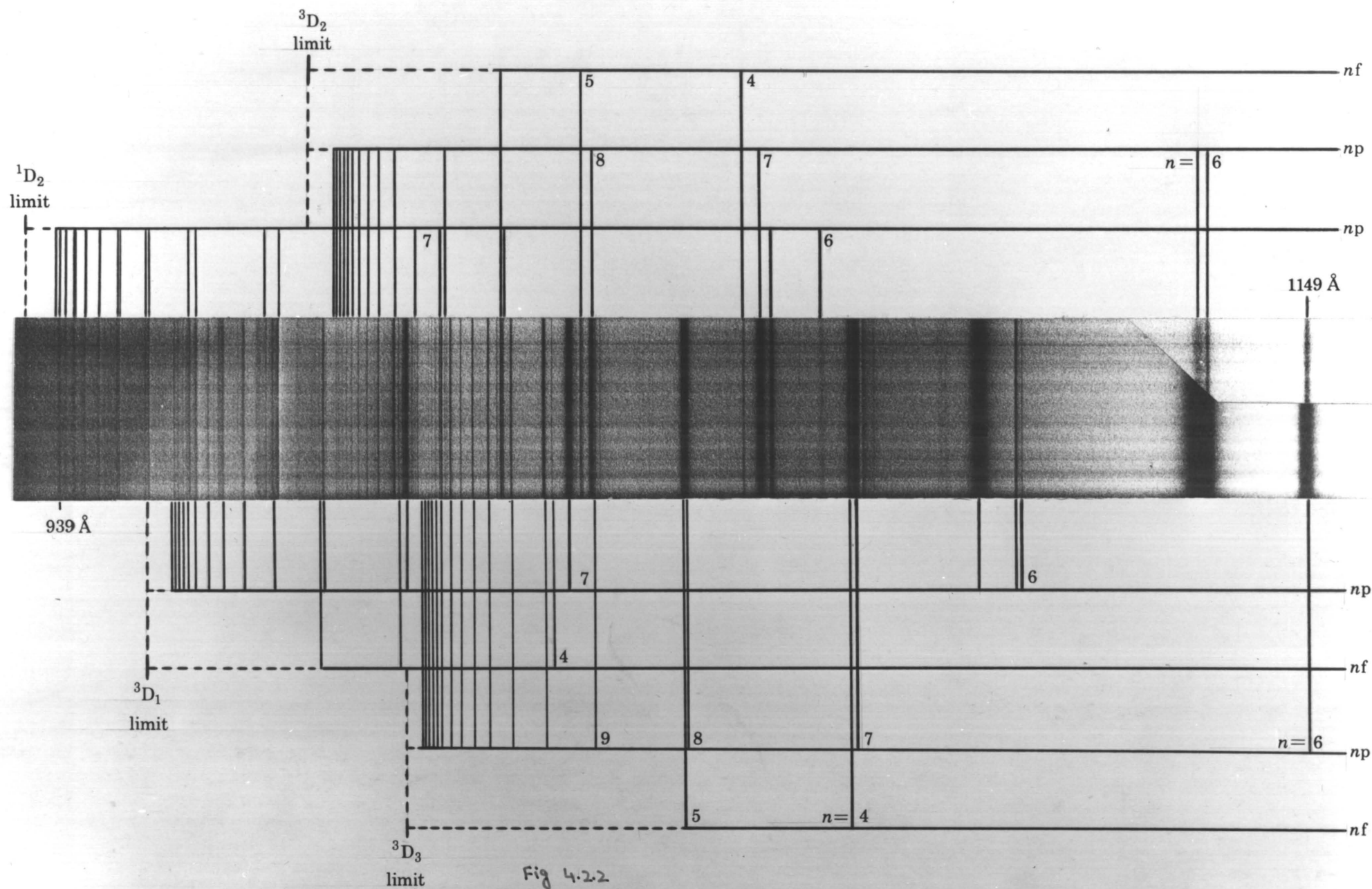


Fig 4.2.2

The observed levels in $4d^95s5p$ configuration are compared below with the intermediate coupling calculations by Connerade and Mansfield (1978) using unscaled LS-dependent Hartree-Fock parameters.

$\lambda/\text{\AA}$	<u>Expt.</u> ν/cm^{-1}	<u>Calc.</u> ν/cm^{-1}	<u>Identification</u>
1709.27	58505	58285	$(5s5p\ ^3P) 4d^9\ ^4P^0_{3/2}$
1652.01	60529	60110	$(5s5p\ ^3P) 4d^9\ ^4P^0_{1/2}$
1632.86	61242	61183	$(5s5p\ ^3P) 4d^9\ ^4F^0_{3/2}$
1574.05	63531	63684	$(5s5p\ ^3P) 4d^9\ ^2D^0_{3/2}$
1548.60	64574	64180	$(5s5p\ ^3P) 4d^9\ ^2P^0_{1/2}$
1515.60	65980	65725 65814	$(5s5p\ ^3P) 4d^9\ ^2P^0_{3/2}$ and $^4D^0_{1/2}$
1507.37	66341	66453	$(5s5p\ ^3P) 4d^9\ ^4D^0_{3/2}$
1388.22	72035	76171	$(5s5p\ ^1P) 4d^9\ ^2P^0_{3/2}$
1306.52	76539	80308	$(5s5p\ ^1P) 4d^9\ ^2P^0_{1/2}$
1283.11	77935	81981	$(5s5p\ ^1P) 4d^9\ ^2D^0_{3/2}$
- - - - -			

We have arranged all the observed transitions into Rydberg series, one intense series converging on the $4d^95s(^3D_3)$ limit, two series converging to $4d^95s(^3D_2)$, one strong series converging on $(^3D_1)$ which shows 'Beutler-Fano' resonances above the $(^3D_2)$ limit and two strong series converging on the $(^1D_2)$ limit. The $4d^95s(^3D_{3,2,1}, ^1D_2)nf$ series have also been found.

4.2.4c $4d^9 5s(^3D_3)np$ Series

This is the most intense of the observed series. The line at $1548.60 \text{ \AA}$ acts as an apparent first member yielding $n^* = 1.75$, but is, in fact, a transition to $(^3P)^2P_{1/2}$. With Martin and Sugar's (1969) values for the parameters, this transition should be assigned $^4D_{1/2}$. Connerade's (1978) calculations suggest that a $^2P_{1/2}$ assignment is marginally better.

Shenstone (1940) has made an accurate measurement for this line, in emission, and the reversal width was measured as $4 \text{ \AA}$. The second members of this series at $1148.84 \text{ \AA}$ has also been observed by Paul (1937) and is listed by Johannsen and Lincke (1975) as a transition to $4d^9 5s6p$, which is in consistent agreement with our present identification. According to Jk coupling only one np series to 3D_3 is accessible

$$4d^9 5s(^3D_3)np [2]_{3/2}$$

which seems a more appropriate coupling scheme for silver.

This series has been observed up to $n=22$ having a smooth course of quantum defects. The wavelengths in $\text{\AA}$, the value of the level in cm^{-1} and the Rydberg denominator $n^* = (R/T)^{1/2}$ are reported in Table (4.2.1).

4.2.4d $4d^9 5s(^3D_2)np$ Series

This is a strong and broad series having two components up to $n=11$, afterwards the two components merge together. The leading members of this series are $1515.60 \text{ \AA}$ and $1507.37 \text{ \AA}$.

The line at $1515.60 \text{ \AA}$ was measured by Shenstone (1977) in emission and the reversal width was measured as $17 \text{ \AA}$. The second member at $1132.09 \text{ \AA}$ is listed by Paul (1937) and Johannsen and Lincke (1975) as a transition to $4d^9 5s5p$, which is in agreement with our

interpretation. The assignment in Ls coupling for the leading members is $5s5p(^3P)4d^9\ ^2P_{3/2}$.

In Jk coupling (Racah (1942) and Cowan and Andrew (1965)) the accessible series are

$$4d^9 5s(^3D_2)np \begin{bmatrix} 2 \end{bmatrix}_{3/2}, \begin{bmatrix} 1 \end{bmatrix}_{3/2,1/2}$$

Assuming the $\begin{bmatrix} 1 \end{bmatrix}_{3/2,1/2}$ series are merged, the Racah (1942) formula yields

$$(^3D_3)np \begin{bmatrix} 2 \end{bmatrix} \quad f_2 = 0.175$$

$$(^3D_2)np \begin{bmatrix} 1 \end{bmatrix} \quad f_2 = 0.175$$

Thus the longer wavelength series is $(^3D_2)np \begin{bmatrix} 1 \end{bmatrix}_{1/2,3/2}$, while the shorter wavelength series is $(^3D_2)np \begin{bmatrix} d \end{bmatrix}_{3/2}$. This interpretation is consistent with the interpretation of the 1515.60 Å line as merged transitions to $J=1/2$ and $J=3/2$ upper levels. This line is explained as a mixture of $^4D_{1/2}$ and $^2P_{3/2}$ terms. The line at 1507.37 Å is explained as $^4D_{1/2}$.

These series have been observed up to $n=20$ and the wavelength in Å, the value of the level in cm^{-1} and the Rydberg denominator $n^* = \sqrt{\frac{R}{T}}$ are reported in Table (4.2.2).

4.2.4e $4d^9 5s(^3D_1)np$ Series

The leading member of this series is a broad feature at 1388.22 Å and is described as $5s5p(^1P)4d^9\ ^2P_{3/2}$ according to calculations by Connerade et al. (1978). The $n=6$ member is split into three components rather than two components. According to Jk coupling the following series are accessible :

$$4d^9 5s(^3D_1)np \begin{bmatrix} 0 \end{bmatrix}_{1/2} \quad f_2 = -0.25$$

$$4d^9 5s(^3D_1)np \begin{bmatrix} 2 \end{bmatrix}_{3/2} \quad f_2 = -0.025$$

$$4d^9 5s(^3D_1)np \begin{bmatrix} 1 \end{bmatrix}_{1/2,3/2} \quad f_2 = +0.125$$

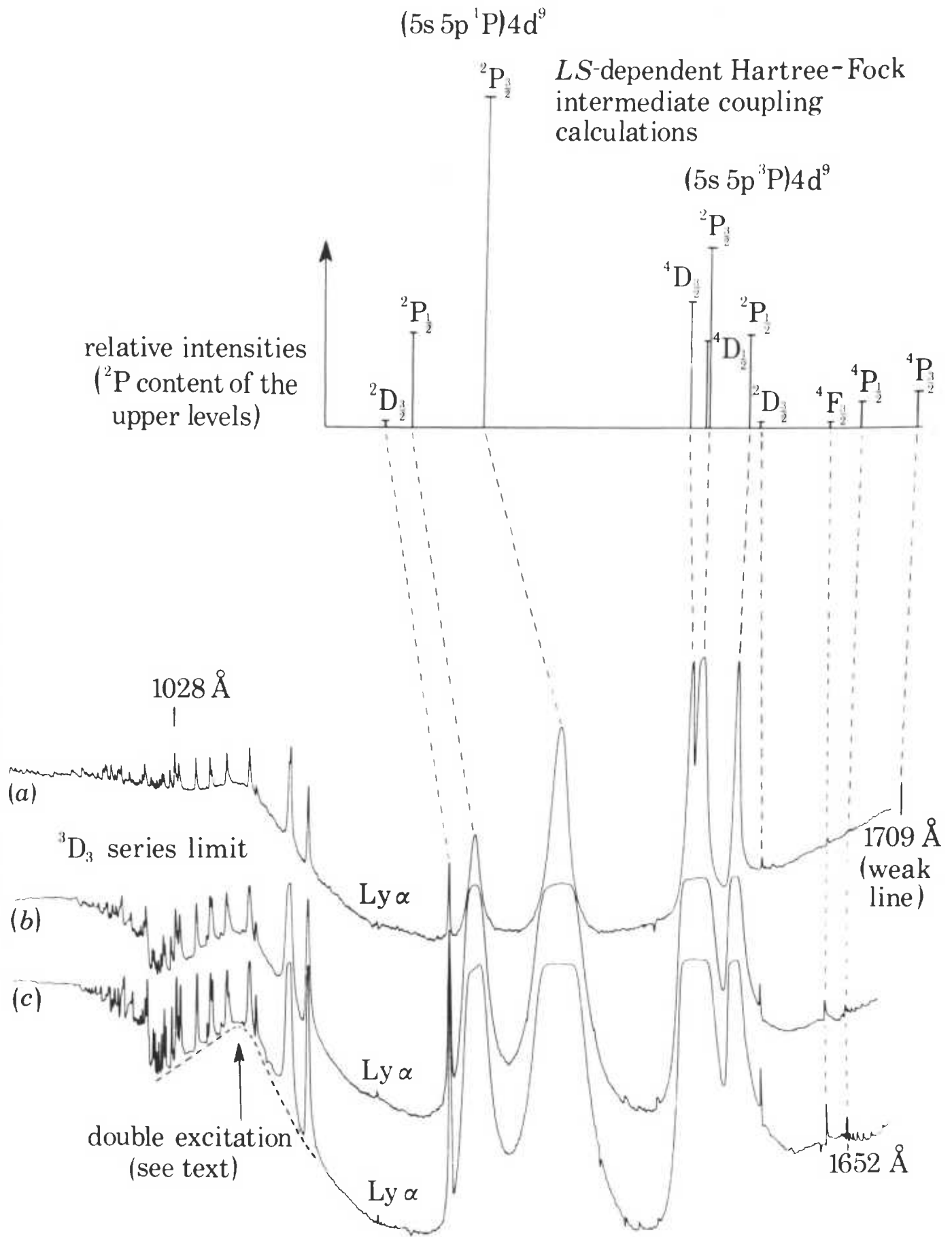


Fig 4.2.3

which accounts for the observation of three members at $n=6$. The higher members are easy to pick out even in the overlapped region and show Fano-type resonance above the $4d^9 5s(^3D_2)$ limit. This series has been observed up to $n=18$ and wavelengths are collected in Table (4.2.3).

4.2.4f $4d^9 5s(^1D_2)np$ Series

This series shows doublet components which are resolved up to $n=11$. The leading members are at $1306.52 \text{ \AA}$ described as $(5s5p^1P)4d^9 2P_{1/2}^0$ and at $1283.11 \text{ \AA}$ assigned as $(5s5p^1P)4d^9 2D_{3/2}^0$. According to Jk coupling the accessible series are

$$4d^9 5s(^1D_2)np \quad [1]_{1/2,3/2} \quad f_2 = -0.175$$

$$4d^9 5s(^1D_2)np \quad [2]_{3/2} \quad f_2 = +0.175$$

in order of increasing energy. This is consistent with the interpretation of the line at $1283 \text{ \AA}$ as a transition to a level with $J=3/2$. The transition at $1388 \text{ \AA}$ together with one at $1306 \text{ \AA}$ can be considered as the leading members of the series which merge into $4d^9 5s(^1D_2)np \quad [1]_{1/2,3/2}$ for $n > 6$.

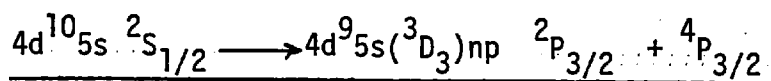
This series also shows asymmetric resonances above the $(^3D_1)$ limit and it is observed up to $n=17$. The identifications and wavelengths are presented in Table (4.2.4).

In addition to the np series we have also identified the nf series converging on $4d^9 5s(^3D_3)$, $4d^9 5s(^3D_2)$ and $4d^9 5s(^3D_1)$ levels of the ion. The assignment was based on the residual quantum defect as has been reported in the d -subshell excitation of Zn, Cd and Hg by Garton and Connerade (1969).

4.2.5 Double Excitation Series

At higher energy than the $4d^9 5s$ threshold we observe many transmission windows which are mostly too weak for accurate measurement

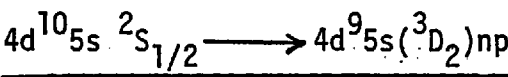
TABLE 4.2.1

4d Excitation Spectra of Ag I

$$\text{Limit} = 100270.46 \text{ cm}^{-1}$$

n	$\lambda/\text{\AA}$	ν/cm^{-1}	n^*
5	1548.60	64574	1.75
6	1148.84	87044	2.87
7	1072.80	93214	3.94
8	1044.05	95781	4.94
9	1028.93	97188	5.97
10	1020.33	98008	6.96
11	1014.80	98541	7.97
12	1010.93	98919	9.01
13	1008.32	99175	10.01
14	1006.26	99378	11.09
15	1004.92	99510	12.02
16	1003.82	99619	12.98
17	1002.92	99709	13.98
18	1002.15	99786	15.05
19	1001.53	99847	16.09
20	1001.01	99900	17.20
21	1000.59	99941	18.25
22	1000.26	99974	19.25

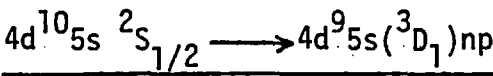
TABLE 4.2.2



Limit = 101847.56 cm⁻¹

n	$\lambda/\text{\AA}$	ν/cm^{-1}	n*
5	1515.60)	65980	1.75
	1507.37)	66341	1.76
6	1132.09)	88332	2.85
	1130.63)	88446	2.87
7	1057.76)	94539	3.88
	1056.84)	94621	3.90
8	1028.93)	97188	4.85
	1028.25)	97253	4.89
9	1013.45)	98673	5.88
	1013.10)	98707	5.91
10	1004.57)	99545	6.90
	1004.21)	99581	6.96
11	999.11)	100089	7.90
	998.85)	100115	7.96
12	995.19	100483	8.97
13	992.57	100749	9.99
14	990.69	100939	10.99
15	989.22	101090	12.03
16	988.10	101205	13.06
17	987.26	101291	14.04
18	986.64	101354	14.91
19	986.02	101418	15.98
20	985.54	101467	16.99

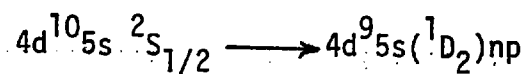
TABLE 4.2.3



Limit = 104845.26 cm⁻¹

n	λ/Å	ν/cm ⁻¹	n*
5	1388.22	72035	1.83
6	1101.07)	90821	2.80
	1099.99)	90910	2.81
	1093.70)	91433	2.86
7	1024.61	97598	3.89
8	997.25	100276	4.90
9	983.30	101698	5.91
10	974.86	102579	6.96
11	969.84	103110	7.95
12	966.32	103486	8.99
13	963.92	103744	9.98
14	961.90	103961	11.14
15	960.72	104088	12.04
16	959.69	104200	13.04
17	958.90	104286	14.01
18	958.13	104370	15.19

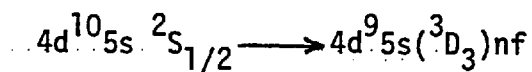
TABLE 4.2.4



$$\text{Limit} = 107152.26 \text{ cm}^{-1}$$

n	$\lambda/\text{\AA}$	ν/cm^{-1}	n^*
5	1306.52)	76539	1.89
	1283.11)	77935	1.94
6	1067.09)	93713	2.86
	1058.76)	94450	2.94
7	1003.12)	99689	3.83
	999.11)	100089	3.94
8	975.75)	102485	4.85
	973.77)	102694	4.96
9	961.90)	103961	5.86
	960.90)	104069	5.97
10	953.86)	104837	6.88
	953.41)	104887	6.96
11	949.00)	105374	7.86
	948.61)	105417	7.95
12	945.46	105769	8.91
13	943.08	106035	9.91
14	941.26	106240	10.97
15	939.95	106388	11.99
16	939.05	106491	12.88
17	938.25	106582	13.87

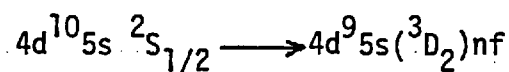
TABLE 4.2.5



$$\text{Limit} = 100270.46 \text{ cm}^{-1}$$

n	$\lambda/\text{\AA}$	ν/cm^{-1}	n*
4	1071.83	93299	3.97
5	1043.58	95824	4.97
6	1028.93	97111	5.97

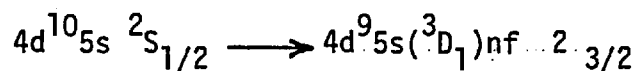
TABLE 4.2.6



$$\text{Limit} = 101847.56 \text{ cm}^{-1}$$

n	$\lambda/\text{\AA}$	ν/cm^{-1}	n*
4	1053.99	94878	3.97
5	1026.57	97412	4.97
6	1012.42	98774	5.98

TABLE 4.2.7



$$\text{Limit} = 104845.26 \text{ cm}^{-1}$$

n	$\lambda/\text{\AA}$	ν/cm^{-1}	n*
4	1021.58	97887	3.97
5	996.00	100402	4.97
6	982.70	101760	5.96

and are similar in appearance to transmission windows above the $3d^9 5s$ threshold in Rb I (Connerade and Mansfield, 1978). These transmission windows ~~which~~ have the weak and diffuse appearance characteristic of simultaneous excitation of two electron from different subshells. Thus this structure can be attributed to simultaneous excitation of one 4d and one 5s electron.

4.3 5d-Excitation in Gold

4.3.1 Introduction

Gold has a single valence electron outside the filled 5d shell, therefore the excited states of the s electron correspond to systems of terms of the same type as in the case of atoms of the alkali metals. As the binding energy of 's' and 'd' electrons are approximately the same, new states are possible due to the excitation of a 'd' electron.

Early classifications in the arc spectrum of Gold were made by Thorsen (1923), who found the sharp and diffuse series and McLennen and McLay (1931), who studied extensively the $5d^9 6s n x$ configuration. Platt and Sawyer (1941) observed the spectrum in the region 600-10,000 Å and reported 2000 new lines. Ehrhardt and Davis (1971) reinvestigated the spectra of Au I in the region 400-9600 Å and report an accurate line list along with information on the hyper-fine structure of lines in Au I.

Absorption spectra were first observed by Garton (1962), who found some autoionization resonances in the ultraviolet region but neither wavelengths nor assignments are given. Tegeder and Lincke (1971) determined the relative photoionization cross section in the spectral region 1200 to 1600 Å using crossed beam photoelectric technique. However, no identification was proposed by Tegeder and Lincke (1971) who simply give a line list.

More recently Brown and Ginter (1978) have observed the high resolution absorption spectrum in the region 1300-1900 Å using third and fourth orders of a 6.6 m vacuum spectrograph and microwave excited Xenon and Krypton lamps as background continuum. Apart from the extension of the principal series, they also observed $5d \rightarrow 6p$ transitions and made tentative assignments based on a comparison with parametric calculations by Martin and Sugar (unpublished).

Apart from the above mentioned investigations, there do not appear to have been any absorption studies below 1300 Å where the bulk of the discrete structure due to $5d \rightarrow np, nf$ excitation is expected to occur.

The 3d excitation spectrum in Cu I has been studied by Tondello (1973), and the 4d excitation spectrum in Ag I has been the subject of the previous sections, and the 5d-excitation in Au I completes this family of spectra, which provide useful data to compare d-subshells in Atoms and Solids. The properties of the d-subshells are more easily studied in the atom than in the solid because the different excitation processes are more easily separated from each other in energy.

4.3.2 Results

We have observed the absorption spectra of Au I between 950-1350 Å finding 57 new transitions corresponding to the excitation of a single electron from the 5d-subshell. The spectra were recorded in the first order of a 1 m normal incidence spectrograph equipped with a 1200 lines/mm grating. Approximately ten grams of pure gold metal was placed in a tungsten boat. The furnace tube was of molybdenum 0.3 mm thick and 30 cm long and was heated to temperatures ranging from 1300 to 1700°C.

It was discovered on opening the furnace system that the molybdenum tube and the tantalum liner had been attacked by the metal,

a difficulty which was not encountered for Ag I but which also occurs for Cu I.

4.3.3 Analysis

The absorption spectrum of Au I in the region 930-1310 Å is reproduced in Fig.(4.3) showing the $5d^9 6s(^1,^3D)np$ and nf series. The ground state configuration of Au I is $5d^{10} 6s^2 S_{1/2}$ and excitation of the outermost 's' electron to 'p' orbitals yield principal series converging on the ground state 1S_0 of the ion Au II. Absorption spectra in the region 1300-1900 Å have been studied by Brown and Ginter (1978) and their observations include $5d^{10} 6s^2 S_{1/2} \rightarrow 5d^{10} np^2 P^0_{3/2,1/2}$ transitions for $n=7$ through to $n=40$, $5d^9 6s^2 D_{5/2} \rightarrow np^2 P^0_{3/2}$ for $n=8$ through to $n=12$ and transitions from $6s^2 S_{1/2}$ to levels associated with the interloper configurations $5d^9 6s 6p$ and $5d^8 6s^2 6p$. Brown and Ginter (1978) determined the accurate value of the ionization potential of Au I $74408.88 \text{ cm}^{-1} \pm 0.17 \text{ cm}^{-1}$ from the $np^2 P$ series. Perturbation was also detected in both of the $^2P^0$ series at $n=7$ and $n=8$ and again between $n=10$ and $n=11$.

In the present experiment, we also found the principal series but with very low intensity because of short path lengths $\approx 40 \text{ cm}$ use by us, and our measured wavelengths are in good agreement with those of Brown and Ginter (1978).

4.3.4a $5d^9 6s np, nf$ Configurations

The excitation of a single electron from the d-subshell corresponds to the transition which lies above the first ionization limit. All the states from the configuration $3d^9 6s n l$ fall above the first ionization limit and can interact with the accompanying continua, $5d^{10} \epsilon p^2 P^0$. As a result, lines will appear broadened due to autoionization and the broadening will be larger the nearer the upper states are to the first ionization limit.

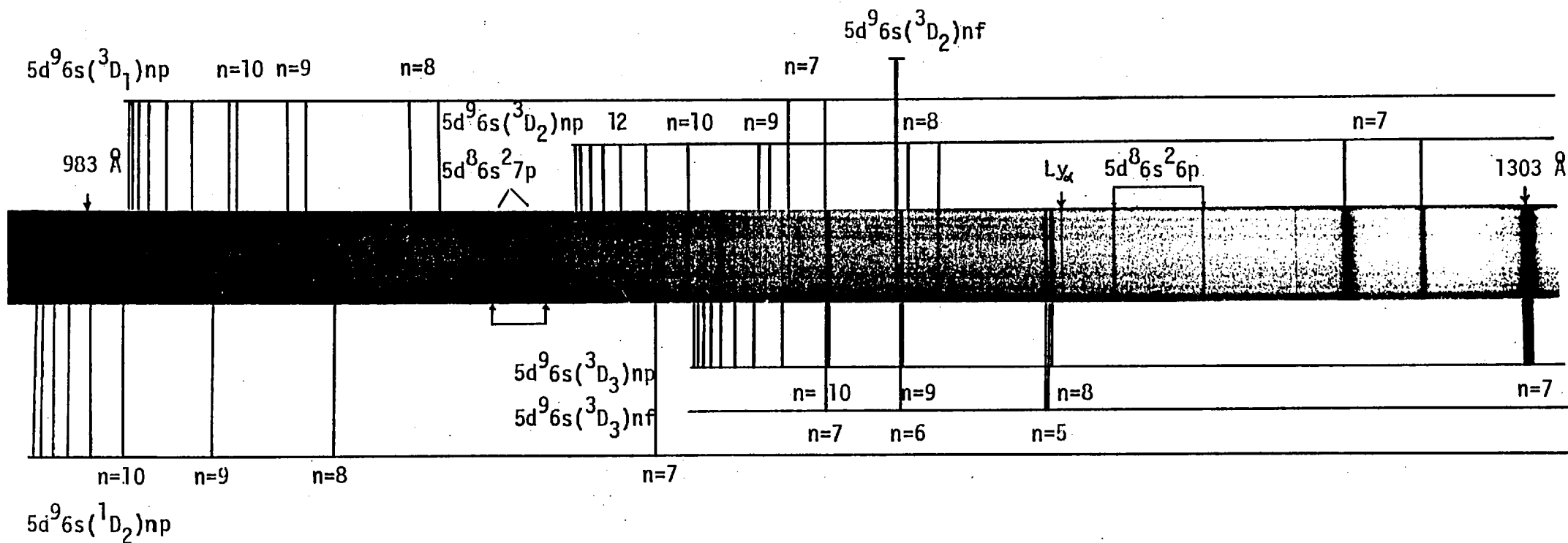
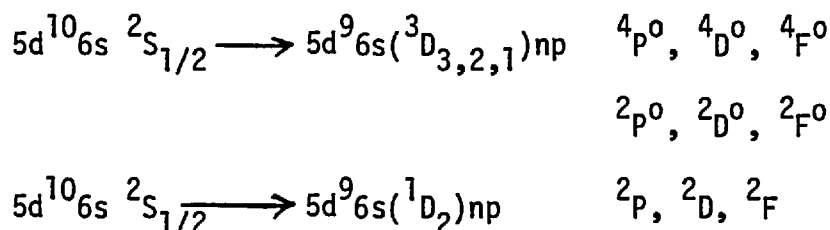


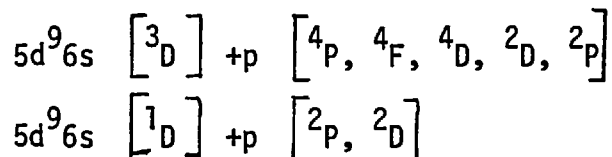
FIGURE 4.3.1 - The absorption spectrum of Ag I in the vacuum ultraviolet, showing the $5d^9 6s(^1,^3D)np$ and nf series.

Thus the configuration arising from the excitation of the inner 5d-electron to a 'p' orbital in Au I is



Similar configurations will arise by promoting an electron from the 5d-shell to the 'f' orbitals. These configurations converge onto the excited states $5d^9 6s(^3D)$ and $5d^9 6s(^1D)$ of Au I. The 3D_3 is at 89447.88 cm^{-1} , 3D_2 at 92048.28 cm^{-1} , 3D_1 at $102173.38 \text{ cm}^{-1}$ and 1D_2 is at $104024.68 \text{ cm}^{-1}$ above the ground state $^2S_{1/2}$ of Au I.

Various transitions are expected from the ground state $5d^{10}6s \ ^2S_{1/2}$ to the final bound states according to the dipole selection rules; thus the $5d^9 6snp$ configuration gives the terms

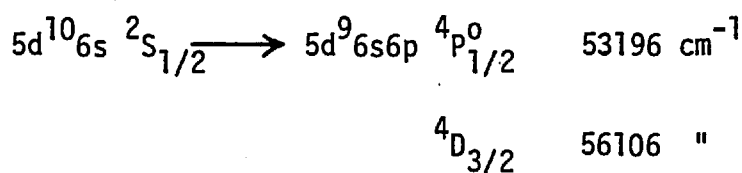


We have listed only $J=1/2$ or $3/2$ levels omitting $(^3D)^2F$ and $5d^9 6s(^1D)^2F$.

4.3.4b $5d^9 6s6p$ Configuration

This configuration will give terms $^4P_{1/2,3/2}$, $^4F_{3/2}$, $^4D_{1/2,3/2}$, $^2P_{1/2,3/2}$, $^2D_{3/2}$ built on the $5d^9 6s(^3D)$ core and $^2D_{3/2}$ and $^2P_{1/2,3/2}$ built on the $5d^9 6s(^1D)$ core. All the levels of this configuration lie below the first ionization limit in contrast to the situation in Ag I where all the levels due to $4d^9 5p$ configuration lie above the first ionization limit except the $^4P_{1/2,3/2}$ levels.

Brown and Ginter (1978) attribute seven lines to the transitions



$5d^{10}6s\ ^2S_{1/2}$	$\longrightarrow$	$5d^96s6p\ ^2P_{3/2}$	58846 cm^{-1}
		$^2P_{1/2}$	60979 "
		$^2D_{3/2}$	61564 "
		$^2P_{1/2}$	62569 "
		$^2P_{3/2}$	63006 "

in order of increasing energy. Platt and Sawyer (1941) observed levels which were tentatively correlated with $5d^96s6p$ ($J=1/2$ and $J=3/2$) configuration.

The analysis given by Brown and Ginter (197) is based on intermediate coupling calculations of the $J=1/2$ and $J=3/2$ levels by Martin and Sugar (unpublished) who have apparently treated the Slater-Condon integrals as adjustable parameters, fitting them as well as possible to the best possible data.

Connerade (private communication) performed single configuration Hartree-Fock calculations of the configuration $5d^96snp$ paying special attention to the possible LS dependence of Slater-Condon parameters for $(6snp\ ^1,^3P)5d^9$ and pointed out that there is a significant change in the magnitude of the Slater-Condon parameters between the configuration average and $(6snp\ ^1P_1)$ based levels. The effect of the LS dependence on calculations of $5d^96s6p$ structure in Au I appears to be much less pronounced than for the $4d^95s5p$ configuration of Ag I.

Mansfield (private communication) performed calculations with full configuration mixing in a Hartree-Slater scheme using the 'Zealot' suite of programmes (Cowan, 1978) with the following combinations.

- (1) $5d^96s6p \times 6s7p \times 6s8p \times 6s5f$
- (2) $5d^96s6p \times 6p6d \times 5d^86s^26p$
- (3) $5d^96s6p \times 6s7s \times 5d^86s^26p$

A large change in energies and intensities is produced by the introduction of $5d^8 6s^2 6p$ configuration in the calculations. Mansfield (private communication) also performed calculations with the same scheme for the corresponding configuration in Ag I and these indicate that the influence of $5d^8 6s^2 6p$ on $5d^9 6s 6p$ is much larger than for the corresponding configurations in Ag I, because the configurations with two vacancies in the 4d subshell lie relatively much higher in energy for Ag I than configurations with two vacancies in the 5d-subshell of Au I. All the observed lines were arranged into Rydberg series except two strong lines at $1250 \text{ \AA}$ and $1228 \text{ \AA}$. These lines were also observed by Tegeder and Lincke (1971). According to the calculations, these can be clearly regarded as a transition involving double vacancy production, $5d^8 6s^2 6p$.

In Tables (4.3.1) and (4.3.2) we give a comparison between the results of Mansfield's calculations and experiment for $n=6$ and $n=7$ levels. For comparison we also include the parametric results of Martin and Sugar (1978), which are somewhat different.

We have used jj coupling for the whole configuration $5d^9 6s 6p$, which is more appropriate than LS coupling.

In Fig.(4.3.2) we show a comparison between our data and the measurements of Tegeder and Lincke (1971) in the wavelength region $1200\text{--}1350 \text{ \AA}$ which corresponds to the $5d^9 6s 7p$ configuration.

The $5d^9 6s(^3D_3)np$ Series

This is the most strong and well defined series observed in the spectrum of Au I. The level at $1303 \text{ \AA}$, observed by Tegeder and Lincke (1971) and Brown and Ginter (1978) has been assigned as the second member of this series yielding $n^* = 2.78$. According to the Jk coupling only one series to $(^3D_3)$ is accessible

$$5d^9 6s(^3D_3)np \quad [2]_{3/2}$$

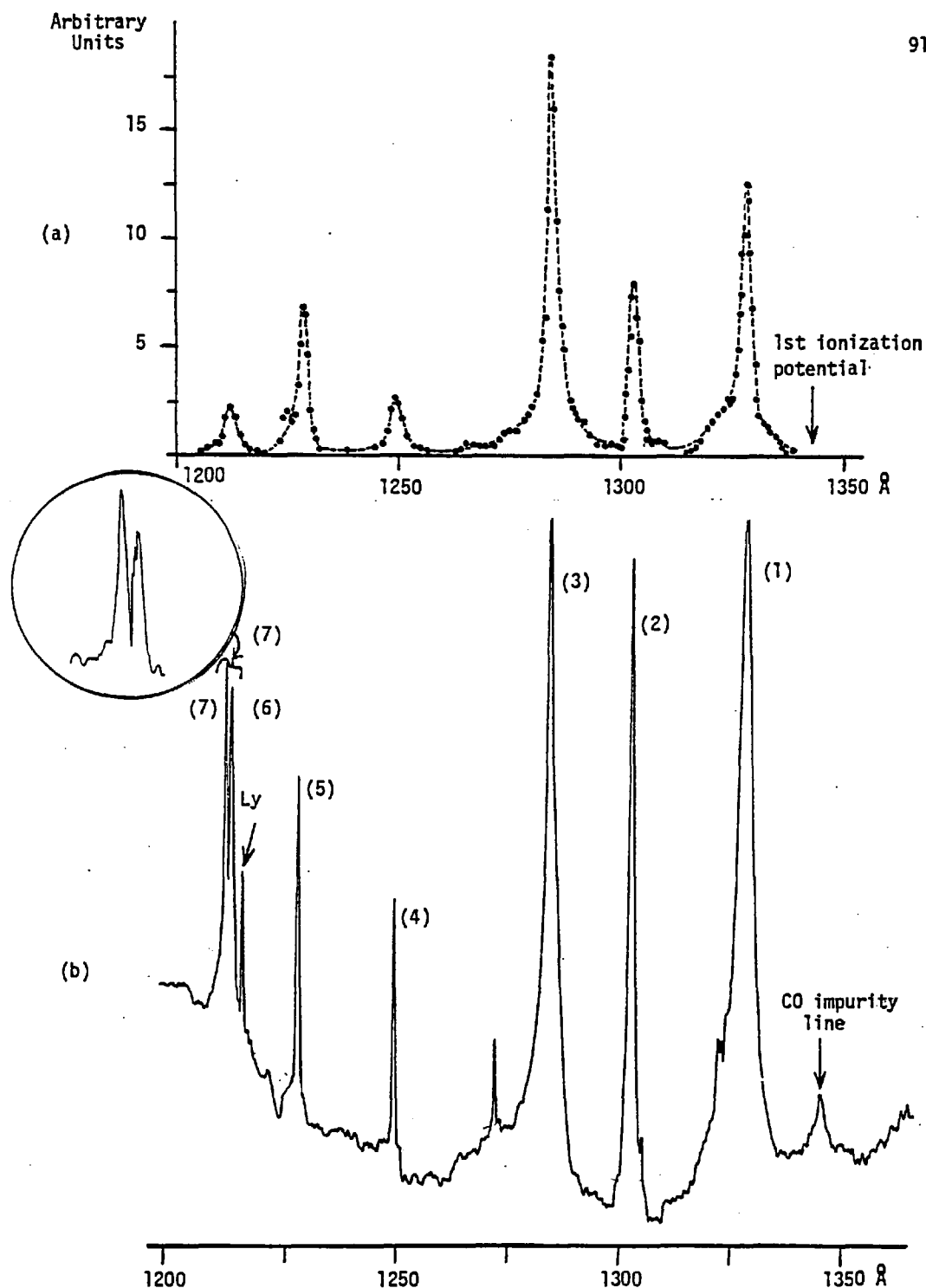


FIGURE 4.3.2 - Comparison between (a) photoionization measurements on an Au atomic beam (Tegeder & Lincke 1971) and (b) photoabsorption data using synchrotron radiation and an inductively heated furnace (present experiments) showing the lowest energy 5d excitation lines recorded in the present experiments.

This series has been observed up to $n=17$ yielding a smooth course of quantum defects. The wavelength in Å, the value of the level in cm^{-1} and the Rydberg denominator $n^* = (R/T)^{1/2}$ are reported in Table (4.3.2).

The $5d^9 6s(^3D_2)np$ Series

This strong and broad series consists of doublet components of comparable intensity. After $n > 11$ the two components merge. The lines at 1303 Å and 1284.5 Å which were previously identified by Tegeder and Lincke (1971) are assigned as the second member of this series. In Jk coupling, Racah (1942) and Cowan and Andrew (1965), the accessible series are

$$5d^9 6s(^3D_2)np \left[2 \right]_{3/2}, \left[1 \right]_{1/2, 3/2}$$

The transitions to the $\left[1 \right]_{1/2}$ levels appear to be very weak.

Therefore, the line at 1303 Å can be assigned $5d^9 6s(^3D_2)7p \left[1 \right]_{3/2}$ and the line at 1284.52 Å can be assigned as

$$5d^9 6s(^3D_2)7p \left[2 \right]_{3/2}$$

This series has been observed up to $n=17$ and wavelengths in Å, terms in cm^{-1} and the Rydberg denominator $n^* = \sqrt{\frac{R}{T}}$ are reported in Table (4.3.3).

4.3.4c $5d^9 6s(^3D_1)np$ Series

Observed transitions consist of doublet components resolved up to $n=11$. According to Jk coupling, the accessible series are

$$5d^9 6s(^3D_1)np \left[0 \right]_{1/2}$$

$$5d^9 6s(^3D_1)np \left[2 \right]_{3/2}$$

$$5d^9 6s(^3D_1)np \left[1 \right]_{1/2, 3/2}$$

We observe only two series. The line at 1158 Å is identified as $5d^9 6s(^3D_1)7p \left[0 \right]_{1/2}$ and the 1148.95 Å line as $5d^9 6s(^3D_1)7p \left[1 \right]_{3/2}$.

TABLE 4.3.1

Comparison between experimental energies and theory for the
 $5d^9 6s 6p \times 5d^8 6s^2 6p$ configurations of Au I

(a) $J = 1/2$ levels

Parametric cm^{-1}	Ab initio cm^{-1}	Experiment cm^{-1}	Identification (largest compositions)
52464	52793	53196*	69% $(\frac{5}{2} \frac{1}{2} \frac{3}{2})$
59505	60148	60979*	55% $(\frac{5}{2} \frac{1}{2} \frac{3}{2}) + 37\% (\frac{3}{2} \frac{1}{2} \frac{3}{2})$
68739 ⁺	61142	61564*	51% $(\frac{3}{2} \frac{1}{2} \frac{1}{2}) + 24\% (\frac{5}{2} \frac{1}{2} \frac{3}{2})$
72077 ⁺	74413	73396	53% $(\frac{3}{2} \frac{1}{2} \frac{3}{2}) + 22\% (\frac{3}{2} \frac{1}{2} \frac{1}{2})$

(b) $J = 3/2$ levels

Parametric cm^{-1}	Ab initio cm^{-1}	Experiment cm^{-1}	Identifications (largest compositions)
46823	46731	47007 $\neq$	23% $(\frac{5}{2} \frac{1}{2} \frac{3}{2}) + 62\% (\frac{5}{2} \frac{1}{2} \frac{1}{2})$
51065	50958	51231 $\neq$	68% $(\frac{5}{2} \frac{1}{2} \frac{3}{2}) + 10\% (\frac{5}{2} \frac{1}{2} \frac{1}{2})$
56085	55984	56106*	55% $(\frac{5}{2} \frac{1}{2} \frac{3}{2}) + 37\% (\frac{3}{2} \frac{1}{2} \frac{3}{2})$
58847	60649	58846*	46% $(\frac{3}{2} \frac{1}{2} \frac{1}{2}) + 12\% (\frac{5}{2} \frac{1}{2} \frac{3}{2})$
64536 ⁺	61965	62569*	58% $(\frac{3}{2} \frac{1}{2} \frac{3}{2})$
71870 ⁺	64623	63006*	55% $(\frac{5}{2} \frac{1}{2} \frac{3}{2}) + 18\% (\frac{3}{2} \frac{1}{2} \frac{1}{2})$
73701 ⁺	79286	80004	20% $(\frac{3}{2} \frac{1}{2} \frac{3}{2}) + 35\% (2\frac{1}{2})$
- -	81965	81415	70% $(1\frac{1}{2}) + 16\% (2\frac{3}{2})$

* Already attributed to $5d^9 6s 6p$ by Borwn & Ginter (1978).

$\neq$ Platt and Sawyer (1941).

+ Tentative correlations with other experimental levels are given by Brown and Ginter (1978)

TABLE 4.3.2

Comparison between experimental energies and calculated
structure for the $5d^9 6s 7p$ configuration of Au I

Ab initio λ cm ⁻¹	Experiment λ cm ⁻¹	No	Identification
75275	75292	1	$(5d^9 6s \ ^3D_3) 7p \ [2]_{3/2}$
77111)	76739	2	$(5d^9 6s \ ^3D_2) 7p \ [1]_{3/2}$
77729)			
78450	77850	3	$(5d^9 6s \ ^3D_2) 7p \ [2]_{3/2}$
85974)	86346	-	$(5d^9 6s \ ^3D_1) 7p \ [0]_{1/2}$
86450)			
87011)	87036	-	$(5d^9 6s \ ^3D_1) 7p \ [1]_{3/2}$
87391)			
90244	89619	-	$(5d^9 6s \ ^1D_2) 7p \ [1]_{3/2}$
91602	91980		
92059	92926		

The ab initio calculations are obtained from a four-configuration treatment (set (1) in text) and have been raised in energy by 7000 cm^{-1} . The numbers for the first three peaks refer to Fig.2. The identification given refers to the most intense component. Peak 2 has a very weak line on the long wavelength side which may be the $[1]_{1/2}$ transition.

TABLE 4.3.3

5d excitation spectrum of Au I
 $5d^{10}6s\ ^2S_{1/2} \rightarrow 5d^96s\ (^3D_3)np\ [2]_{3/2}$
Series Limit: 89447.88 cm⁻¹

n	λ (Å)	ν cm ⁻¹	n*
7	1328.16	75292	2.78
8	1213.33	82418	3.95
9	1176.93	84967	4.95
10	1158.49	86319	5.92
11	1147.18	87170	6.94
12	1140.16	87707	7.94
13	1135.39	88075	8.94
14	1131.87*	88349	9.99
15	1129.65	88523	10.89
16	1127.96	88656	11.77
17	1126.39	88779	12.81

* Blended line.

This series consists of broad and intense transitions.

TABLE 4.3.4

5d excitation spectrum of Au I
 $5d^{10}6s\ 2S_{1/2} \rightarrow 5d^96s(^3D_2)np[1,2]_{3/2}$

Series Limit: 92048.28 cm⁻¹

n	λ (Å)	ν cm ⁻¹	n*
7	1303.11	76739	2.68
	1284.52	77850	2.78
8	1185.40	84360	3.78
	1178.34	84865	3.91
9	1143.29	87467	4.89
	1141.94	87570	4.95
10	1124.32	88943	5.94
11	1114.27	89745	6.90
	1113.81	89782	6.96
12	1107.49	90294	7.91
13	1102.92	90668	8.92
14	1099.82	90924	9.88
15	1097.58	91110	10.81
16	1096.00	91241	11.66
17	1094.41	91373	12.75

This series consists of broad and intense transitions, Identifications are given in J_cK coupling and the order of k values is given in Table 4.3.2.

TABLE 4.3.5

5d Subshell excitation spectrum of Au I

$5d^{10}6s^2S_{1/2} \rightarrow 5d^96s(3D_1)np [0]_{1/2}, [1]_{3/2,1/2}$

Series limit: 102173.38 cm⁻¹

n	λ (Å)	ν cm ⁻¹	n*
7	1158.13	86346	2.63
	1148.95	87036	2.69
8	1064.10	93976	3.66
	1056.57	94646	3.82
9	1030.71	97021	4.62
	1024.98	97563	4.88
10	1012.93	98724	5.64
	1010.14	98996	5.88
11	1002.51	99750	6.73
12	996.04	100398	7.86
13	992.29	100777	8.86
14	989.91	101019	9.75
15	987.95*	101220	10.73
16	986.36	101383	11.78

* Very weak.

This series consists of broad and intense transitions.

TABLE 4.3.6

5d Subshell excitation spectrum of Au I

$5d^{10}6s\ 2S_{1/2} \rightarrow 5d^96s\ ({}^1D_2)np\ [1]_{3/2,1/2}, [2]_{3/2}$

Series limit: 104029.68 cm⁻¹

n	λ (Å)	ν cm ⁻¹	n*
6	1532.83	65239	1.68
7	1115.84	89619	2.76
8	1037.42	96393	3.79
9	1006.70	99334	4.83
10	991.55	100852	5.88
11	983.06	101726	6.90
12	--	--	-
13	974.74	102591	8.74

This series consists of fairly strong broad transitions, becoming noticeably broader above the ³D₂ threshold.

TABLE 4.3.7

5d subshell excitation spectrum of Au I
 $5d^{10}6s\ 2S_{1/2} \longrightarrow 5d^96s(^3D_3)nf\ [0,1,2]$

n	$\lambda\ (\text{\AA})$	νcm^{-1}	n^*
5	1213.10	82433	3.96 ⁺
	1212.82	82452	3.96 ⁺
	1212.03	82506	3.98 ⁺
6	1176.35	85009	4.97
7	1158.13	86346	5.95

+ See the inset at peak No.7 in Fig.2.

TABLE 4.3.8

5d subshell excitation spectrum of Au I
 $5d^{10}6s\ 2S_{1/2} \longrightarrow 5d^96s(^3D_2)nf\ [1,2]$

n	$\lambda\ (\text{\AA})$	νcm^{-1}	n^*
5	1175.52	85069	3.97 [1] _{1/2,3/2}
	1175.34	85082	3.97 [2] _{3/2}

TABLE 4.3.9

5d subshell excitation spectrum of Au I
 $5d^{10}6s\ 2S_{1/2} \longrightarrow 5d^96s(^3D_1)nf\ [2]_{3/2}$

n	$\lambda\ (\text{\AA})$	νcm^{-1}	n^*
5	1050.34	95207	3.97

The lines listed in Tables above are all weak and comparatively sharp. Where possible k values are given, but, for n=6 and above, all the transitions with different k values are probably degenerate in energy.

The higher members up to $n=16$ have been observed and are reported in Table (4.3.4).

4.3.4d $5d^9 6s(^1D_2)np$ Series

This series consists of fairly strong transitions becoming noticeably broader above the 3D_2 threshold. According to the jk coupling, the accessible series are

$$5d^9 6s(^1D_2)np \quad [1]_{1/2,3/2}$$

$$5d^9 6s(^1D_2)np \quad [2]_{3/2}$$

The line at 1115.34 Å is attributed to $5d^9 6d(^1D_2)7p \quad [1]_{3/2}$ and the higher members are observed up to $n=13$. In this region there were some impurity lines as well which create problems in extending this series. The line list with identifications is given in Table (4.3.4).

In addition to the np -series we have also identified the $5d^9 6s(^3D_3)nf \quad [0,1,2]$ levels from $n=5$ to $n=7$. This level, $5d^9 6s(^3D_3)5f$, splits into three components which can be seen in the Fig.(4.3.2). The same splitting of f levels were detected in Hg I by Garton and Connerade (1969). We have interpreted this level at 1175.52 Å and 1175.34 Å as transitions to $5d^9 6s(^3D_2)5f \quad [1]_{1/2,3/2}$, $[2]_{3/2}$ yielding $n^* = 3.97$. The line at 1050.34 Å, which is a very sharp transition is identified as $5d^9 6s(^3D_1)5f \quad [2]_{3/2}$, yielding $n^* = 3.97$.

4.4 3d-subshell Excitation in Mn I

4.4.1 Introduction

The manganese atom has twentyfive extranuclear electrons with ground state electron configuration $3d^5 4s^2 \quad ^6S_{5/2}$ and the spectrum of Mn I is expected to be very complex because of overlapping structure due to excitation from the 4s-shell and the 3d-shell. The emission

spectrum of Mn I has been extensively studied in the past and Catalan, Meggers and García-Riquelme (1951) have classified all the observed lines between 1785 Å and 1760 Å. Corliss and Sugar (1977) have summarised the existing energy level data on Mn I through Mn XXV.

The absorption spectrum was first observed by Paul (1937) in the region 500-1390 Å using a resistively heated tungsten furnace and Lyman continuum as the background source. Marr and Zico (1971) observed the photoabsorption spectrum above the first ionization limit down to 1200 Å and found some broad features which were tentatively assigned. Brown and Ginter (1978) recorded the high resolution absorption spectra in the region 1305 - 2040 Å using 3rd and 4th order of a 6.6. m vacuum spectrograph and microwave excited Xenon or Krypton lamps as background continuum. Brown and Ginter (1978) extended the principal series upto $n=41$ and reported an accurate value of the first ionization potential $59959.40 \pm 0.10 \text{ cm}^{-1}$, which is 22 cm^{-1} below the previously recommended value, Corliss and Sugar (1977). The region investigated by Brown and Ginter (1978) was particularly interesting because it contains most of the transitions between the $3d^5 4s^2 \ ^6S_{5/2}$ ground level to the excited energy levels converging on the $3d^5 4s \ ^7S_3$ (ground), $3d^5 4s \ ^5S_2$ (first excited state) and $3d^6 \ ^5D_{4,3,2,1,0}$ levels of Mn II. Brown and Ginter (1978) also identified some quadrupole transitions.

Manganese has a half filled d-shell and all the five electrons have parallel spins; it is therefore very interesting for electron scattering studies experiments because, besides sextet states, spin exchange can also excite quartet and octet states. Williams et al. (1978) have reported the electron scattering studies in manganese vapour in the 10-100 eV impact energy and found quartet, sextet and octet excitations. Williams et al. (1978) observed many peaks below the first ionization limit and found two strong peaks at 7.74 eV and

8.73 eV, which were attributed to double scattering.

Connerade et al. (1977) reported the absorption spectrum of Mn I in the energy region 40-70 eV corresponding to excitation of the 3p-subshell and found a broad feature followed by some discrete levels. The spectrum was interpreted by comparison with ab initio Hartree-Fock calculations.

In the present investigation we have observed the vacuum ultraviolet absorption spectra of Mn I vapour extending over the full range from 700-1800 Å. Rich, but surprisingly simple structure has been found converging on 4s and 3d ionization thresholds. It is shown that all the structures Williams et al. (1978) observed by electron impact excitation, above the first ionization threshold, are in fact optically allowed by the dipole selection rules. The simplicity of the Mn I absorption spectrum is attributed to the validity of the spectator electrons model and the observed structures are interpreted by comparison with ab initio Hartree-Fock calculations of the excited configurations.

4.4.2 Results

In the present investigation we have covered the spectral range 700-1900 Å and found very interesting features due to excitation of 4s and 3d electrons. The Mn I vapour was produced by heating the metal in an induction furnace with tantalum as furnace tube at temperatures from 1100-1400°C taking care not to heat the tube above the melting point of Mn I for a long period in order to inhibit chemical attack. In spite of this, after the experiment, when the furnace was dismantled, the furnace tube was found to be badly damaged. Spectra were recorded in the first order of a 1 m normal incidence spectrograph equipped with a 1200 lines/mm grating. To avoid the overlapping of higher spectral orders, a LiF window was used in some exposures. Other experimental details are discussed in Chapter III.

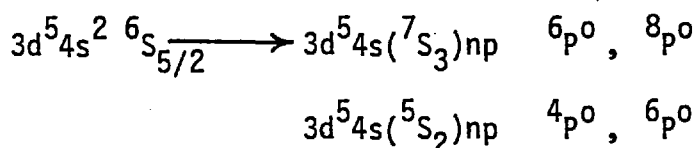
4.4.3 Analysis

The absorption spectrum of Mn I in the region 850-1760 Å is reproduced in Fig.(4.4.1) where all the observed transitions are marked with identifications. The lines are arranged into Rydberg series converging on the ground state and higher excited levels of Mn II. We discuss all the transitions separately.

4.4.3a $3d^5 4snp$ Configuration

Manganese is placed in the Periodic Table where competition occurs between the d and s states in filling of the d-shell. The ground state configuration is represented by $3d^5 4s^2 {}^6S_{5/2}$. The 3d and 4s levels have very close energy therefore the levels corresponding to the configurations $3d^4 4s^2$, $3d^5 4s$ and $3d^6$ lie very close in Mn II. All these levels have the same parity because both 'd' and 's' states are even, therefore electric dipole transitions between these levels are not possible. The atom can be excited by the excitation of one of the 3d or 4s electrons into the np orbitals.

In the Mn I 3d shell, all the electrons have parallel spins and the addition of a 4s electron with $3d^5 {}^6S_{5/2}$ will form 5S_2 and 7S_3 terms, which are separated by about 9473 cm^{-1} . This large separation between the two s-terms is due to the interaction between $s = 5/2$ of the parent term and $s = 1/2$ of the added electron. The addition of an np electron with $3d^5 4s({}^7S_3, {}^5S_2)$ core will change the multiplicity and the resulting terms will be ${}^4P, {}^6P$ & 8P . The interaction between the spin of the parent term and the spin of the np electron will separate the resultant P terms. Thus, the excitation of a 4s electron to np orbitals $n \geq 4$ will result in a Rydberg series converging on the 7S_3 and 5S_2 levels of Mn II.



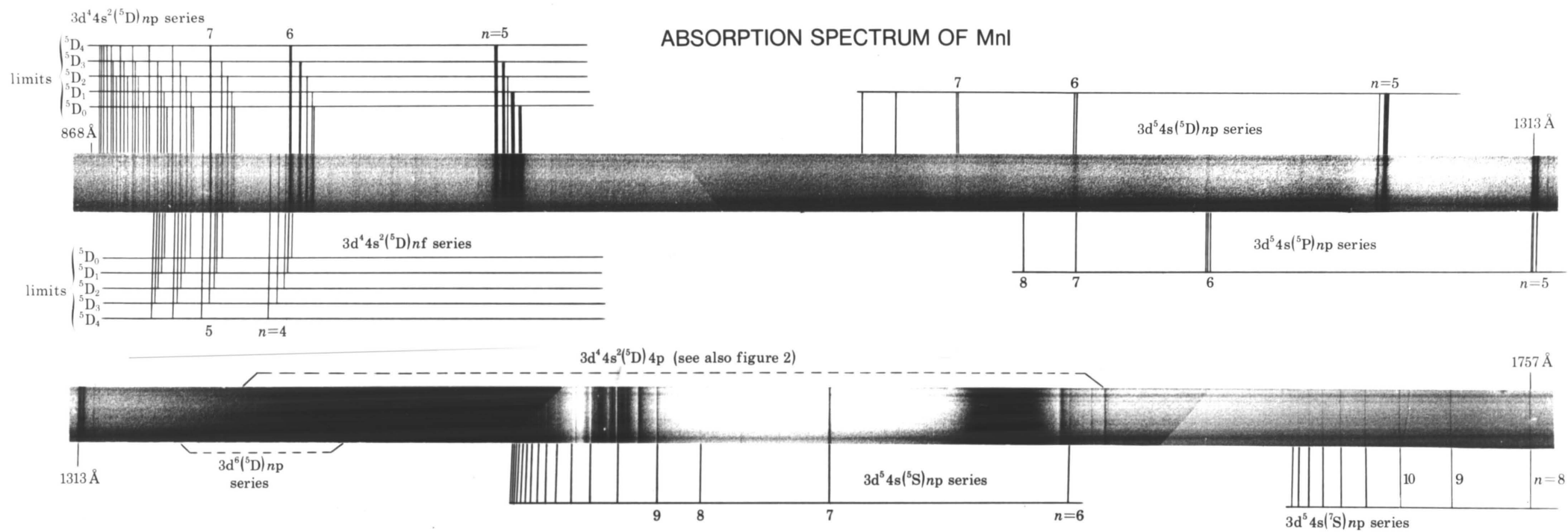
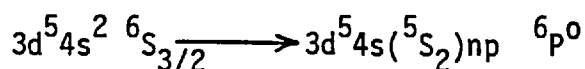


Fig 4.4.1

The first series in the principal series have been observed up to $n=41$ by Brown and Ginter (1978) yielding a more accurate value of the first ionization potential $59959.40 \pm 0.10 \text{ cm}^{-1}$. In the present experiment we have also observed this series which can be seen in Fig.(4.4.1). Brown and Ginter (1978) were able to resolve all the fine components of the $6P_{3/2,5/2,7/2}$ levels. A weak series was also detected due to $3d^5 4s(7S_3)np^8 P_{5/2,7/2}$ up to $n=22$.

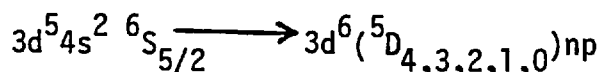
Considering now the Rydberg series converging on $5S_2$ level of the ion, which is the first excited state of Mn II. This series has the most pronounced feature of Beutler-Fano resonances and is very strongly developed on our plates. A very low vapour pressure was sufficient to observe this series and a small increment in temperature results in saturation of the line profiles. Brown and Ginter (1978) reported this autoionizing series up to $n=35$.



The assignment of this series as $6P^0$ was based on the fact that this is strong in arc spectrum. Autoionization in this series is due to the interaction with $3d^5 4s(7S_3) \epsilon l$ continua. Several perturbations also occur, particularly at $3d^5 4s6p$; a broad feature and autoionization resonances occur and the intensity of the $3d^5 4s 8p$ line is attenuated. We made densitometer traces for this section of the spectrum and this is reproduced in Fig.(4.4.2) along with the identification and comparison with theoretical calculation - Roth (1970).

4.4.3b $3d^6(5D)np$ Configuration

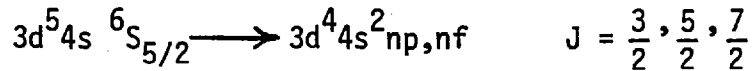
The excitation of one of the 4s electrons to the 3d orbital will form the core $(5S_{4,3,2,1,0})$ and the addition of a 'p' electron will give Rydberg series due to double excitation of both the 4s electrons, converging on the $5D_{4,3,2,1,0}$ levels of Mn II.



This double excitation may arise due to strong configuration mixing in the parent ion - Brown and Ginter (1978) have reported these series and the broad features overlapped on the $3d^5 4s(^5S_2)np$ series were explained due to $3d^6(^5D)5p, 6p$ and $7p$ levels. After crossing the limit of $3d^5 4s(^5S_2)$ series, all the levels of the $3d^6(^5D)np$ series show transmission windows and with very weak intensity.

4.4.3c $3d^4(^5D)4s^2np$ Configuration

Excitation of one electron from the $3d$ subshell of Mn I to the np and nf orbitals will result from the excitation scheme



This excitation scheme is very complex because the $3d^4 4s^2$ configuration of the parent ion gives rise to the term

$${}^1_0S, {}^1_4S, {}^3_2P, {}^1_2D, {}^1_4D, {}^5_4D, {}^1_4F, {}^3_4F, {}^1_2G, {}^1_4G, {}^3_4H \text{ and } {}^1_4I$$

(The leading subscript is the seniority number).

The introduction of the spectator electrons approximation (Sugar, 1972; Mansfield and Connerade, 1976) results in a good simplification of the one electron excitation scheme.

If we assume that the relative angular momentum orientations of all but one of the $3d$ electrons in the ground state configuration of Mn I are unchanged during the $3d \longrightarrow 4p$ transition, then it turns out that there is one and only one relevant limit, namely 5_4D . The reason for this is illustrated in Fig.(4.4.3).

In the ground state of Mn I, the spins of all five electrons in $3d^5$ are aligned and has $L = 0$, therefore the angular momenta have a simple arrangement, which is shown in Fig.(4.4.3). They have the same ordering of angular momenta for $3d^4$, no matter which electron is removed. Thus, if the electrons in $3d^4$ retain the angular momentum

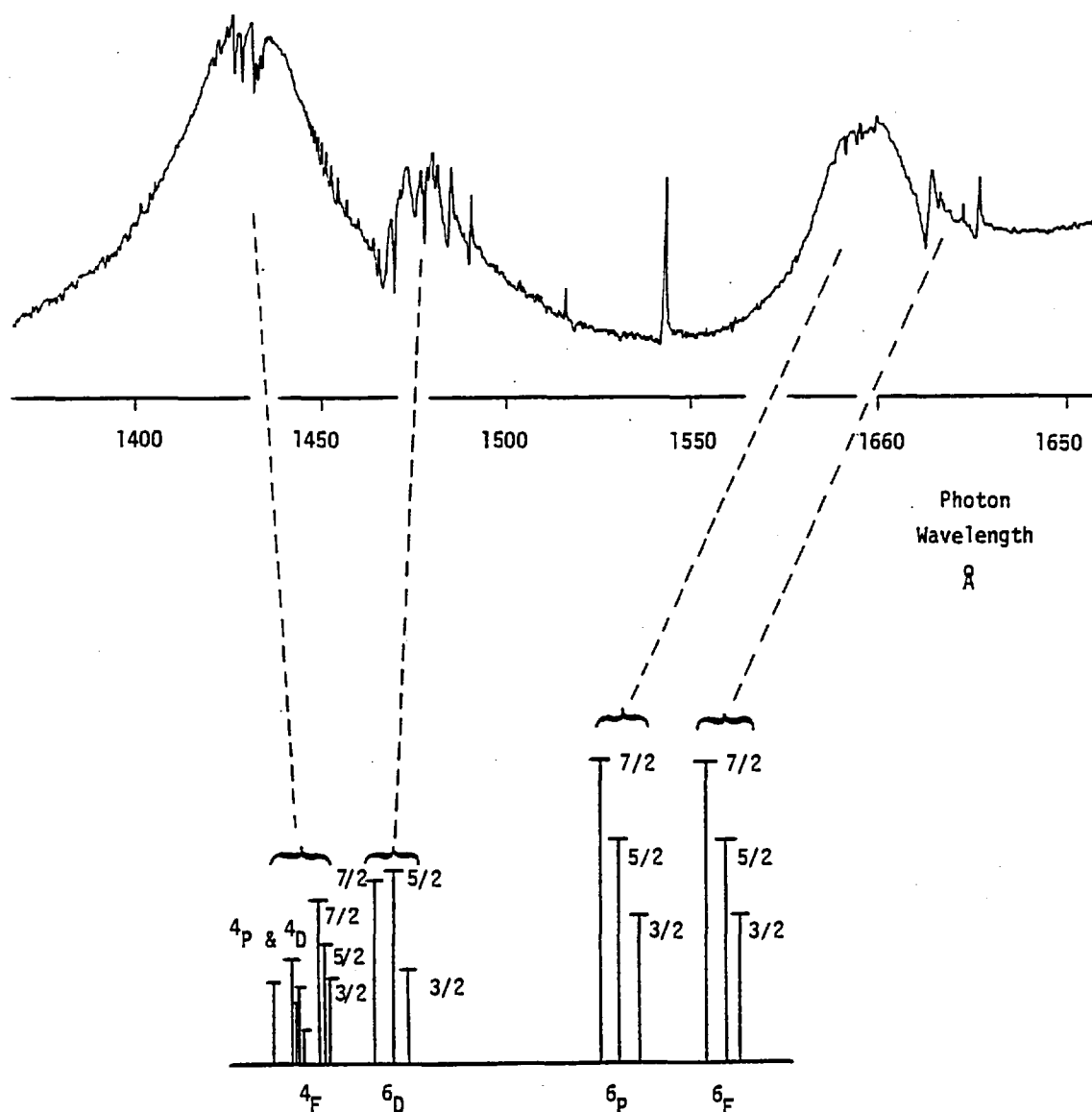


FIGURE 4.4.2

Comparison between the calculations of Roth (1970) for $3d \rightarrow 4p$ excitation in Mn I and experiment. The stick diagram does not represent intensities, but the $3d^4 4s^2 ({}^5D)4p$ content as derived from Roth's (1970) table.

orientations, $3d^5$, the only prominent excitation series must run to the $3d^4 4s^2 {}^5D_4$ limit.

In the present experiment we confirm that the only strong absorption series converge on the $3d^5 4s^2 ({}^5D_{0,1,2,3,4})$ limit and no structure associated with any other $3d^4 4s^2$ limit is observed down to 700 Å. Both np and nf series have been observed and the n^* values and identifications are collected in Tables.

The lowest member of the np series lie in the energy region studied by Brown and Ginter (1978), who do not attribute any transition to the $3d^5 4s^2 {}^6S_{5/2} \longrightarrow 3d^4 4s^2 ({}^5D)4p$ configuration.

We show a densitometer trace of several intense transitions which are assigned by Brown and Ginter (1978) as $3d^6 5p$, $3d^6 6p$ and $3d^6 7p$ upper configurations. Large intensities and breadths cannot only originate from the $3d^5 4s^2 {}^6S_{5/2} \longrightarrow 3d^6 ({}^5D)np$ channel, because all other members of this channel with $n > 7$ appear as very weak transmission windows. We have assigned these broad features as

$$3d^5 4s^2 {}^6S_{3/2} \longrightarrow 3d^4 4s^2 ({}^5D)4p$$

transitions, which is consistent with the n^* value of the higher members. These assignments provide an explanation for the large intensity associated with broad feature which remained unidentified in the previous experiments. They do not invalidate the description of many sharp overlapping features as transitions to $3d^5 ({}^6S)4s {}^5S$ np and $3d^6 ({}^5D)np$ assigned by Brown and Ginter (1978).

A pronounced interchannel mixing effect between the broad and the sharp features is observed. As the higher series members of the $3d^5 4s ({}^5S_2)np$ series approaches $3d^4 4s^2 ({}^5D)4p {}^4F$, their intensity is enhanced.

Roth (1970) performed the full intermediate coupling calculations of the configuration $(3d+4s)^6 4p$ including mixing between relevant

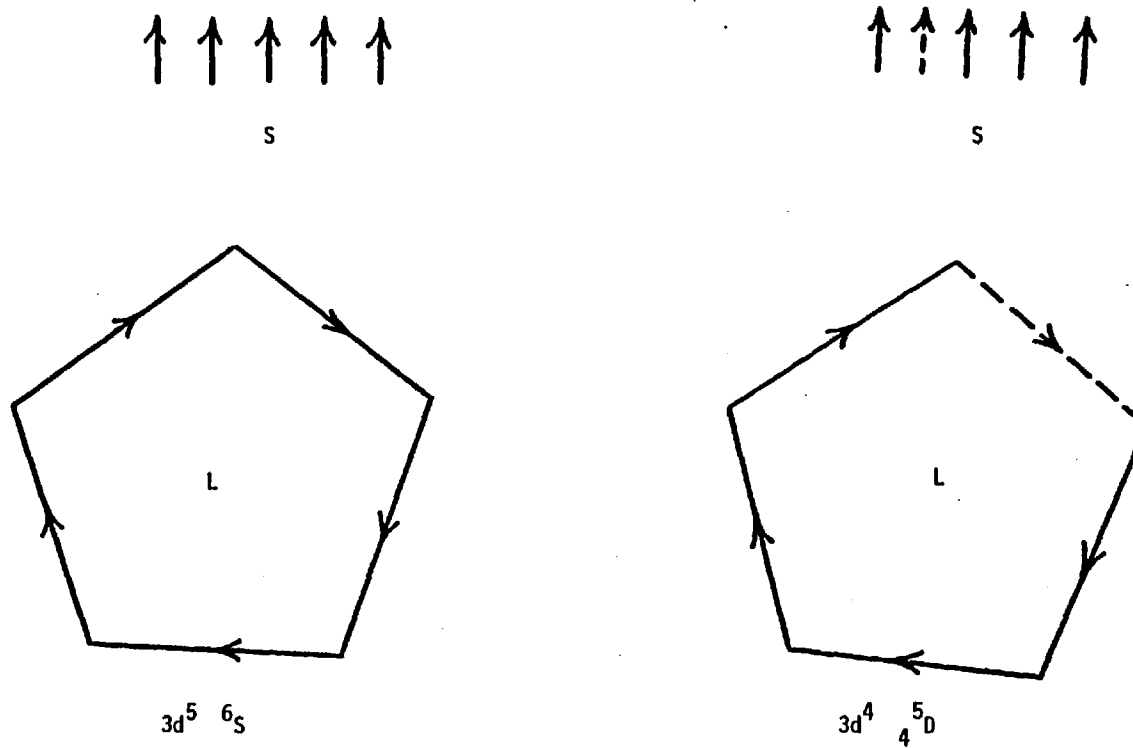


FIGURE 4.4.3

Showing schematically how the spectator electron model accounts for the high intensity of transitions to $3d^4 4s^2 ({}^5D)np$ rather than any other accessible series.

configurations. Roth (1970) listed many levels with appreciable $3d^4 4s^2 ({}^5D)4p$ content but cautions against large uncertainties in the empirically derived parameters for $3d^4 4s^2 4p$ in Mn I.

If we consider only those levels which possess $3d^4 4s^2 ({}^5D)4p$ character, the calculated span is 3500 cm^{-1} , whereas the observed span is $10,000 \text{ cm}^{-1}$. We have further introduced a shift of 4843 cm^{-1} towards lower energies in all the levels to compare with the experiment which is shown in Fig.(4.4.2).

Connerade (1979) has also performed ab initio Hartree-Fock calculations for the $3d^4 4s^2 4p$ configurations in Mn I which show that the spatial overlap between 3d and np wavefunctions becomes large at $n=4$, which shows qualitatively why the Slater-Condon parameters, which determine the energy splittings, are greater for $3d^4 4s^2 np$ than for higher members of the series.

Neglecting the non-diagonal terms which couple $3d^4 4s^2 {}^5D$ -based terms to other terms in the energy matrix of $3d^4 4s^2 np$, we obtain the following formula in pure LS coupling (Slater, 1960).

$$({}^5D) {}^6F^0 = E({}^5D) - \frac{2}{35} F^2(pd) - \frac{12}{30} G^1(pd) - \frac{72}{980} G^3(pd)$$

$$({}^5D) {}^6D^0 = E({}^5D) + \frac{7}{35} F^2(pd) - \frac{12}{30} G^1(pd) - \frac{252}{980} G^3(pd)$$

$$({}^5D) {}^6P^0 = E({}^5D) - \frac{7}{35} F^2(pd) + \frac{8}{30} G^1(pd) - \frac{252}{980} G^3(pd)$$

$$({}^5D) {}^4F^0 = E({}^5D) - \frac{2}{35} F^2(pd) + \frac{13}{30} G^1(pd) + \frac{228}{980} G^3(pd)$$

$$({}^5D) {}^4D^0 = E({}^5D) + \frac{7}{35} F^2(pd) + \frac{13}{30} G^1(pd) + \frac{273}{980} G^3(pd)$$

$$({}^5D) {}^4P^0 = E({}^5D) - \frac{7}{35} F^2(pd) + \frac{8}{30} G^1(pd) + \frac{273}{980} G^3(pd)$$

Using the values of F^2 , G^1 and G^3 , Connerade (private communication), and neglecting the spin orbit interaction, we obtain a distribution of energies in quite good agreement with the observed energy span.

TABLE 4.4.1

Spectrum of Mn I

$$\underline{3d^5\ 4s^2\ ^6S_{5/2} \longrightarrow 3d^4\ 2s^2(^4_4\ ^5D_0)np}$$

Series Limit : 114805.64 cm⁻¹

n	$\lambda \text{ \AA}$	$\nu \text{ cm}^{-1}$	n^*
5	998.75	100125	2.73
6	933.99	107068	3.77
7	909.10	109999	4.78
8	896.54*	111540	5.80
9	889.48*	112425	6.79
10	885.07	112985	7.77
11	881.97†	113383	8.78
12	879.80†	113662	9.80
13	878.38†	113846	10.70

* Blended lines.

† Overlapped lines.

(Footnote to all the Tables:)

The transitions are assigned to different series on the basis of effective quantum numbers (quantum defects) obtained from the experimental transition energies and known limit structure (Moore 1958). Since many configurations overlap in energy, the ordering into channels must be regarded as a first approximation. When the quantum numbers are incompletely specified, it can be assumed that the observed transitions correspond to a blend of transitions to all the K and J upper levels for a given nl and core.

The same formula also predicts a much large span (7540 cm^{-1} for $3d^4 4s^2 4p$) but nevertheless smaller than the observed $10,000\text{ cm}^{-1}$.

In the vicinity of $3d^6(^5D)$ and $3d^4 4s^2(^5D)$ levels, we observed some weak features which are arranged into two Rydberg series converging on $3d^5 4s(^5P)$ and $3d^4 4s(^5D)$ level of the ion. The intensity of these lines decreases very rapidly and only $n=5$ members are stronger. The wavelengths and identifications are given in Tables.

TABLE 4.4.2

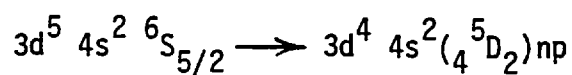
Spectrum of Mn I

$3d^5\ 4s^2\ ^6S_{5/2} \longrightarrow 3d^4\ 4s^2(^5D_1)np$

Series Limit : 114897.59 cm^{-1}

n	$\lambda \text{\AA}$	$\nu\text{ cm}^{-1}$	n^*
5	996.41	100360	2.75
6	933.56	107117	3.76
7	908.39	110085	4.78
8	895.87	111623	5.79
9	888.62†	112534	6.81
10	884.26✕	113089	7.79
11	881.16	113487	8.82
12	879.03	113762	9.83
13	877.48†	113963	10.84
14	-	-	-
15	875.41†	114232	12.84

TABLE 4.4.3

Spectrum of Mn I

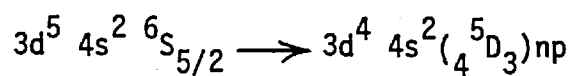
Series Limit : 115075.71 cm⁻¹

n	$\lambda \text{ \AA}$	$\nu \text{ cm}^{-1}$	n*
5	994.78	100525	2.75
6	931.95	107302	3.76
7	907.17	110233	4.76
8	894.47†	111798	5.79
9	887.33	112698	6.79
10	882.82†	113273	7.80
11	879.79†	113663	8.82
12	877.45†	113967	9.93
13	-	-	-
14	874.99†	114287	11.80
15	874.08*	114406	12.80
16	873.27†	114512	13.95
17	872.84	114569	14.71

* Blended lines.

+ Overlapped lines.

TABLE 4.4.4

Spectrum of Mn I

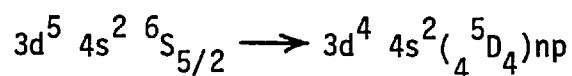
Series Limit : 115331.08 cm⁻¹

n	λ Å	ν cm ⁻¹	n*
5	993.57	100647	2.73
6	929.71	107560	3.76
7	904.17	110599	4.82
8	892.46	112050	5.78
9	885.37	112947	6.79
10	880.83 †	113529	7.81
11	877.82 †	113919	8.81
12	875.76	114187	9.79
13	874.08 *	114406	10.89
14	872.98 †	114550	11.86
15	872.08 *	114668	12.87
16	-	-	-
17	870.79	114838	14.93
18	870.38 †	114892	15.82
19	869.95	114949	16.94
20	869.61 †	114994	18.05

* Blended lines.

+ Overlapped lines

TABLE 4.4.5

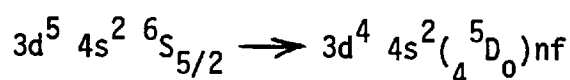
Spectrum of Mn I

Series Limit : 115656.39 cm⁻¹

n	$\lambda \text{ \AA}$	$\nu \text{ cm}^{-1}$	n*
5	991.18	100890	2.73
6	926.76†	107903	3.76
7	901.81	110888	4.80
8	889.90	112372	5.78
9	882.82†	113273	6.79
10	878.38†	113846	7.79
11	875.41†	114232	8.78
12	873.27†	114512	9.79
13	871.56*	114737	10.93
14	-	-	-
15	869.61†	114994	12.87
16	868.87†	115092	13.94
17	868.37*	115158	14.84
18	867.88	115223	15.91
19	867.57	115264	16.74

* Blended lines

+ Overlapped lines

Spectrum of Mn I

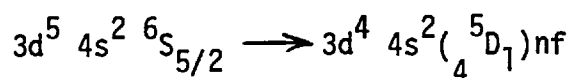
Series Limit : 114805.64 cm⁻¹

n	$\lambda \text{ \AA}$	$\nu \text{ cm}^{-1}$	n*
4	927.63	107802	3.96
5	+ 906.36 *	110331	4.95
6	895.21	111706	5.95
7	888.62 †	112534	6.95
8	884.49 †	113060	7.93

* Blended lines

† Overlapped lines

TABLE 4.4.7

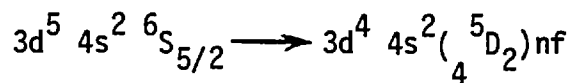
Spectrum of Mn I

Series Limit : 114897.59 cm⁻¹

n	$\lambda \text{ \AA}$	$\nu \text{ cm}^{-1}$	n*
4	926.76 †	107903	3.96
5	905.31 *	110459	4.97
6	894.47 †	111798	5.95
7	887.92	112623	6.95
8	883.70	113161	7.95
9	880.83 †	113529	8.96
10	878.79	113793	9.97
11	-	-	-
12	876.18	114132	11.97

* Blended lines

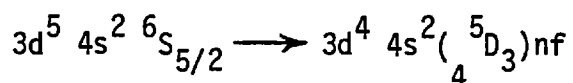
TABLE 4.4.8

Spectrum of Mn I

Series Limit : 115075.71 cm⁻¹

n	λ Å	ν cm ⁻¹	n [*]
4	925.35	108067	3.96
5	904.17	110597	4.95
6	893.07	111973	5.95
7	886.50	112803	6.95
8	882.30	113340	7.95
9	879.47	113705	8.95

TABLE 4.4.9

Spectrum of Mn I

Series Limit ; 115331.08 cm⁻¹

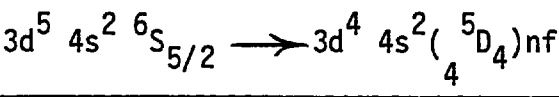
n	λ Å	ν cm ⁻¹	n [*]
4	923.16	108324	3.96
5	901.96*	110870	4.96
6	891.02	112231	5.95
7	884.49†	113060	6.95
8	880.33	113594	7.95

* Blended lines

† Overlapped lines

TABLE 4.4.10

Spectrum of Mn I



Series Limit : 115656.39 cm⁻¹

n	λ Å	ν cm ⁻¹	n*
4	920.49	108638	3.95
5	899.49	111174	4.95
6	888.49	112551	5.94
7	881.97†	113383	6.95
8	877.82†	113919	7.95
9	874.99†	114287	8.95
10	872.98†	114550	9.96
11	871.56†*	114737	10.93
12	870.38†	114892	11.99
13	869.61†	114994	12.87
14	868.87†	115092	13.94

* Blended lines

† Overlapped lines.

TABLE 4.4.11

Spectrum of Mn I

 $3d^5 4s(^5P)np$ and $3d^5 4s(^5D)np$ Series

Wavelength	Wavenumber	Designation	n*
1318.95	75818)	$3d^5 4s(^5P)5p \quad ^6D^0$	2.80
1317.19	75919)		
1317.08	75926)		
1314.10	76098)	$3d^5 4s(^5P_3)5p$	2.82
1313.10	76156)	$3d^5 4s(^5P_2)5p \quad ^6P^0$	2.83
1312.65	76182)	$3d^5 4s(^5P_1)5p$	2.83
1267.56	78892)	$3d^5 4s(^5D)5p$	2.82
1267.38	78904)		
1267.16	78916)		
1264.97	79053)		
1213.68	82394)	$3d^5 4s(^5P_3)5p$)	3.84
1212.61	82466)	$3d^5 4s(^5P_2)6p$)	3.85
1211.91	82514)	$3d^5 4s(^5P_1)6p$)	3.85
1171.92	85330	$3d^5 4s(^5P_3)7p$)	4.93
1171.81	85334	$3d^5 4s(^5P_2)7p$)	4.92
1171.72	85344	$3d^5 4s(^5P_1)7p$)	4.90
1171.24	85379)	$3d^5 4s(^5D)6p$	3.85
1170.75	85415)		
1135.43	88072)	$3d^5 4s(^5D)7p$	4.86
1134.22	88167)		
1133.52	88221)		
1115.67	89633	$3d^5 4s(^5D)8p$	5.87
1104.68	90524	$3d^5 4s(^5D)9p$	6.92

TABLE 4.4.12

Transitions to the $3d^4 4s^2(^5D)4p$ Upper Configuration in Mn I

Identification	λ Å	ν cm ⁻¹	n [*]
$3d^4 4s^2(^5D)4p \quad ^6F_{3/2}$	1622.71	61625	1.44
5/2	1619.54	61746	1.44
7/2	1614.00	61958	1.44
$3d^4 4s^2(^5D)4p \quad ^6P_{3/2}$	1599.04	62538	1.45
5/2	1594.77	62705	1.45
7/2	1592.63	62789	1.45
$3d^4 4s^2(^5D)4p \quad ^6D_{3/2}$	1484.52	67362	1.52
5/2	1479.54	67589	1.52
7/2	1475.06	67794	1.53
$3d^4 4s^2(^5D)4p \quad ^4F_{3/2}$	1441.02	69395	1.55
5/2	1437.82	69550	1.56
7/2	1435.69	69653	1.56
$3d^4 4s^2(^5D)4p \quad ^4D_{3/2}$	1434.62	69705	1.56
5/2	1433.05	69781	1.56
7/2	1428.54	70002	1.56
$3d^4 4s^2(^5D)4p \quad ^4P_{3/2}$	1431.63	69850	1.56
	1426.93	70081	1.56

CHAPTER V

SPECTRA OF DI-ATOMIC MOLECULES

5.1 Introduction

The fundamental difference between atomic and molecular spectra is due to two additional modes of motion which do not occur for atoms. Firstly, the molecule can rotate as a whole about an axis passing through the centre of gravity and perpendicular to the internuclear axis and, secondly, the atoms can vibrate relative to each other along the internuclear axis. Therefore, molecular spectra consist of rotational, vibrational and electronic transitions. To a first approximation, the energy of a molecule can be represented by three parts, the electronic, the vibrational and the rotational energy: $E = E_e + E_v + E_r$. Corresponding to the three kinds of energy, we have three kinds of spectra: (i) rotation spectra, in which transitions take place from the rotational level of a given vibrational level in a given electronic state to other rotational levels of the same vibrational and electronic state; (ii) rotation-vibration spectra, in which transitions take place from the rotational levels of a given vibrational level to the rotational levels of another vibrational level of the same electronic state; and (iii) electronic spectra, in which transitions from the rotational levels of the various vibrational levels of one electronic state take place to the rotational and vibrational levels of another electronic state. From the rotational frequencies, we obtain accurate information about the geometrical arrangement of the nuclei in the molecule and values of the internuclear distances. From the vibrational frequencies, the force between the atoms in the molecule and the heat of dissociation can be calculated. The study of electronic structure leads to a theoretical understanding of chemical valence.

The wavenumbers of the spectral lines corresponding to the transitions between two electronic states are given by

$$\nu = T' - T'' = (T'_e - T''_e) + (G' - G'') - (F' - F'')$$

where the single primed letters refer to the upper state and the double primed letters refer to the lower state. For a given electronic transition $(T'_e - T''_e)$ is a constant and is called the origin of the band system. Neglecting $(F' - F'')$, which in general is small compared to the vibrational frequency, we obtain an expression which represents all possible transitions between the different vibrational levels of the two participating electronic states:

$$\nu = \nu_e + \omega_e(v' + \frac{1}{2}) - \omega_e x'_e(v' + \frac{1}{2})^2 - \omega_e(v'' + \frac{1}{2}) + \omega_e x''_e(v'' + \frac{1}{2})^2$$

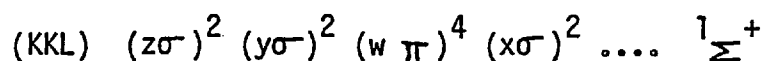
The representation of the electronic structure of a molecule by electron configuration is only an approximation but we can derive from it the electronic states of any molecule. In order to obtain the electronic state, we begin by placing the electrons in the lowest possible orbitals thus obtaining the ground state. In a many-electron system each electron may be considered separately as moving in a approximately axial field of the nuclei and the other electrons.

Each electron in this approximation can be described by the quantum number n , ℓ and λ where n is the principal quantum number,

ℓ is the orbital angular momentum and λ is the component of the orbital angular momentum along the internuclear axis. The possible values of λ are $0, 1, 2, 3, \dots$, according to which of these values, the electron has, it is called a $\sigma, \pi, \delta, \dots$ electron respectively.

Consider the simplest example of the H_2 molecule which has only two electrons. The ground state of H_2 is the state in which both electrons are in the lowest orbital, 1σ which is a $1\Sigma_g^+$ state. The excited states result from one of the electrons going

from the lowest orbital to one of the higher orbitals $2s\sigma$, $2p\sigma$, $2p\pi$, Similarly the lowest electronic configuration for the CH molecule, with seven electrons, is $K(2s\sigma)^2(2p\sigma)^2(2p\pi)$ which gives a $^2\Sigma^+$ state as the ground state. If the two atoms that form a molecule belong to different periods of the periodic system then we take no account of the closed shells of the separated atoms, these are essentially unaffected by molecule formation, and consider only the electrons outside these closed shells. These electrons will arrange themselves in orbitals similar to those for the corresponding molecules consisting of atoms from the second period of the periodic system. A molecule like SiO has the same number of outer electrons as CO or N_2 , therefore the electronic configuration of the ground state can be written as



In such a configuration formula, the order in which the symbols are written is the order of decreasing binding energy. The letters z, y, x, w, v, preceding σ or π are used to distinguish different kinds of σ or π electrons. The symbols (KKL) refer to the most firmly bound electrons in the molecule.

The molecular orbitals describing the electrons in the molecule can be divided into three classes: (i) core orbitals: these are localized close to the nucleus of an atom and describe very strongly bound electrons that are hardly affected by molecule formation; (ii) occupied valence orbitals: these molecular orbitals are derived from the atomic orbitals of the valence electron shells; (iii) virtual molecular orbitals, which are unoccupied in the ground state of the molecule but can be used for the description of excited electrons.

With visible or ultraviolet radiation, the electrons can be promoted from the occupied valence molecular orbitals into the

unoccupied orbitals, whereas the strongly binding core electrons can only be promoted with X-rays, which have much higher energies. In the visible and ultraviolet region, absorption spectra of molecules consist of valence states and the Rydberg transitions lie in the VUV region. Considering molecules with ten outer electrons, CO, SiO, GeO, CS, PN, N₂, P₂ the electronic configuration of the ground state can be represented as:

$$(\text{core}) (z\sigma)^2 (y\sigma)^2 (w\pi)^4 (x\sigma)^2 \dots {}^1\Sigma^+$$

The first excited states arise from the configuration:

$$(\text{core}) (z\sigma)^2 (y\sigma)^2 (w\pi)^4 (x\sigma)(v\pi) \dots {}^1\Pi, {}^3\Pi$$

Since the $(v\pi)$ orbital is antibonding these two π states are expected to have B and ω values smaller than those of the ground state and the ${}^1\Pi$ state is expected to combine strongly with the ground state.

The next valence electron configuration,

$$(\text{core}) (z\sigma)^2 (y\sigma)^2 (w\pi)^3 (x\sigma)^2 (v\pi) \dots {}^1\Sigma^+, {}^1\Sigma^-, {}^1\Delta \\ {}^3\Sigma^+, {}^3\Sigma^-, {}^3\Delta$$

gives rise to six electronic states, promoting an electron from the $(w\pi)$ orbital to the $(v\pi)$ orbital. This configuration has only three $(w\pi)$ bonding and one antibonding $(v\pi)$ orbitals. The magnitudes of the B and ω values of these states are expected to be smaller than those of states belonging to the above mentioned configuration.

The other possible valence transition may arise from the configurations :

$$(\text{core}) (z\sigma)^2 (y\sigma)^2 (w\pi)^3 (x\sigma)(v\pi)^2 \dots {}^1\Pi(3), {}^1\Phi, {}^3\Pi_i(2) \\ {}^3\Pi_r(2), {}^3\Phi_i, {}^5\Pi_i \\ (\text{core}) (z\sigma)^2 (y\sigma)^2 (w\pi)^4 (x\sigma) - (u\sigma) \dots {}^1\Sigma^+, {}^3\Sigma^+.$$

In the last configuration the ($u\sigma$) electron is not a Rydberg electron. Rydberg states arise when the most loosely bound electron ($x\sigma$) is taken into orbitals with higher principal quantum numbers. These states can be represented by the configuration:

$$(\text{core}) (z\sigma)^2 (y\sigma)^2 (w\omega)^4 (x\sigma) (n\ell\lambda)$$

where n and ℓ are the principal quantum number and the angular momentum quantum number of atom-like orbitals and λ is the quantum number representing the component of ℓ along the internuclear axis. Taking away the Rydberg electron we obtain the configuration of the ground state of the ion. The Rydberg states are expected to have the same B and w values as the ground state of the ion. For a given value of ℓ , the various states of different λ have different values of $\delta_{\ell\lambda}$, and the spread of these values depends on the deviation from spherical symmetry of the core. As n increases, the Rydberg states fall into groups, called ℓ -complexes, which merge more closely as the angular momentum ℓ becomes progressively uncoupled from the internuclear axis. A Rydberg p-electron will give a Σ and a Π state. For zero rotation, these states are separated by $A\Lambda^2$ where A is a coupling constant determined by the strength of the interaction between ℓ and the figure axis (Hill and Van Vleck (1928)). When the molecule is considered to rotate, ℓ begins to uncouple from the figure axis and to couple with the molecular rotation, i.e. ℓ -uncoupling occurs, which forms a p-complex. Similarly, from a Rydberg d-electron a 'd-complex' is expected to occur. Such ℓ -complexes have been observed for a number of molecules; H_2 - Richardson (1934); BH - Bauer et al. (1964); He_2 - Ginter and Ginter (1968); N_2 - Carroll and Yoshino (1972); BF - Caton and Douglas (1970); and Sr H - Khan et al. (1976).

The electronic energies of Rydberg states are usually represented by

$$T_{n\ell\lambda} = T_{\infty} - \frac{R}{(n^*)^2} = T - \frac{R}{(n - \delta_{\ell\lambda})^2}$$

where $T_{n\ell\lambda}$ is the term value, T_{∞} is the ionization potential, R is the Rydberg constant, n is the principal quantum number and $\delta_{\ell\lambda}$ is quantum defect.

The Rydberg transitions can be arranged into Rydberg series and the assignment to the Rydberg series are made by inspection of the quantum defect which is small for states derived from nd electrons, somewhat larger for np electrons and appreciably larger for ns electrons. The convergence limit of the Rydberg series will give an accurate value of the ionization potential.

Other Rydberg states are also expected by promoting an inner electron to the Rydberg orbitals, which can be represented by the configuration

- (i) (core) $(z\sigma)^2(y\sigma)^2(\omega\pi)^3(x\sigma)^2 (n\ell\lambda)$
- (ii) (core) $(z\sigma)^2(y\sigma)(\omega\pi)^4(x\sigma)^2 (n\ell\lambda)$
- (iii) (core) $(z\sigma)(y\sigma)^2(\omega\pi)^4(x\sigma)^2 (n\ell\lambda)$

These transitions will lie in the vuv and xuv regions and will yield an accurate value of the ionization potentials for the inner electrons. From the size of the quantum defect, one can judge the symmetry of the Rydberg orbital, and from the selection rules one can sometimes correlate an ionization potential with a certain molecular orbital.

Schirmer (1978) pointed out that it is useful to divide the four valence orbitals into two outer valence orbitals and two inner orbitals because different features result upon ionization. Schirmer (1978) also found that the independent particle picture of ionization

fails to reproduce the correct ordering and reliable values of the ionization potentials; this breakdown of Koopman's theorem occurs in PN, CS and P_2 molecules. The observation of absorption spectra in the vuv region is therefore very helpful to interpret photoelectron data. In this spectral region, interesting spectral features are expected to occur due to autoionization, configuration interaction and simultaneous excitation of two electrons. These features have been extensively studied in the absorption spectra of atoms. Extensions to the absorption spectra of molecules with high resolution will be of great importance.

In the present investigation, we have photographed the absorption spectra of SiO, GeO, PN, AlF and P_2 molecules. Previous studies in SiO have been extended by the observation of Rydberg series converging on the ground state of SiO^+ , and another Rydberg series originates due to excitation of an electron from the inner valence orbital. The spectra of the GeO molecule comprises Rydberg series yielding more accurate value of the first ionization potential of GeO. Weak features have been detected in PN and AlF molecules near the first ionization limits.

5.2 Vacuum Ultraviolet Spectrum of SiO

5.2.1 Summary

The absorption spectrum of SiO in the 700-1500 Å wavelength range has been observed using synchrotron radiation as the background continuum. The known band systems have been extended, and a Rydberg series converging on the $X^2\Sigma^+$ state of SiO^+ has been found from which an improved value of the ionization potential is derived (11.584 ± 0.011 eV). A further Rydberg series above the first ionization threshold is found to converge on the $B^2\Sigma^+$ state of SiO^+ at 14.805 eV.

5.2.2 Introduction

The Si O molecule has the same number of valence-shell electrons as CO. If Si O and CO are compared, the observations of electronic transitions of Si O in the vuv region are seen to be incomplete. The Si O molecule in the uv region has been extensively studied by many investigators. Jevons (1924) was the first to detect the emission spectrum of Si O in the region 2100-2930 Å, and the transition was assigned as $D^1\Pi - X^1\Sigma^+$. This band system was later studied by Lagerqvist and Uhler (1953) who performed a vibrational and rotational analysis and changed this assignment to $A^1\Pi - X^1\Sigma^+$ analogous to the CO $A^1\Pi$ -system, which is the first singlet excited state of these molecules. The study of perturbation in this system led Lagerqvist and Uhler (1953) to suggest the existence of four new electronic states, three of them being singlets $F^1\Pi$ or $^1\Delta$, $G^1\Pi$ or $^1\Delta$ and $^1\Sigma$ and one triplet $e^3\Sigma^-$. Singh et al. (1972) reinvestigated the $A^1\Pi$ -system and analysed three more vibrational bands. The perturbation in this band system was studied by Deutsch et al. (1975) and Bredohl et al. (1976), while Field et al. (1976, 1977) have reported a detailed investigation of the perturbation and of the low-lying electronic states.

Nagraj and Verma (1970) reported the emission spectrum of Si O in the region 4200-4300 Å corresponding to the $^3\Sigma^- - ^3\Pi$ transition. Cornet and Dubois (1972) have observed and analysed a transition $^3\Pi_i - a^3\Pi_r$ in the region 3700-3950 Å and also found another system at 2950 Å which was tentatively identified as a $^3\Sigma^+ - a^3\Pi_r$ transition.

Barrow and Rowlinson (1954) were the first to observe the absorption spectrum of Si O in the Schumann region, using a Lyman tube as the source of background continuum. They found five new band systems which were named E, F, G, H and I-systems in the region

1250-2000 Å. The $E^1 \Sigma^+ - X^1 \Sigma^+$ system in the region 1650-2000 Å has been rotationally analysed by Elander and Lagerqvist (1971). Lagerqvist et al. (1973) extended the observed spectral range using a flash-absorption technique and analysed eleven band systems in the region 1200-1500 Å. Spectra were recorded in the 8th and 9th orders of a 10.5 m vacuum spectrograph equipped with a 600 lines/mm grating. Lagerqvist and Renhorn (1974) reported the Si^{18}O absorption spectrum, changing some of the early vibrational assignments by considering the isotopic shift. The interaction between two near-lying states, $I^1\Pi$, $G^1\Pi$, in the region 1300-1470 Å have been treated by Lagerqvist and Renhorn (1979).

No previous investigations of the Si O spectrum below 1200 Å are known in the literature. The purpose of the present investigation was to extend the observed spectral region in the vacuum ultraviolet region where numerous Rydberg transitions were expected analogous to the CO molecule.

5.2.3 Results

In the present investigation we have recorded the absorption spectrum of Si O in the region 700-2000 Å using synchrotron radiation as the background continuum and a 1 m normal incidence vacuum spectrograph equipped with a 1200 lines/mm grating. The column of Si O vapour was produced by two different methods in our vapour containment system. Firstly, only Si O commercially available was heated in an induction furnace up to temperatures 1100-1300°C and, secondly, a mixture of Si + Si O₂ was used. At higher temperatures there was not any difference in the observed spectrum, which suggests that Si O₂ dissociates at higher temperature forming Si O. When the tantalum furnace tube was dismantled after the experiment, no oxidation was detected confirming that Si O was not dissociated.

5.2.4 Analysis

The ground state electronic configuration of Si O can be written by analogy with CO as

$$\text{KKL } (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)^2 \dots 1\Sigma^+$$

which is normally denoted as $X^1\Sigma^+$. The excitation of an outer electron to the antibonding ($v\pi$) valence orbital will give rise to two electronic states:

$$\text{KKL } (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)(v\pi) \dots A^1\Pi, b^3\Pi_r$$

The two states are the lowlying singlet and triplet states. The $A^1\Pi$ -state has been thoroughly studied by many investigators, whereas the $b^3\Pi_r$ -state has only recently been detected. The vibrational and rotational constants for these states were observed, as expected, smaller than for the ground state.

The next configuration

$$\text{KKL } (z\sigma)^2(y\sigma)^2(\omega\pi)^3(x\sigma)^2(v\pi) \dots C^1\Sigma^-, D^1\Delta, E^1\Sigma^+ \\ e^3\Sigma^-, d^3\Delta, a^3\Sigma^+$$

gives six states. This configuration has three ($\omega\pi$) orbitals which are strongly bonding and only one antibonding ($v\pi$) orbital. The magnitude of the vibrational and rotational constants of these states are expected to be smaller than those of states belonging to the above mentioned configuration.

The other possible excitation schemes are

$$\text{KKL } (z\sigma)^2(y\sigma)^2(\omega\pi)^3(x\sigma)(v\pi)^2 \dots 1\Pi_r(3), 1\Phi, 3\Pi_i(2) \\ 3\Pi_r(2), 3\Phi_i, 5\Pi_i$$

$$\text{KKL } (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)(v\sigma) \dots 1\Sigma^+, 3\Sigma^+$$

These above mentioned transitions were for the valence states.

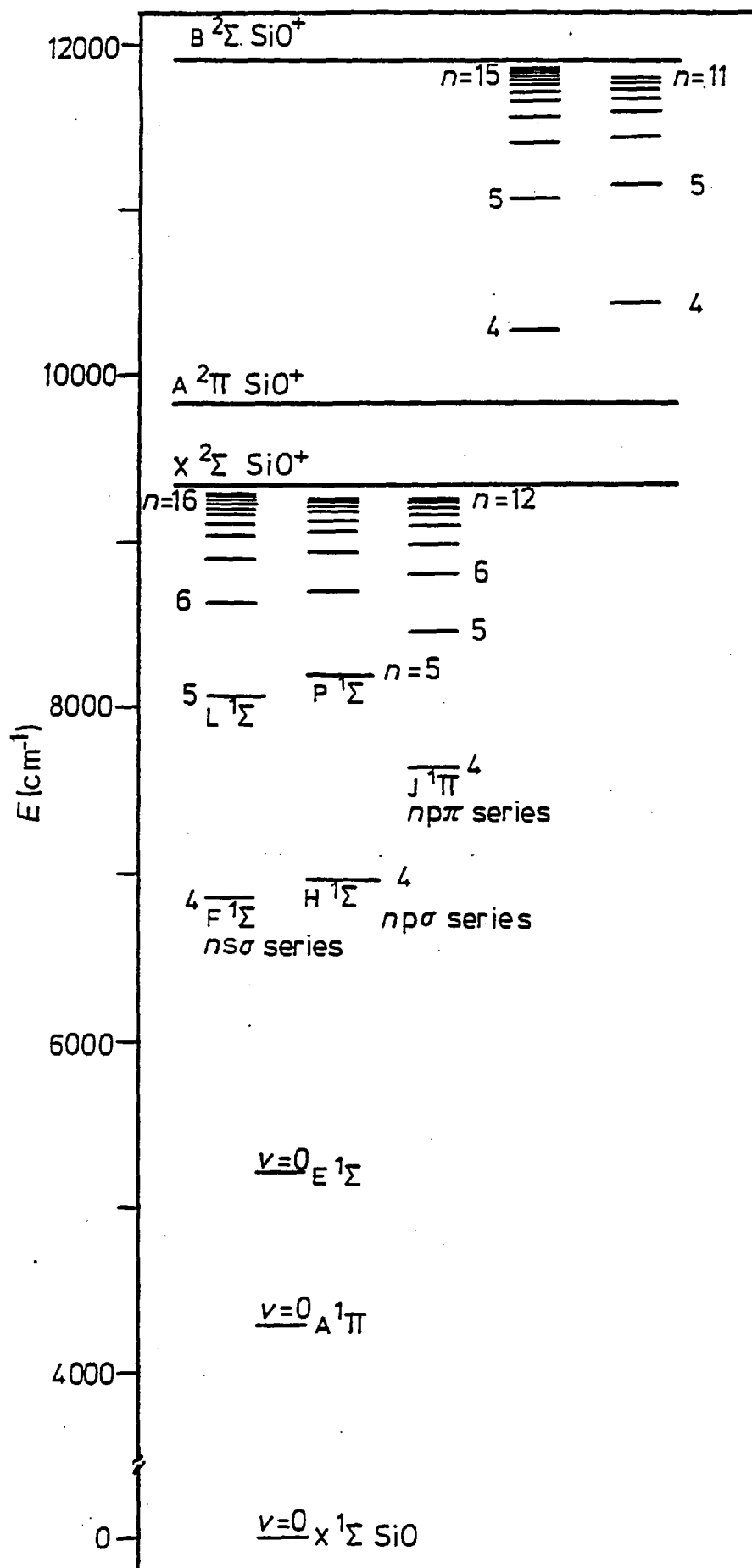


FIGURE 5.2.1 - Term diagrams of the SiO molecule.

The Rydberg states can be represented by the configuration

$$\text{KKL } (z\sigma^-)^2(y\sigma^-)^2(\omega\pi)^4(x\sigma^-) \dots n\ell\lambda$$

where n is the principal quantum number of the Rydberg electron, ℓ is its angular momentum and λ is the component of ℓ along the internuclear axis.

For atomic Rydberg states the quantum numbers n and ℓ are well-defined, while for molecular Rydberg states the meaning is less precise. Taking away the Rydberg electron, we obtain the configuration for the ground state $^2\Sigma^+$ of $\text{Si } 0^+$. The molecular Rydberg series are the lowest in energy because they arise by excitation of the outermost valence electrons and therefore converge on the $X^2\Sigma^+$ ground state of $\text{Si } 0^+$. The Rydberg states originating from this configuration are expected to have the same B and ω values as the ground state of $\text{Si } 0^+$. Rydberg series of progressively higher energies are obtained as deeper valence electrons are excited and they converge on excited states of $\text{Si } 0^+$. In Fig.(5.2.1) we represent the Rydberg series accessible in absorption from the ground state of $\text{Si } 0$ and converging on the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of $\text{Si } 0^+$.

We will discuss now (i) the various band systems which arise by excitation of an $x\sigma^-$ electron to $ns\sigma^-$, $np\sigma^-$, and $np\pi$ orbitals, (ii) the arrangement of the (0,0) bands of the system into Rydberg series converging on $X^2\Sigma^+$ state, and (iii) a further Rydberg series of band systems converging on the $B^2\Sigma^+$ state of $\text{Si } 0^+$.

5.2.4a $ns\sigma^-$ Band Systems

We have observed a series of bands, which are designated $1\Sigma^+ - 1\Sigma^+$ transition. The longest wavelength member of this series, corresponding to the deepest lying Rydberg state of the $ns\sigma^-$

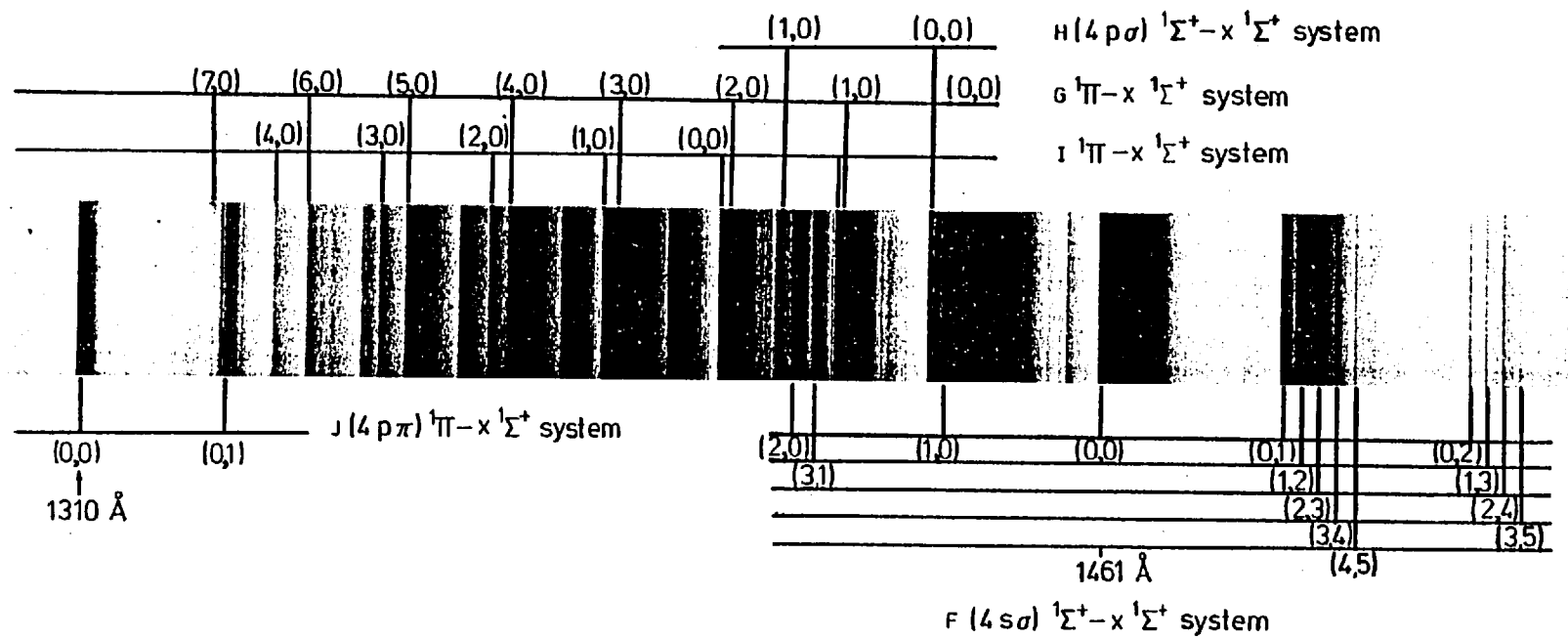


FIGURE 5.2.2 - Known band systems of the Si O molecule between 1500 and 1300 Å.

series was analysed by Lagerqvist et al. (1973). It is assigned $F(ns\sigma)^1 \Sigma^+$ and originates from the configuration

$$KKL (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)(ns\sigma) F^1 \Sigma^+.$$

which is analogous to the $B^1 \Sigma^+$ state of CO. Lagerqvist et al. (1973) analysed the (0,0), (1,0), (2,0), (3,1) and (0,1) bands of this system and the $n=4$ assignment of the Rydberg state was supported by the values of the vibrational and rotational constants deduced from the observations. The next member of this series is $L^1 \Sigma^+$ which was interpreted as the $5s\sigma L^1 \Sigma^+$ Rydberg state, consisting of (0,0), (1,0) and (2,0) bands. These two members have been reproduced in Fig.(5.2.2). The other members of this series up to $n=16$ have been observed for the first time in the present investigation and are listed in Table (5.2.1). The dispersion available in the present experiment was not sufficient to enable a rotational analysis of the new band systems but the ionization potential of Si 0 was determined from this series.

5.2.4b $np\sigma$ Band Systems

Lagerqvist et al. (1973) observed two band systems which belong to this series, namely $H(4p\sigma)^1 \Sigma^+$ at 1435 Å and $P(5p\sigma)^1 \Sigma^+$ at 1220 Å. The $H^1 \Sigma^+ - X^1 \Sigma$ system consists of (0,0) and (1,0) bands whereas the $P^1 \Sigma^+ - X^1 \Sigma$ system has (0,0), (1,0) and (2,0) bands. The band systems have the same vibrational and rotational constants which is consistent with the interpretation as Rydberg states. This is the most intense series of bands in the absorption spectrum of Si 0 and has been extended up to $n=13$. Fig. (5.2.3) shows all the observed Rydberg series converging on the ground state of Si 0^+ . Wavelengths, wavenumbers and effective quantum numbers for these systems are collected in Table (5.2.2).

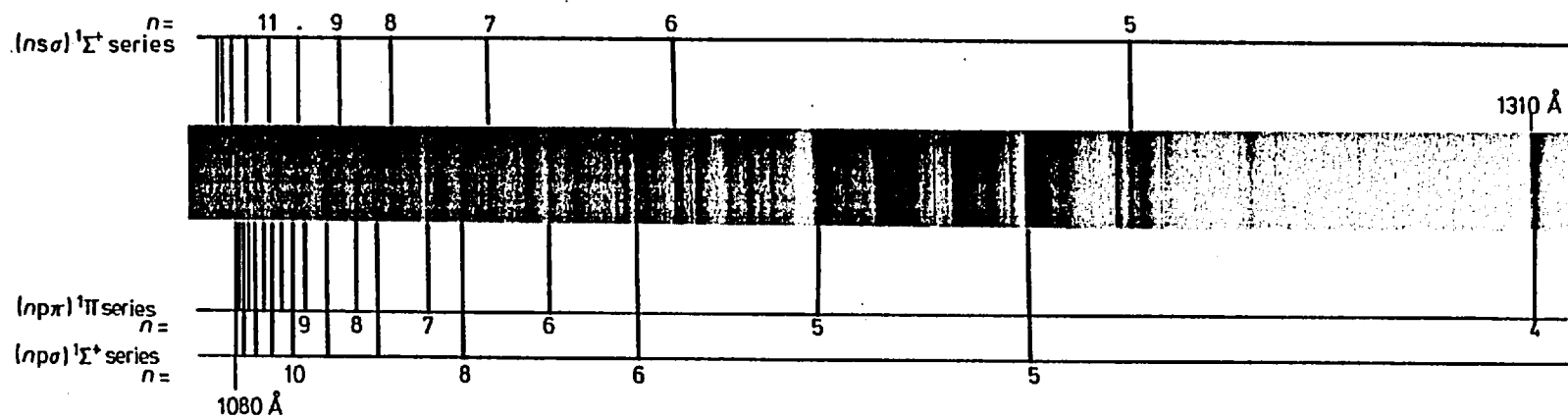


FIGURE 5.2.3 - Rydberg series converging on the $X^2 \Sigma^+$ state of Si O^+ .

5.2.4c np π Band Systems

The leading member of this series at 1310 Å has been analysed by Lagerqvist et al. (1973) and is assigned as a transition to $(4p\pi)J^1\pi-X^1\Sigma^+$. Lagerqvist et al. (1973) observed (1,0), (0,0) and (0,1) bands but only the (0,0) band was rotationally analysed. All the other members upto $n=12$ are reported here for the first time. This is a weak series with consistent quantum defect which merges with other series to the same limit above $n=12$. This state originates from the configuration

$$KKL (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma) (np\pi) ^1\pi$$

Wavelengths, wavenumbers and effective quantum numbers are collected in Table (5.2.3).

5.2.5 Rydberg Series Converging on the $X^2\Sigma^+$ State of $Si\ 0^+$

The observed structure between 1070 Å and 1500 Å can be arranged into three Rydberg series which are designated by the upper configurations $KKL (z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma) (ns\sigma) ^1\Sigma^+$

$$(np\sigma) ^1\Sigma^+$$

$$(np\pi) ^1\pi$$

These series converge on the ground state of the ion and the series limit will give an accurate value of the first ionization potential of Si 0. We have fitted the observed Rydberg series to the formula

$$T_{n\ell\lambda} = T_{\infty} - \frac{R}{(n^*)^2} = T_{\infty} - \frac{R}{(n - \delta_{\ell\lambda})^2}$$

where $T_{n\ell\lambda}$ is the term value, T_{∞} is the ionization potential, R is the Rydberg constant and n is the principal quantum number. The quantum defect $\delta_{\ell\lambda}$ is plotted against $(n^*)^{-2}$ in Figure (5.2.4). Here ℓ is the angular momentum of the Rydberg electron and λ is the component of ℓ along the internuclear axis.

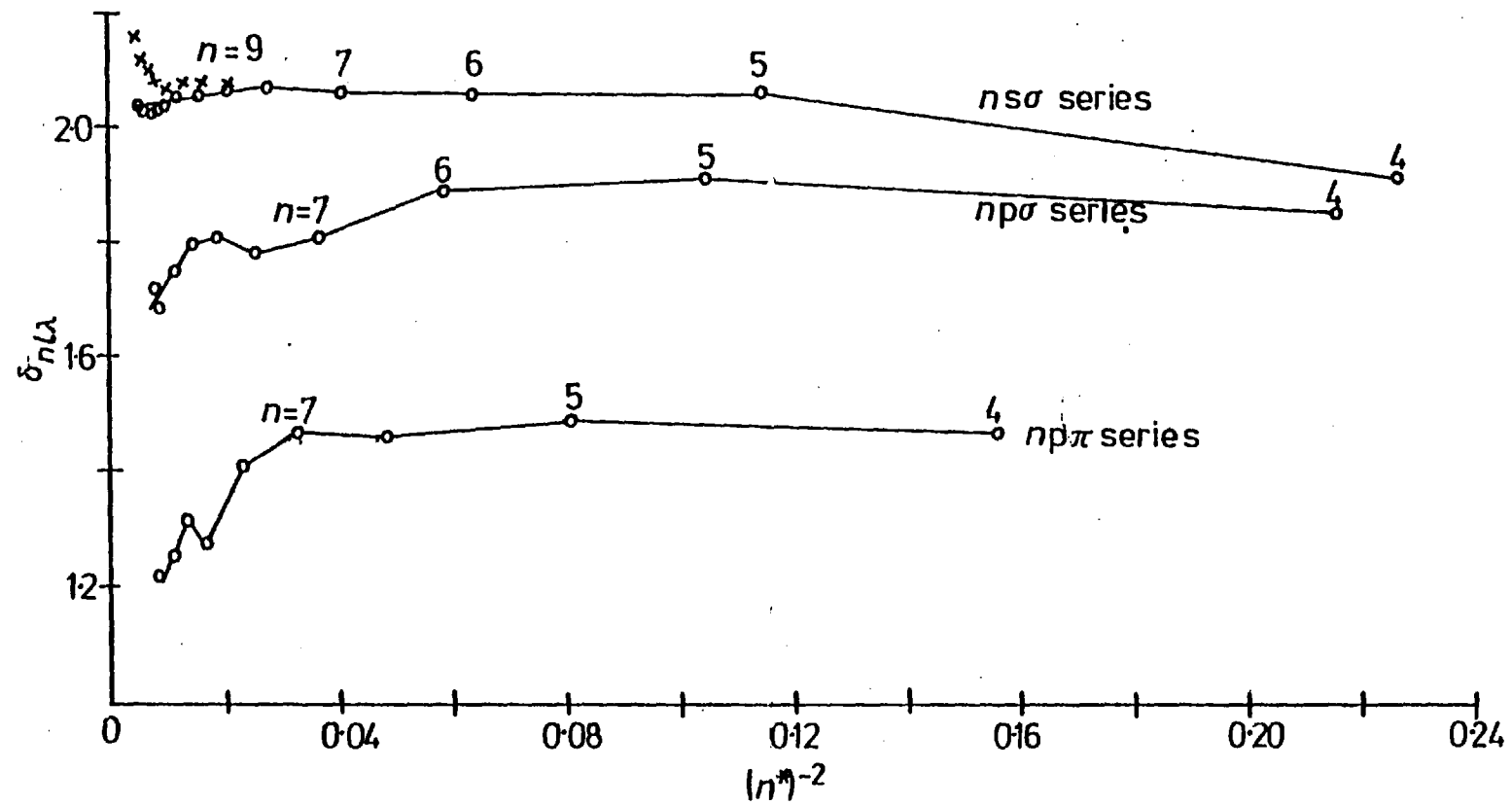


FIGURE 5.2.4 - Edlen plot for the determination of the ionization potential.

The quantum defect of each series is calculated for $T_{\infty} = 93430 \text{ cm}^{-1}$ (11.584 eV) and the values of $\delta_{\ell\lambda}$ lie approximately on straight lines, but if the ionization potential were changed by 10 cm^{-1} the points marked as crosses in Fig.(5.2.4) would be obtained, which indicates a statistical error of about $\pm 10 \text{ cm}^{-1}$ in the determination of the ionization potential. Since the values reported are for the band heads, our accuracy also depends on the difference $\mathcal{V}_{\text{head}} - \mathcal{V}_{\text{origin}}$; this could only be extracted from a complete rotational analysis, which becomes progressively more difficult at higher n values even when high dispersion is available. However we are able to calculate the probable difference because the rotational constants of the $X^2\Sigma^+$ of Si O $B_0 = 0.71780 \text{ cm}^{-1}$ (Singh et al. 1973), and of the $X^1\Sigma^+$ of Si O $B_0 = 0.72442 \text{ cm}^{-1}$ (Elander and Lagerqvist, 1971) are known. Using the formula

$$\mathcal{V}_{\text{head}} - \mathcal{V}_{\text{orig}} = - \frac{(B' + B'')^2}{4(B' - B'')}$$

we obtain the value 78.55 cm^{-1} , which is larger than the statistical error from the quantum-defect fit. The systematic shift could, of course, be allowed for but it is perhaps more realistic to quote a larger error. We thus arrive at the figure $11.584 \pm 0.011 \text{ eV}$.

The reported values of the ionization potential of Si O are 11.43 (Lagerqvist and Renhorn, 1974) estimated from optical spectroscopy, $11.69 \pm 0.16 \text{ eV}$ (Kuande and Wahlbeck, 1976), $11.58 \pm 0.10 \text{ eV}$ (Hildebrande, 1971), $11.6 \pm 0.2 \text{ eV}$ (Hildebrande and Murad, 1969) from electron impact mass spectroscopy and $11.61 \pm 0.01 \text{ eV}$ (Colbourn et al. 1978) from photoelectron spectroscopy.

5.2.6 Rydberg Series converging on the $B^2\Sigma^+$ State of Si O⁺

The absorption spectrum of Si O in the region 850-1000 Å shows rather simple features which are reproduced in Figure (5.2.5). As all these levels lie above the first ionization threshold, they

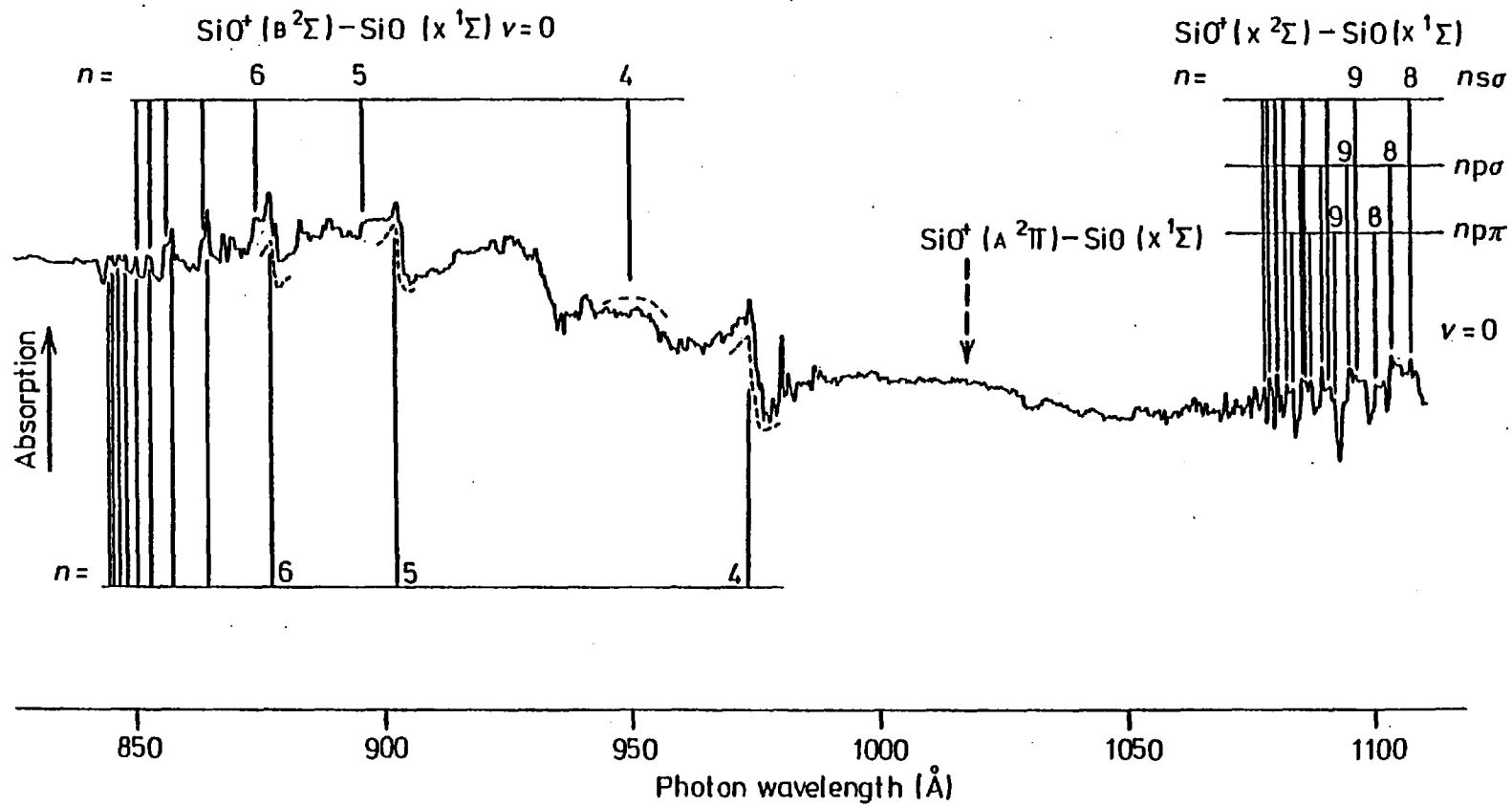


FIGURE 5.2.5 - Densitometer trace of the spectrum of the Si O molecule between 850-1000 Å.

show asymmetric line profiles due to the autoionization phenomena. We have made densitometer traces of this region to show the effect more clearly.

The bands are classified into four Rydberg series converging on the $B^2\Sigma^+$ state of Si 0. One of the series, which consists of symmetrical features, is similar in appearance to the analogous series converging on the $B^2\Sigma^+$ state of CO^+ (Ogawa and Ogawa, 1972) and $B^2\Sigma^+$ state of N_2^+ (Ogawa and Tanaka, 1962), while the other consists of intense asymmetric Beutler-Fano absorption profiles.

The effective quantum numbers for these series have been calculated using the limit 119410 cm^{-1} . This value can be compared with the value calculated from $B^2\Sigma^+ - X^2\Sigma^+ = 26016.55\text{ cm}^{-1}$ given by Singh et al. (1973) and T_∞ value for the first ionization limit of Si 0 obtained in the present experiment - 93430 cm^{-1} .

$T_{B^2\Sigma^+} + T_\infty = 119446.55\text{ cm}^{-1}$, whereas the value deduced from the series limit is 119410 cm^{-1} . The agreement between the observed and calculated values is within the experimental error for excitation from the $v=0$ level.

Excitation of the $B^2\Sigma^+$ state in the photoelectron spectrum of Si 0 has recently been reported by Colbourn et al. (1978) who gave the value $14.80 \pm 0.01\text{ eV}$, which is in good agreement with the present observation : $14.805 \pm 0.003\text{ eV}$.

The observed Rydberg bands might be due to the transition between the upper $1\Sigma^+$ or 1Π state and the $X^1\Sigma^+$ ground state of Si 0. The possible electron configurations and the upper states of the observed Rydberg series are as follows.

$$\begin{array}{l}
 \text{KKL } (z\sigma)^2(y\sigma)(\omega\pi)^4(x\sigma)^2 \quad (ns\sigma) \quad 1\Sigma^+ \\
 \quad \quad \quad (np\sigma) \quad 1\Sigma^+ \\
 \quad \quad \quad (np\pi) \quad 1\Pi \\
 \quad \quad \quad (nd\sigma) \quad 1\Sigma^+ \\
 \quad \quad \quad (nd\pi) \quad 1\Pi
 \end{array}$$

TABLE 5.2.1

$(ns\sigma)^{-1} \Sigma^{+}$ Series converging on the
 $\chi^2 \Sigma^{+}$ state of Si 0^{+}

n	System	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	n^{*}
4	$F(4s\sigma)^{-1} \Sigma^{+}$	1460.14	68486.58	2.10
5	$L(5s\sigma)^{-1} \Sigma^{+}$	1238.68	80731.10	2.94
6	-	1157.60	86386	3.95
7	-	1124.46	88932	4.94
8	-	1107.30	90310	5.93
9	-	1098.08	91068	6.82
10	-	1090.64	91689	7.94
11	-	1086.28	92057	8.94
12	-	1083.15	92323	9.96
13	-	1081.29	92482	10.76
14	-	1079.05	92674	12.05
15	-	1077.94	92769	12.89
16	-	1076.86	92862	13.90

TABLE 5.2.2

$(np\sigma)^1 \Sigma^+$ series converging on the
 $\chi^2 \Sigma^+$ state of Si 0^+

n	System	λ (Å)	ν (cm ⁻¹)	n^*
4	H(4p σ) ¹ Σ^+	1434.82	69695.15	2.15
5	P(5p σ) ¹ Σ^+	1219.97	81969.23	3.09
6	--	1150.38	86928	4.11
7	--	1119.06	89361	5.19
8	--	1103.84	90593	6.22
9	--	1095.21	91307	7.19
10	--	1089.37	91796	8.20
11	--	1085.26	92144	9.24
12	--	1082.30	92396	10.30
13	--	1080.33	92564	11.26

TABLE 5.2.3

$(np\pi)^1\Pi$ Series converging on the $X^2\Sigma$ state of $Si\ O^+$

n	System	$\lambda\ (\text{\AA})$	$\nu\ (\text{cm}^{-1})$	n^*
4	$J(4p\pi)^1\Pi^+$	1309.76	76349.87	2.53
5	--	1182.97	84533	3.51
6	--	1134.93	88111	4.54
7	--	1114.27	89745	5.46
8	--	1100.08	90902	6.59
9	--	1091.81	91591	7.72
10	--	1087.30	91971	8.67
11	--	1083.77	92271	9.73
12	--	1081.29	92482	10.76

TABLE 5.2.4

Rydberg series converging on the $B^2\Sigma^+$ state of $Si\ O^+$

Series limit = $119410\ \text{cm}^{-1}$

n	$\lambda\ (\text{\AA})$	$\nu\ (\text{cm}^{-1})$	n^*
4	948.32	105450	2.80
5	894.21	111830	3.80
6	871.82	114703	4.83
7	860.26	116244	5.89
8	853.70	117137	6.95
9	849.89	117662	7.92
10	847.17	118040	8.95

This series consists of intense asymmetric resonances.

TABLE 5.2.5

Rydberg series converging on the $B^2 \Sigma^+$ state of $Si\ O^+$

Series Limit = 119410 cm^{-1}

n	λ (Å)	ν (cm^{-1})	n^*
4	973.24	102750	2.57
5	901.87	110881	3.59
6	874.90	114299	4.53
7	862.42	115953	5.63
8	855.29	116919	6.64
9	850.69	117552	7.69
10	847.74	117960	8.70
11	845.66	118251	9.73
12	844.25	118448	10.68
13	843.11	118608	11.76
14	842.29	118724	12.65

This is a series of broad symmetrical features.

TABLE 5.2.6

Rydberg series converging on the $B^2 \Sigma^+$ state of $Si\ O^+$

Series Limit = 119410 cm^{-1}

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	n^*
912.99	109530	3.33
881.45	113449	4.29
865.63	115523	5.31
857.73	116587	6.23

TABLE 5.2.7

Rydberg series converging on the $B^2 \Sigma^+$ state of $Si\ O^+$

Series Limit = 119410 cm^{-1}

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	n^*
922.63	108386	3.16
888.37	112566	4.00
866.91	115352	5.20

Inspection of the effective quantum numbers suggests that the series listed in Table 5.2.4 might be due to the configuration

$$\text{KKL } (z\sigma)^2(y\sigma)(\omega\pi)^4(x\sigma)^2 n\sigma^{-1} \Sigma^+$$

whereas the series listed in Tables (5.2.5) and (5.2.6) have the upper states $(np\pi)^1\pi$ and $(np\sigma)^1\Sigma^+$.

Colbourn et al. (1978) also report the $A^2\pi$ state of $\text{Si } 0^+$ at 12.19 eV and calculate the internuclear distance for the state. In Figure (3) of their paper, potential curves for $X^2\Sigma^+$, $A^2\pi$ and $B^2\Sigma^+$ are given. The internuclear distance for $A^2\pi$ is about 0.1 Å larger than for the other two states. We find very weak features in the vicinity of the $A^2\pi$ limit but these are too diffuse to be measured. The weakness of the features can be attributed to the fact that the $A^2\pi$ level has a larger internuclear distance than the ground state which reduces the transition probability. The potential curves for $X^2\Sigma^+$ and $A^2\pi$ cross above the $v=0$ level of $X^2\Sigma^+$, which explains why prominent series converge on the $v=0$ level of $X^2\Sigma^+$, but there are no series to $v=1$ or higher vibrational levels of $X^2\Sigma^+$.

5.3 Vacuum Ultraviolet Spectrum of Ge 0

5.3.1 Summary

The absorption spectrum of the Ge 0 molecule in the region 1000-1800 Å has been observed and extended below 1500 Å for the first time. A number of new Rydberg states have been discovered which are assigned to Rydberg series converging on the $X^2\Sigma^+$ -state of $\text{Ge } 0^+$. An accurate value of the first ionization potential of Ge 0 is determined as $90730 \pm 30 \text{ cm}^{-1}$ ($11.249 \pm 0.004 \text{ eV}$).

5.3.2 Introduction

The absorption spectrum of the Ge 0 molecule in the ultraviolet region was studied by Shaw (1937) who found twentyone red degraded

bands and assigned them to the $D^1\Pi - X^1\Sigma^+$ transition. This system was later observed by Sen-Gupta (1937) who extended the observed spectral region to 3300-2340 Å recording 46 bands of this system. Sen-Gupta (1939) performed the rotational analysis of this system and identified this transition as $^1\Sigma - ^1\Sigma$. Lagerqvist et al. (1959) investigated the analogous system in Sn O and from the rotational analysis established the electronic transition responsible for this system $^1\Pi - ^1\Sigma^+$ analogous to the $A^1\Pi - X^1\Sigma^+$ system of Co and Si O. Lagerqvist et al. (1959) argued that the rotational analysis of the corresponding system in Ge O, Sen-Gupta (1939), is incorrect and that the latter system also corresponds to a $^1\Pi - ^1\Sigma^+$ transition.

Sharma and Padur (1967) observed the spectrum of the chemiluminescence produced during the reaction of germanium tetrahydride and atomic oxygen in the region 5100-2450 Å. In addition to extensions of the $D^1\Pi - X^1\Sigma^+$ system, they identified a new electronic transition on the long wavelength side of the $D^1\Pi$ -state which was interpreted as the transition analogous to the B-X systems in Pb O and Sn O. Tewari and Mohan (1971) reported the thermal emission spectrum of Ge O in the region 5100-4600 Å using high temperature vacuum graphite furnace and rephotographed the B-X system.

The absorption studies were initiated by Shapiro et al. (1932), Drummond and Barrow (1952) and Barrow and Rowlinson (1954). The work of Barrow and Rowlinson (1954) in the ultraviolet region revealed strong absorption band systems of Si O, Ge O and Sn O molecules. Some of the observed transitions were interpreted as the Rydberg states corresponding to the deepest laying members of the $(ns\sigma)^1\Sigma^+, (np\sigma)^1\Sigma^+$ and $(np\pi)^1\Pi$ series. The work on Si O was extended to the vacuum ultraviolet region by Lagerqvist et al. (1973). More recently Baig and Connerade (1979) reported the spectrum of Si O in the region 2000-700 Å and observed the Rydberg series converging on the $X^2\Sigma^+$

and $B^2\Sigma^+$ states of $Si\ O^+$.

The $Ge\ O$ molecule possesses the same valence electron configuration in the ground state as CO and $Si\ O$. Therefore, one should expect similar structure in the vacuum ultraviolet region. A minor difference in structure will result from the heavier nucleus leading to smaller vibrational frequency intervals. Therefore, by promoting the valence shell electron to higher Rydberg orbitals one should observe the series converging on the corresponding upper configurations. These Rydberg series enable a more accurate value of the first ionization potential to be deduced.

Three Rydberg series have been observed in the far ultraviolet absorption spectrum converging to the $X^2\Sigma^+$ -state of the $Ge\ O^+$ ion. The first ionization potential is found to be $90730 \pm 30\text{ cm}^{-1}$ (11.249 eV).

5.3.3 Results

The absorption spectrum of $Ge\ O$ was recorded using synchrotron radiation of the 500 MeV electron accelerator at Bonn, Connerade et al. (1974). The $Ge\ O$ was produced by heating $Ge\ O_2 + Ge$ in an induction furnace in the temperature range 1100-1300°C. The sample was loaded into the 0.3 mm thick tantalum tube 30 cm long with six tantalum baffles and an inner tube of 4 mm inner diameter in it.

The spectra were recorded in the first order of a 1 m normal incidence vacuum spectrograph equipped with a 1200 lines/mm grating. The exposure time ranged from 20-40 min. on Ilford Q2 plates.

5.3.4 Analysis

The absorption spectrum of $Ge\ O$ in the region 1000-1550 Å is reproduced in Fig.(5.3.1). For comparison, we also show the absorption spectra of $Si\ O$ in the same region which facilitates the identification of corresponding transitions in the two molecules.

We discuss all the observed band systems below.

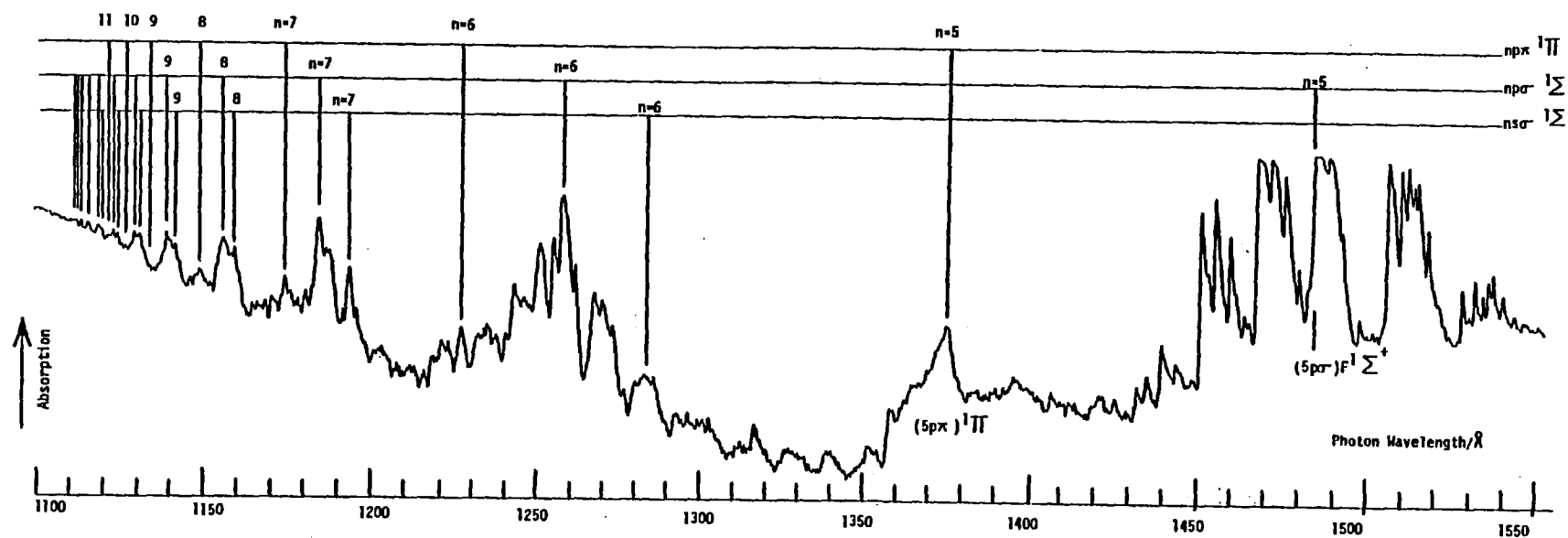


FIGURE 5.3.1 - Absorption spectrum of Ge 0 between 1000-1550 Å showing the Rydberg series.

(a) $F^1 \Sigma^+ - X^1 \Sigma^+$ Transition

This band system was previously observed in absorption by Barrow and Rowlinson (1954) who performed the vibrational analysis and interpret this transition as a Rydberg state analogous to the $B^1 \Sigma^+$ state of CO and $F^1 \Sigma^+$ -state of Si O. This band system is very well developed on our plates (see Fig.5.3.1) and we adopt the vibrational assignment of Barrow and Rowlinson (1954). We interpret this state as a member of the $(np\sigma)^1 \Sigma^+$ series converging on the $X^2 \Sigma^+$ state of Ge O⁺. This interpretation is suggested by its correlation with the higher members of this series yielding consistent quantum defects and a smooth course of intensities. This series of the Rydberg bands has been observed up to n=16 (Table 5.3.1) for the first time, and possesses similar quantum defects to those reported for the $(np\sigma)^1 \Sigma^+$ series in Si O.

(b) $J^1 \Pi - X^1 \Sigma^+$ Transition

There are three bands observed for this system. (0,0) at 1374.6 Å, (1,0) at 1357.7 Å and (0,1) at 1393 Å. We have identified the transition corresponding to the deepest lying Rydberg state of the $(np\Pi)^1 \Pi$ series. This band system lies in the expected region for a $^1 \Pi - ^1 \Pi$ transition analogous to the $(4p\Pi)J^1 \Pi$ -state of Si O (Lagerqvist et al. 1973). The same nomenclature has been retained here. The vibrational assignment is straightforward yielding the value of $\Delta G'(v + 1/2) = 907 \text{ cm}^{-1}$ which is a reasonable value for the Rydberg state. The (0,1) band of this system is very weak and could not be measured very accurately.

Higher members of this series have been observed up to n=12 (Fig. 5.3.2). The quantum defect is also in agreement with the analogous $(np\Pi)^1 \Pi$ series in Si O.

(c) $L^1 \Sigma^+ - X^1 \Sigma^+$ Transition

Only two bands of this system were identified as (0,0) at 1283.04 Å and (1,0) at 1269.99 Å. The value of the vibrational constant is found to be $\Delta G'(v + 1/2) = 800 \text{ cm}^{-1}$. We have interpreted this state as a member of the $(ns\sigma)^1 \Sigma^+$ -series which has a limit at $X^2 \Sigma^+$ -state of Ge 0⁺. This identification is supported by comparison with the analogous state in Si 0 $(5s\sigma)L^1 \Sigma^+$ and the consistency of the quantum defect with those of higher members of this series which are reported up to $n=12$. The second argument in support of the above interpretation is similar n^* value which has been reported for the analogous $(ns\sigma)^1 \Sigma^+$ series in Si 0.

(d) $P^1 \Sigma^+ - X^1 \Sigma^+$ Transition

This is the strong band system having comparable intensity to that of the $F^1 \Sigma^+$ -system. Three bands (0,0) at 1257.63 Å, (1,0) at 1243.65 Å and (0,1) at 1273.28 Å have been identified. We have used the same name for this system as for the analogous transition in Si 0 (Lagerqvist et al. 1973), Baig and Connerade 1979). The wavenumbers of the observed band heads have been fitted in the formula (Herzberg 1950).

$$T_{v',v''} = \nu_e + \omega'_e(v' + \frac{1}{2}) - \omega'_e x'_e(v' + \frac{1}{2})^2 - \omega''_e(v'' + \frac{1}{2}) + \omega''_e x''_e(v'' + \frac{1}{2})^2$$

where v' and v'' correspond to the upper and lower vibrational levels respectively. The vibrational constants obtained in this way are

$$\begin{aligned}\nu_e &= 79557 \text{ cm}^{-1} \\ \omega_e &= 902 \text{ cm}^{-1} \\ \omega'_e x'_e &= 4 \text{ cm}^{-1} \\ \omega''_e &= 985.5 \text{ cm}^{-1} \\ \omega''_e x''_e &= 4.29 \text{ cm}^{-1}\end{aligned}$$

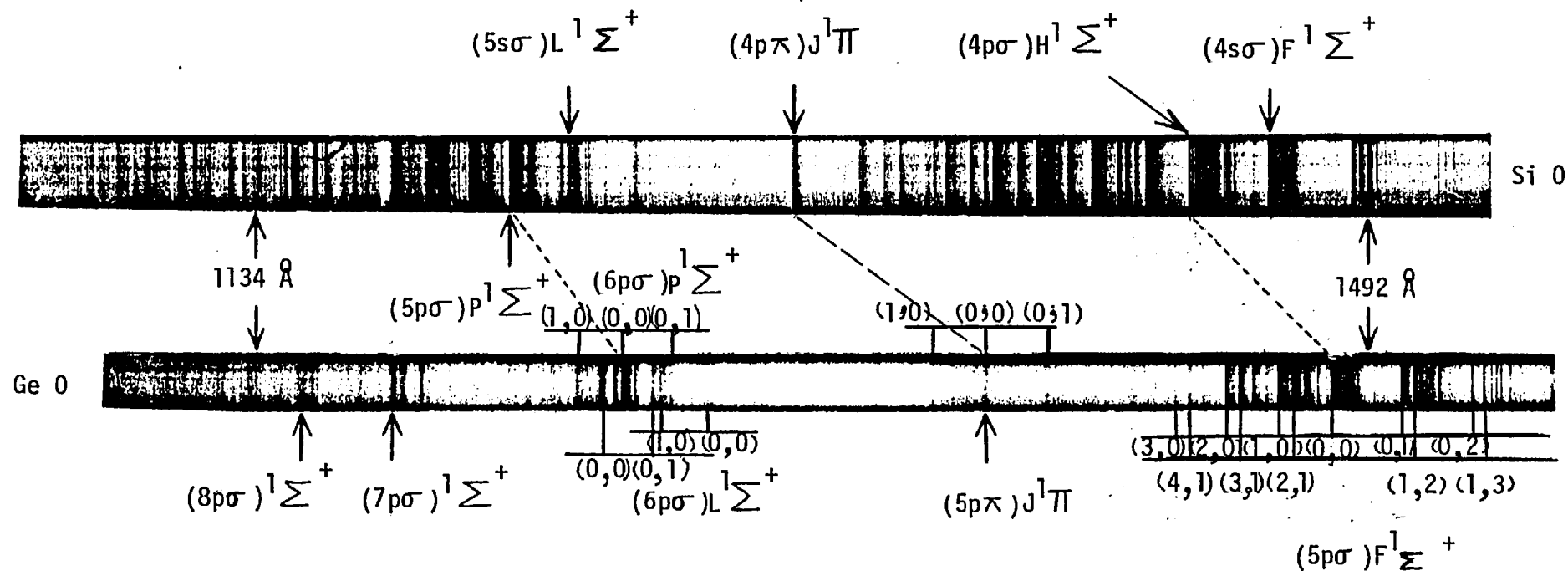


FIGURE 5.3.2 - Absorption Spectra of Ge 0 and Si 0 showing the corresponding transitions in both species.

We have interpreted this Rydberg state as the second member of the $(np\sigma)^1 \Sigma^+$ series. This series is easily followed to high n values since the intensity distribution and the quantum defect behave in a regular manner.

There are some more band systems in this spectral region which we could not fit into the analysis. Two strong bands have been tentatively identified as the (0,0) at 1251.8 Å and (0,1) at 1267.25 Å bands of another electronic transition which may be called $N-X^1 \Sigma^+$.

The other bands can be attributed to excitation of the valence states. A more complete analysis would be possible only if a higher dispersion spectrum were available. Such an extension is planned but, in the present investigation, we only report observations of the Rydberg series converging on the ground state of the $\text{Ge } 0^+$, from which a more accurate value of the first ionization potential of Ge 0 has been calculated.

5.3.5 Rydberg Series converging on $X^2 \Sigma^+$ State

The ground state electron configuration of Ge 0 is

$$\text{KKLM } (z\sigma)^2 (y\sigma)^2 (\omega\pi)^4 (x\sigma)^2 \dots X^1 \Sigma^+$$

The Rydberg states are obtained by promoting the $(x\sigma)$ electron to various Rydberg orbitals. Thus

$$\text{KKLM } (z\sigma)^2 (y\sigma)^2 (\omega\pi)^4 (x\sigma) (n\ell\lambda)$$

where n is the principal quantum number of the Rydberg electron, ℓ is its angular momentum and λ is the component of ℓ along the internuclear axis. The Rydberg series converge on the $X^2 \Sigma^+$ state of $\text{Ge } 0^+$ and the possible configurations for the upper state are

$$\begin{aligned} \text{KKLM } (z\sigma)^2 (y\sigma)^2 (\omega\pi)^4 (x\sigma) \quad & (ns\sigma)^1 \Sigma^+ \\ & (np\sigma)^1 \Sigma^+ \\ & (np\pi)^1 \Pi \end{aligned}$$

TABLE 5.3.1

(ns σ) $^1\Sigma^+$ Series (0, 0) Bands

n	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	n^*
6	1283.04	77940	2.93
7	1193.22	83807	3.98
8	1159.22	86265	4.96
9	1140.81	87657	5.98
10	1130.22	88478	6.98
11	1123.19	88874	7.98
12	1118.95	89369	8.98

(The wavelengths given here and in the following tables refer to bandheads rather than origins).

TABLE 5.3.2

(np σ) $^1\Sigma^+$ Series (0,0) Bands

n	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	n^*
5	1483.90	67390	2.17
6	1257.63	79515	3.13
7	1184.44	84428	4.17
8	1154.65	86606	5.16
9	1138.72	87818	6.14
10	1128.68	88599	7.18
11	1122.46	89090	8.18
12	1118.29	89422	9.16
13	1115.24	89667	10.16
14	1112.95	89851	11.17
15	1111.30	89985	12.14
16	1109.95	90094	13.14

$(np\pi)^1\Pi$ Series (0,0) Bands

n	λ (Å)	$\tilde{\nu}$ (cm ⁻¹)	n^*
5	1374.68	72744	2.47
6	1227.23	81484	3.45
7	1174.05	85175	4.44
8	1148.98	87034	5.45
9	1135.14	88095	6.45
10	1126.86	88742	7.43
11	1121.20	89190	8.44
12	1117.37	89496	9.43

TABLE 5.3.4

New Band Systems

(i) <u>$(5p\pi)^1\Pi - X^1\Sigma^+$</u>	v'/v''	λ (Å)	
	(0,0)	1374.68	
	(1,0)	1357.75	
	(0,1)	1393	$\Delta G'(v+\frac{1}{2}) = 907 \text{ cm}^{-1}$
(ii) <u>$(5s\sigma)^1\Sigma^+ - X^1\Sigma^+$</u>	(0,0)	1283.04	
	(1,0)	1269.99	$\Delta G'(v+\frac{1}{2}) = 800 \text{ cm}^{-1}$
(iii) <u>$(6p\sigma)^1\Sigma^+ - X^1\Sigma^+$</u>	(0,0)	1257.63	
	(1,0)	1243.65	$\omega'_e = 902 \text{ cm}^{-1}$
	(0,1)	1273.28	$\omega'_e X'_e = 4 \text{ cm}^{-1}$
(iv) <u>$N - X^1\Sigma^+$</u>	(0,0)	1251.8	
	(0,1)	1267.25	

All these Rydberg series have been identified and the wavelength and wavenumbers along with the identification is given in Tables.

The Rydberg series were fitted to the formula

$$T_e = I_0 - \frac{R}{(n-\delta)^2}$$

where T_e is the electronic energy, I_0 is the ionization potential, R the Rydberg constant, n the principal quantum number associated with the Rydberg electron and δ is the quantum defect.

It is assumed that the series limit corresponds to the ground state $X^2\Sigma^+$ of the $\text{Ge } O^+$ ion. Using the value of 90730 cm^{-1} (11.249 eV) for I_0 in the above equation, very consistent effective quantum numbers were obtained.

$I_0 = 90730 \text{ cm}^{-1}$ was determined from Edlen plots applied to the data for the best developed series, namely $(np\sigma)^1\Sigma^+$. We have estimated the uncertainty in the determination of the ionization potential by considering the effect of a change of $\pm 10 \text{ cm}^{-1}$ on the linearity of the quantum defect plot. An additional uncertainty of 20 cm^{-1} (which is actually a systematic error) arises from the difference in energy between the band origin and band head for each value of n . We therefore report a total error of $\pm 30 \text{ cm}^{-1}$ in the determination of the first ionization potential of $\text{Ge } O$.

The only value for the ionization potential is given by Hildebrand and Murad (1964): $11.5 \pm 0.5 \text{ eV}$, using mass spectroscopy. Within the estimated uncertainty given by Hildebrand and Murad (1964) our value is in agreement with the known one.

5.4 VUV Absorption Spectrum of AℓF Molecule

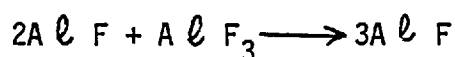
5.4.1 Summary

In the present investigation we have observed the absorption spectra of AℓF in the region $800\text{--}2000 \text{ \AA}$ using synchrotron radiation

as the background source and a 1m normal incidence vacuum spectrograph. All the known band systems have been reproduced and numerous new band systems in the short wavelength end have been recorded. Owing to the low dispersion, a detailed analysis of the band system was not possible. However, there is clear evidence that the molecule was properly generated in our vapour containment system.

5.4.2 Introduction

The absorption spectra of the AlF molecule was first reported by Barrow and Rowlinson (1954) in the region 1250-2000 Å using a Lyman source as the background continuum. The AlF molecule was generated by the following reaction



The mixture of Aluminium and Aluminium Trifluoride was heated in a King furnace with path lengths of about 20-30 cm at temperatures of 1000°C. Barrow and Rowlinson (1954) reported the vibrational analysis for the six new singlet band systems, namely $B^1\Sigma-X^1\Sigma$, $C^1\Sigma-X^1\Sigma$, $E^1\Sigma-X^1\Sigma$, F-X, G-X and H-X. Barrow and Rowlinson (1954) also found numerous strong bands in the region 1340 to 1410 Å, which were not analysed due to their complexity and the bands were attributed to the AlF_3 molecule. This region of the spectrum was of particular interest because the lowest Rydberg series in AlF were expected.

More recently Barrow et al. (1974) have made a detailed investigation of the AlF molecule and report the transitions between nine singlet states, including the ground state and between seven triplet states. All the observed states were arranged into a common energy scheme. The singlet-triplet separation was adjusted from the observation of perturbations in the $v=4, 5$ and 6 levels of $A^1\Pi-X^1\Sigma^+$ system. Barrow et al. (1974) used a hollow cathode discharge with $Al + AlF_3$ in the cathode and H_e carrier gas to study the AlF molecule.

Absorption Spectrum of AlF Molecule

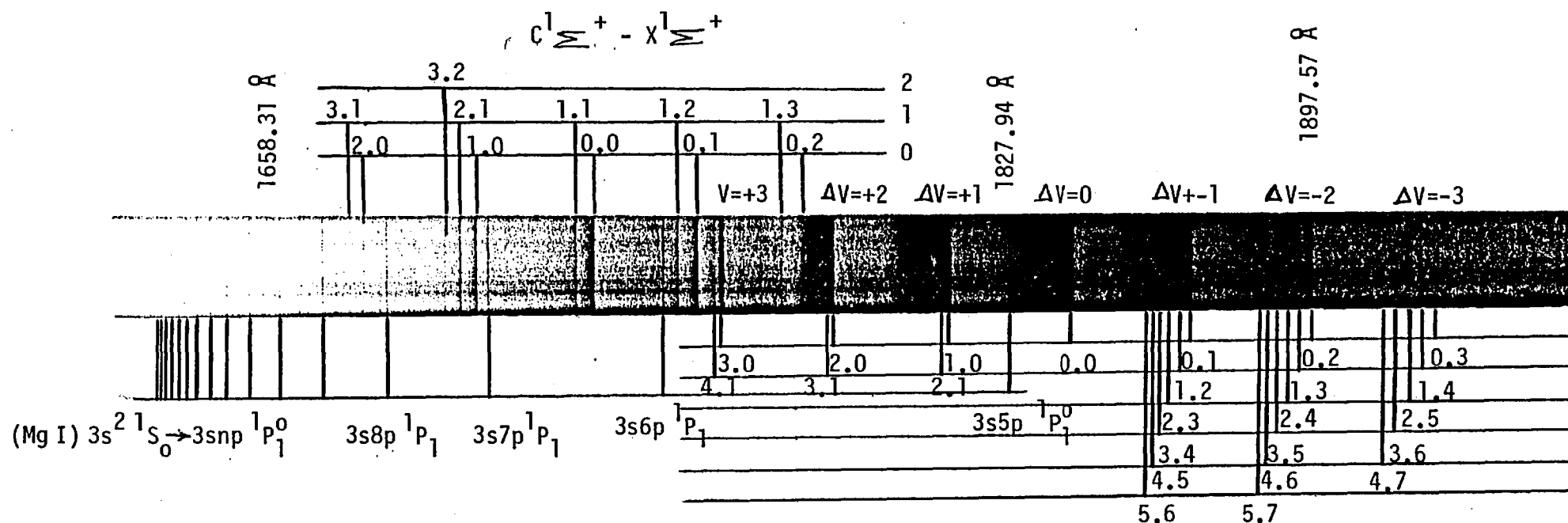


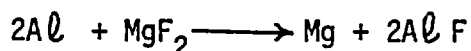
FIGURE (5.4.1) - Showing the $B^1 \Sigma^+ - X^1 \Sigma^+$ and $C^1 \Sigma^+ - X^1 \Sigma^+$ systems recorded in the present investigation. The principal series of magnesium vapour is also marked.

Kopp et al. (1976) reported the rotational analysis of the intercombination band $a^3\Pi-X^1\Sigma$ transition to get a better measurement of the singlet-triplet separation. The spectrum was recorded in absorption using a mixture of AlF_3 and Al powder heated to about $1600^\circ K$ in a King-type furnace in an atmosphere of Ar.

No observations below $1250 \text{ \AA}$ are known to us. In the present investigation we report new observations of the absorption spectrum of AlF molecule in the region $800-2000 \text{ \AA}$. Due to the low dispersion available a detailed analysis was not carried out but there is a clear evidence of Rydberg series converging on the ground state of the ion AlF^+ . The known band systems have been extended to higher vibrational levels.

5.4.3 Experimental Details

In the present investigation, we generate this molecule via different techniques. The powder of Al and MgF_2 was mixed and inserted in the vapour containment system. Six tantalum baffles having 5 mm inner diameter were inserted in the furnace tube which was made of tantalum 30 cm long, 0.3 mm thick. This mixture was heated to about $1200^\circ C$ in an induction furnace. At this temperature, a reaction takes place



The occurrence of this reaction was confirmed by observation of the principal series of atomic Mg which lies in the same region, where strong absorption bands of AlF have been observed.

5.4.4 Results and Discussion

The absorption spectrum of AlF molecule in the region $1600-2000 \text{ \AA}$ is reproduced in Fig.(5.4.1). This region of the spectrum was investigated by Barrow and Rowlinson (1954) who reported a strong band system named $B^1\Sigma-X^1\Sigma$, consisting of $v' = 0, 1, 2$ and $v'' = 0, 1, 2$ vibrational progressions lying between $1780-1900 \text{ \AA}$. The vibrational

Absorption Spectrum of AlF Molecule

New observations

Unclassified Bands

$\text{H} - \text{X}^1\Sigma^+$

(2.0) (1.0) (0.0)

↓ 1250 Å

↓ 1310 Å

↓ 1465 Å

↓ 1480 Å

5.0 4.0 3.0 2.0 1.0
4.1 3.1 2.1
4.2 3.2

$\text{G} - \text{X}^1\Sigma^+$

FIGURE (5.4.2) - The known band systems $\text{G-X}^1\Sigma^+$ and $\text{H-X}^1\Sigma^+$ are marked. The unclassified bands between 1300-1450 Å were reported by Barrow and Rowlinson (1954), which have been observed in the present experiment. Rydberg series are visible converging at ≈ 1250 Å.

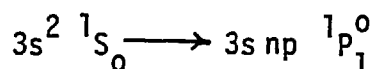
analysis of this band system is straightforward.

Barrow and Rowlinson (1954) also reported a weak band system consisting of (0,0) at 1731.60 Å, (0,1) at 1755.6 Å and (1,2) at 1751.37 Å bands and this transition was named $C^1\Sigma^+ - X^1\Sigma^+$.

On our plates these two band systems are very well developed. We have observed six new vibrational levels in the $B^1\Sigma^+ - X^1\Sigma^+$ system, which are assigned as (3,0), (4,1), (0,3), (1,4), (2,5) and (3,6) bands. Only three bands of the $C^1\Sigma^+ - X^1\Sigma^+$ system were reported by Barrow and Rowlinson (1954). We have extended this system observing six new bands which are designated (1,0), (2,1), (2,0), (3,1), (1,1) and (0,2) bands. The vibrational assignment of the new bands are very simple and can be represented by the formula, Herzberg (1950)

$$T = T_e + \omega'(v' + \frac{1}{2}) - \omega'x'(v' + \frac{1}{2})^2 - \omega''(v'' + \frac{1}{2}) + \omega'x''(v'' + \frac{1}{2})^2$$

In this spectral region, the principal series of Mg due to the transition



are also visible, which confirms that the reaction to produce the vapour column of AℓF is taking place correctly. This series has also been studied by Baig and Connerade (1978) while they were searching for the double excitation spectrum of Mg vapour. This series also serves as the internal wavelength standard.

Barrow and Rowlinson (1954) observed some strong band features in the region 1300-1400 Å. As the spectrum was complicated, they suspected that these bands might be due to the AℓF₃ molecule. We have generated this molecule using a different technique than that used by Barrow and Rowlinson (1954) and all these bands are present on our plates. This independent evidence confirms the reality of these bands and that they do in fact belong to the AℓF molecule.

We have recorded the spectra down to 900 Å and found numerous bands in this region. This part of the spectrum is reproduced in Figure (5.4.2) and it looks as though the Rydberg series are present and converging on the ground state of $\text{A } \ell \text{ F}^+$. As the spectra were recorded using 1 m spectrograph equipped with a 1200 lines/mm grating, it was not possible to perform a detailed analysis. A high resolution absorption spectrum in the region 900-1500 Å will be very useful for detailed vibrational analysis and to calculate a more accurate first ionization potential of $\text{A } \ell \text{ F}$.

5.5 Absorption Spectrum of PN and P_2 Molecules

5.5.1 Introduction

The vacuum ultraviolet absorption spectrum of the PN molecule is of considerable interest because of breakdown of the molecular orbital picture of ionization. The orbital energies of the PN molecule have been calculated using self consistent field procedures by McLean and Yoshimine (1968). Wu and Fehlnner (1975) observed the photoelectron spectra and pointed out that Koopman's theorem fails to predict both the value and order of the ionization potentials. They reported two bands at 11.85 eV and 12.25 eV which were assigned to the 7σ and 2π orbitals of the PN molecule on the basis of the observed vibrational fine structure. The ionization potentials corresponding to the three uppermost orbitals of PN have been calculated by Chong and Takahata (1977) using many-body Rayleigh-Schrodinger perturbation theory. They obtain 11.88 eV and 12.5 eV for the 7σ and 2π ionization potential in good agreement with experimental values. Schirmer et al. (1978) calculate the ionization potentials and spectral intensities for photoionization of the valence electrons applying the one particle Green's function approach (two-particle-hole Tam - Dancoff approximation) and discuss the break-down of the

independent particle picture of ionization in the Cs, PN and P_2 molecules.

The spectra of diatomic phosphorus nitride have been observed in the optical and ultraviolet region by both emission (Curry et al. (1933) and Ghosh and Datta (1933)), and absorption techniques (Moureau et al. (1939)). No observations have been made in the vacuum ultraviolet region where numerous valence and Rydberg states are expected to occur. The purpose of the present investigation was to photograph the Rydberg series of the PN molecule to calculate an accurate value of the first ionization potential and to see the correlation effects due to excitation of inner valence electrons.

In an attempt to generate the PN molecule we employed the techniques used by previous investigators, i.e. by thermal decomposition of P_3N_5 . Wyse et al. (1972) remarked that the decomposition began at 670°C and a running temperature of about 800°C was sufficient for good signal to noise ratios while studying the rotational transitions in the PN molecule. Wu and Fehlner (1975) studied the photoelectron spectra of the vapour over solid P_3N_5 at 1100 K and pointed out that at lower temperatures the reaction of P_3N_5 with residual water produces NH_3 , at about 700 K N_2 was produced and at ≈ 1100 K the pure PN spectrum was recorded. The vapourization of P_3N_5 has been examined mass spectrographically (Carlson et al. (1968)) and it was shown that at 1100 K the major species in the vapour are PN and N_2 .

In our vapour containment system, when P_3N_5 was heated by slowly increasing the temperature, we observed the spectra of P_2 and N_2 molecules. Raising the temperature further, these bands became more developed. At about 800°C , some weak features were detected in the vicinity of the P_2 ionization limit and the beginning of molecular N_2 absorption was found. We have reproduced the spectrum which we believe is due to the PN molecule in Fig.(5.5.2).

ABSORPTION SPECTRUM OF P₂-MOLECULE

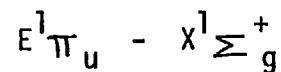
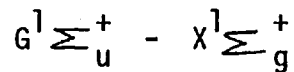
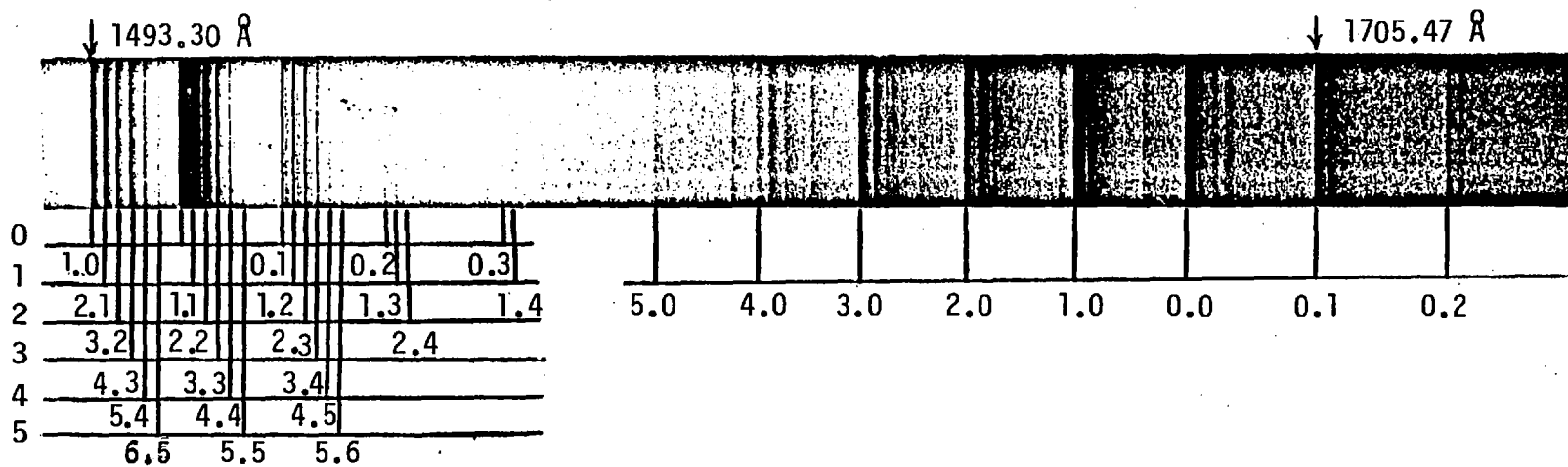

$$\Delta V = +1 \quad \Delta V = 0 \quad \Delta V = -1 \quad \Delta V = -2 \quad \Delta V = -3$$


FIGURE (5.5.1) - Showing the $E^1\Pi_u - X^1\Sigma_g^+$ and $G^1\Sigma_u^+ - X^1\Sigma_g^+$ band systems of the P_2 molecule observed in the present work. Extensions to the $G^1\Sigma_u^+$ -system have been marked with vibrational assignments.

5.5.2 Results and Discussion

(a) P₂ Molecule

The absorption spectrum of the P₂ molecule has been reported by Creutzberg (1969) who analysed eight band systems at high resolution down to 1220 Å. Carroll and Mitchell (1975) observed the spectrum between 1370 and 600 Å and found nine Rydberg series. Four of these converge to the $(5\sigma_g)^2(2\pi_u)^3\ 2\pi_u$ state of the ion which was established as being the ground state; four to the low-lying $(5\sigma_g)(2\pi_u)^4\ A^2\Sigma_g^+$ state and one to $(5\sigma_g)(2\pi_u)^3(2\pi_g)\ F^2\Sigma^+$ state. The first ionization potential was found to be $85229 \pm 15\text{ cm}^{-1}$ (10.567 eV) which is the limit corresponding to the upper component ($^2\Pi_{1/2}$) of the inverted $X^2\Pi_u$ state. This value is in agreement to that reported by Potts, Glenn and Price (1972) using photoelectric spectroscopy. The spectrum in the present investigation was recorded at low resolution (first order of 1200 $\text{\AA}/\text{mm}$ 1 m spectrograph). All the known band systems were identified; $G^1\Sigma_u^+ - ^1\Sigma_g^+$ and $E^1\Pi_u - ^1\Sigma_g^+$ transitions are particularly well developed yielding 10 new vibrational levels. This spectrum is reproduced in Fig.(5.5.1). Above this series limit, weak transitions occur which can be arranged into Rydberg series converging on to a common limit at 11.85 eV. These series could not be assigned either to the P₂-molecule or to the N₂-molecule because the series limits for the P₂ molecule are observed at 87179 cm^{-1} and 125225 cm^{-1} by Carroll and Mitchell (1975). The possibility of the N₂ molecule can be ruled out because N₂-absorption starts above this series limit. We therefore conclude (see also below) that they are due to the PN molecule.

(b) PN Molecule

The ground electron configuration of the PN molecule is given

Absorption Spectrum of P_2 , PN and N_2 Molecules

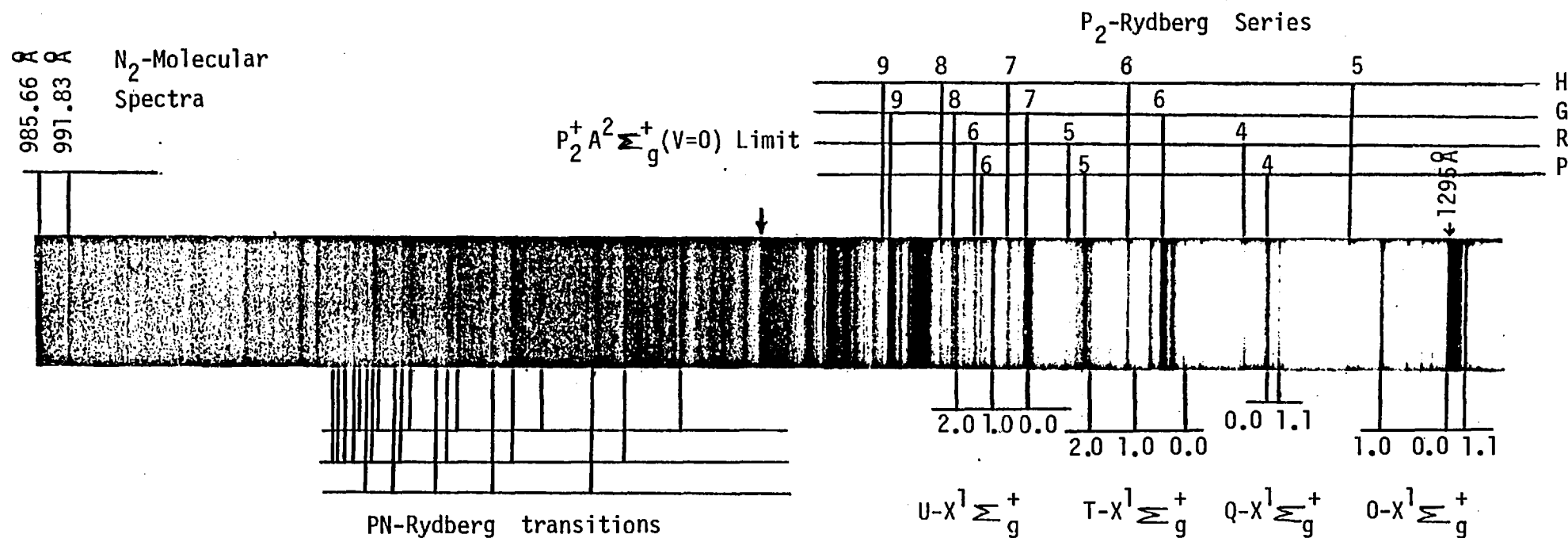


FIGURE (5.5.2) - Showing the absorption spectra of P_2 , PN and N_2 molecules from the thermal decomposition of P_3N_5 at $\approx 1100^\circ K$. The Rydberg series of PN molecule, observed for the first time, are marked.

by

$$KKL(z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)^2 \ ^1\Sigma^+$$

The excitation of an electron from the $(x\sigma)$ orbital to the $(n\ell\lambda)$ molecular orbitals will give Rydberg series converging on the ground state of PN^+ .

$$KKL(z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma) \dots n\ell\lambda$$

where n is the principal quantum number of the Rydberg electron, ' ℓ ' is its angular momentum and ' λ ' is the component of ℓ along the internuclear axis.

The three Rydberg series can be represented as

$$\begin{aligned} KKL(z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma) \quad & (n\sigma\sigma) \ ^1\Sigma^+ \\ & (np\sigma) \ ^1\Sigma^+ \\ & (np\pi) \ ^1\Pi \end{aligned}$$

and the common limit should yield the first ionization potential 11.85 eV reported by photoelectron spectroscopy; Wu and Fehner (1975). Schirmer et al. (1978) pointed out that it is useful to divide the four valence orbitals into two outer valence orbitals and two inner valence orbitals yielding differing features upon ionization.

In the outer valence region, one finds the two ionic state $X^2\Sigma$ and $A^2\Pi$ corresponding to the $x\sigma$ and $\omega\pi$ orbitals. These ionic states are generated by removing a quasi-particle from the initial state or by creating a quasi-hole; Cederbaum (1975).

Excitation of the $\omega\pi$ orbital electron will give Rydberg series converging on the $A^2\Pi$ -state of PN^+ at ≈ 12.25 eV. Schirmer et al. (1978) remarked that the energy of the $z\sigma$ hole state is energetically close to $2h1p$ -TDA* excitation, therefore strong mixing of the $z\sigma$ hole state with the neighbouring excitations occurs producing several final states of comparable intensity.

* Two-particle-hole Tamm-Dancoff Approximation.

On the excitation of two innermost valence orbitals, ($y\sigma^-$) and ($z\sigma^-$), strong correlation effects were expected where the independent-particle picture of ionization fails completely. There is a large energy gap between the valence orbitals ($z\sigma^-$, $y\sigma^-$, $\omega\pi^-$ and $x\sigma^-$) arising from the M and L shells of P and N and the deeper lying core orbitals. The valence orbitals occupy the energy region between 10 and 30 eV whereas the nearest core orbitals associated with the 2p electrons of P lie at approximately 150 eV. Due to this large energy gap, the influence of the core orbitals on the valence energy region will be small.

Unfortunately, this part of the spectrum was overlaid by strong N_2 -absorption and we were unable to pick up any information to compare with the calculations of Cederbaum et al. (1977). A clean spectrum of the PN-molecule at high resolution in the region 10 to 30 eV would be very interesting and this molecule certainly deserves further investigation.

CHAPTER VI

DISCUSSION AND CONCLUSION

Double excitation occurs by a breakdown of the independent electron scheme and, therefore, provides direct evidence of the importance of electron-electron correlations in atoms. For this reason, they have attracted much interest, both experimental and theoretical (Fano, 1975).

We have photographed the absorption spectra of Mg I, Ca I and Sr I due to simultaneous excitation of both valence electrons and found autoionization Rydberg series converging on the $3p\ ^2P$ limit in Mg II, the $4p\ ^2P$ limit in Ca II and the $5p\ ^2P$ limit in Sr II. The spectrum of Mg I was already reported by Esteva et al. (1972) and we have extended their observations by exploiting the experimental advantage of synchrotron radiation. The spectra of Ca I and Sr I are both reported for the first time.

Comparing the doubly excited spectra of Mg I, Ca I and Sr I, remarkable differences were found particularly for the $nd\ np$ transitions. The $3d\ np\ ^1P_1$ levels were sharp in Mg I whereas they are very weak and diffuse in Ca I and Sr I. All the members of this series lie above the first ionization threshold in Mg I. The leading members in Ca I and Sr I serve as the perturbers in the principal series. This difference is attributed to the influence of the centrifugal barrier on the properties of the nd -wavefunction. The nd -wavefunctions are well behaved in Mg I, whereas for Ca I and Sr I the $3d$ and $4d$ wavefunctions collapse. Due to the collapse of $3d$ and $4d$ wavefunctions in Ca I and Sr I, the $4p\ 4d\ ^1P_1^0$ level in Ca I and $5p\ 5d\ ^1P_1^0$ level in Sr I are missing from the spectrum. Connerade (private communication) has performed a detailed *ab initio* intermediate

coupling calculation and finds pronounced potential barrier effects in Ca I and Sr I. The observed doubly excited series are broad and show asymmetric Beutler-Fano resonances, which is understandable within the framework of autoionization theory. A high resolution spectrum may help to see the perturbation in the higher members but it would be difficult to trace the broad features. The spectrum of Sr I is well developed and one can follow the series to higher n values than in Ca I, where all the levels are very broad and diffuse. A photoelectric recording of these spectra will be very helpful to analyse the profiles of the lines.

Copper, Silver and Gold are noted for their remarkable properties of high reflectance and conductivity, possessing filled outermost d-subshells and one s electron in the metallic phase. Rubins (1961) pointed out that the outermost d electrons are not tightly bound and variations in properties between them could be traced to differences in the participation of the d-subshell. The properties of the d-subshell are more easily studied in the atom than in the solid because different excitation processes are more easily separated in energy.

The 3-d subshell excitation spectrum of Cu I was reported by Tondello (1973) and to complete this group of elements, we have photographed the 4d-spectrum of Ag I and 5d-subshell excitation spectrum of Au I. It is remarkable that the inner shell excitation spectra in the noble metals are much simpler than the inner shell spectra in alkalis. This fact is attributed to the competition of filling the 'd' and 's' shells. The binding energies of the 'd' and 's' electrons are approximately the same in alkalis when a vacancy is created in the outermost p subshell which causes a much more complex spectrum due to s-d mixing (Connerade, 1978) whereas the 'd' and 's' energies are well separated in the noble metals so

that s-d mixing is small.

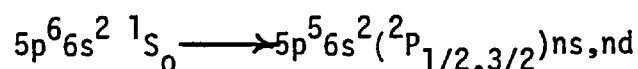
The 4d-spectrum of Ag I is very well developed on our plates and we were able to vary every parameter to record the best spectrum because silver is found to be experimentally a well behaved metal. A difficulty was encountered in recording the spectrum of Gold. We were not able to obtain the same quality of spectrum as was achieved for Ag I because gold attacks our furnace system when it is heated above the melting point. A similar problem was encountered in the studies of Cu I, which suggests that Au I and Cu I have similar properties in the liquid phase. This might be attributed to the fact that Cu I and Au I are preceded by the elements with configurations $3d^8 4s^2$ and $5d^9 6s$ in the periodic table and the Ag I atom is preceded by the Pt atom, the 4d shell of which is completely filled. This indicates that the binding energies of the 's' and 'd' electrons are approximately the same in the case of Cu I and Au I.

Connerade and Mansfield (private communication) have performed ab initio calculations to compare with the observed spectrum and very good agreement was found in Ag I using LS-dependent Hartree-Fock calculations, without including the double d-vacancy. The situation in Au I was different because we observe two strong transitions which we do not fit into the analysis based on the single electron excitation from the 5d-subshell. Connerade and Mansfield performed a multi-configuration Hartree-Fock calculation for Ag I and Au I and point out that the configurations with two vacancies in the 4d subshell lie relatively much higher in energy for Ag I than configurations with two vacancies in the 5d subshell of Au I; therefore, the influence of $5d^8 6s^2 6p$ on $5d^9 6s 6p$ is much larger in Au I. The observed transitions are well represented within the framework of these calculations.

In the short wavelength region, we were unable to record a clean spectrum of Au I due to overlapping impurity lines originating

from the furnace tube. A cleaner spectrum may be useful to see the behaviour of the higher lying members of these Rydberg series.

The 3d-subshell excitation spectrum of Mn I was of particular interest because it has a half filled d-shell and all the electrons have parallel spin while the outermost 's' shell is filled. The absorption spectrum was expected to be very complex but a remarkably simple spectrum was found, because the $3d^4 4s^2$ electrons behave like spectator electrons (Sugar, 1972; Connerade and Mansfield, 1976). Within the framework of this approximation, the $3d^4 4s^2$ electrons retain their identity and mutual angular momentum orientations, and one observes a simple spectrum due to excitation of a single electron from the d-subshell. The breakdown of spectator electrons approximation was found in the 5p-excitation spectrum of Ba I, Connerade et al. (1979) where the outermost 6s subshell shatters and instead of just two series limits according to the one electron excitation scheme



the spectrum was found to consist of 14 series converging on 12 limits. This complexity was attributed to strong s-d mixing.

The configuration $3d^4 4s 4p$ in Mn I is found to be more complex because of the existence of singly and doubly excited levels in the same region. However, the comparison of our observed spectrum shows a good agreement with Roth's (1970) ab initio calculations.

The observation of molecular spectra in the vacuum ultraviolet region was very fruitful because very few molecules have been studied in this region. Rydberg series were found converging on the ground state of the ion. From the Rydberg series, a very accurate value of the first ionization potential can be determined similar to that of atomic Rydberg series. There are a limited number of stable diatomic molecules and many small molecules of intermediate stability can be

prepared using a variety of techniques. One rich source of such species is the vapour above various solids at high temperatures. Only N_2 , CO, NO and O_2 molecules have been extensively studied and, more recently, the spectra of P_2 , CS and BF have been studied using conventional background sources. The experimental advantages of synchrotron radiation have been exploited to observe the spectra of simple diatomic molecules with closed shells in the ground state. In the first instance, we have extended the observations of the Si O molecule in the region 750-2000 Å because this molecule has great astrophysical importance. Secondly, the CO molecule has been extensively studied. The other oxides of the carbon group elements have received less attention. We observed the spectra of Si O and Ge O and found Rydberg series converging on the ground state of $Si\ O^+$ and $Ge\ O^+$. Numerous band systems have been detected but because of the low resolution available, rotational analysis was not possible. However, the observed Rydberg series gave more accurate and reliable first ionization potentials of Si O and Ge O. In the spectrum of Si O we found a new Rydberg series, above the first ionization threshold, converging on the $B^2\Sigma^+$ -state of $Si\ O^+$ and the series limit confirms the investigation of the $Si\ O^+$ emission spectrum by Verma et al. (1979) and Singh et al. (1973).

The spectrum of the Al F molecule was reported up to 1300 Å in the literature and we have extended these observations down to 1000 Å. We produce the Al F molecular spectra using different experimental techniques than were employed by the previous investigators. All the known band systems have been observed with good intensity and numerous band systems have been detected between 1350 Å - 1100 Å. There is clear evidence of Rydberg series converging on the $X^2\Sigma^+$ state of $Al\ F^+$ but the detailed analysis was not undertaken because of the complex structure and low resolution. Barrow and

Rowlinson (1954) reported complex band structure in the region 1300 - 1400 Å but pointed out that these bands might also be due to the AlF_3 molecule. We also observed all these bands using a different technique which provides independent evidence that these bands are really due to the AlF molecule. A high resolution spectrum in this region will provide very useful information regarding this molecule. Techniques to produce this molecule are now known and a high resolution spectrograph in conjunction with synchrotron radiation would be an ideal facility to study its molecular structure.

We were also interested in the PN molecule because it is isoelectronic with SiO. This molecule was observed by Herzberg (1933) yielding an excellent example of vibrational progressions of bands. The photoelectron spectrum has been reported by Wu and Fehlner (1975) and Schrimmer et al. (1978) point out the breakdown of the molecular-orbital picture of ionization for PN. We tried to record the spectrum of the PN molecule by thermal decomposition of P_3N_5 at about 1100°K and found the spectrum of P_2 , N_2 and weak features which we believe are due to the PN molecule. The P_2 molecule has been extensively studied by Creutzberg (1965) in the ultraviolet region and Carroll and Mitchell (1975) found Rydberg series converging on the ground state $X^2\Sigma$ and $F^2\Sigma^+$ state of P_2^+ . The N_2 -molecular spectra is also well known in this region and we found all the known band systems for these two molecules. The photoelectron spectra gives a peak at 11.85 eV for the PN molecule, which is due to the ionization of one electron from (σ^*) orbital. Our observed features seem to form three Rydberg series converging to a common limit at the expected position. Again, a detailed analysis was not possible due to our limitation of low resolution spectra.

As remarked above, extension of the research towards improved resolution will be useful to study correlation effects for excitation of the inner valence orbitals of molecules. The breakdown of the independent-particle picture for the inner valence orbitals for the P_2 , PN and CS molecules has been remarked by Schirmer et al. (1978); therefore, high resolution absorption spectra will be very useful to understand this breakdown which is similar to the one for atoms discussed by Wendin and Ohno (1976). The investigation of the spectra of simple diatomic molecules, which have already been studied in the X-ray and UV regions, will be useful to bridge the observational gap in a region where many interesting physical phenomena are expected to occur.

In conclusion, observations of molecular absorption spectra using an induction furnace and windowless containment system in conjunction with synchrotron radiation have revealed new data for several diatomic molecules. The present investigation provides evidence for the existence of numerous band spectra in the VUV region. This part of the spectral region should be studied further at high resolution as it contains many interesting phenomena; autoionization, configuration mixing and multiple excitations. Much work has been done using photoelectron spectroscopy, Price (1972), Edgqvist et al. (1970), Turner (1970) but less by absorption techniques. Photoelectron spectroscopy gives information about the ionization potentials, vibrational energies and relative intensities of the different vibrational transitions in the ionization process. The Rydberg electron contributes very little to the bonding in the molecule, therefore the vibrational structure of the Rydberg transition should be similar to that of the photoelectron spectroscopy transition. The ionization potentials of the inner electrons can be determined from photoelectron

spectroscopy but a full interpretation of the data requires the use of more than one experimental technique and absorption spectroscopy yields additional information about excited states in the neutral species. The best way to correlate an ionization potential with a certain molecular orbital is often to study the Rydberg transitions.

The studies of these molecules can be extended to the XUV and X-ray region where excitation of the core electrons to Rydberg orbitals will take place. There are other numerous diatomic molecules which have not been observed in the VUX and XUV regions. Many interesting effects occur at these high energies and are worth exploring using synchrotron radiation in conjunction with a high resolution spectrograph, since the characteristic curves for the radiation emitted by most electron accelerators peak in the soft X-ray region.

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