

Laser Based Study of Interacting Autoionising Resonances
in the Spectra of Calcium, Barium and Strontium

by

Shahid Munir Farooqi

*Thesis Submitted for the Degree of Doctor of
Philosophy in the University of London*

1991

Imperial College of Science, Technology and Medicine
London

To My Mother

Her Sweet Memories Are the Treasure of My Life

Abstract

A *hot-wire* thermionic diode detector has been developed and tested using both synchrotron radiation source and a tunable coherent vacuum ultraviolet radiation source obtained by four-wave mixing in a rare gas. This combination was used to study autoionising spectra of the elements calcium, strontium and barium, all of which present peculiarities of structure due to the interaction between overlapping resonances. The cases of particular theoretical interest are that of the doubly excited $3dnp\ ^1P_1$ series in Ca I, and the doubly excited series in barium converging to the $6p\ ^2P_{1/2}^o$ series limit. The former exhibits a pronounced width fluctuation around $n = 6$, and the later exhibits a peculiar disappearance of fluctuations at a specific excitation energy well below the associated series limit. The present experimental report provides the first experimental data on the line profiles of the resonances in the region of interaction, and is discussed in the light of many-body perturbation theory, R-matrix and semi-empirical multichannel quantum defect calculations, and within the framework of analytic K-matrix theory.

Acknowledgement

All thanks and praises to Allah, the most gracious, most merciful. Allah taught man that which he knew not.

My stay at the Imperial college is a very pleasant part of my life. There are so many friends and colleagues who have contributed a lot to make this period successful in many respects.

Firstly I would like to thank Prof. J P Connerade, my supervisor, for his guidance and encouragement throughout. He has always been very kind, friendly, easy to reach and helpful. His advice and suggestions have been most valuable during the course of this work.

I wish to thank Dr. S Ning (now at U.C.L.) for helpful discussions over the subject, and helping me setup my experiments. I am thankful to Dr. J P Marangos for his help to run the VUV system.

I am very thankful to my dear friends and colleagues Mr. M. Nawaz, Mr. W.A. Farooq, Mr. R. Ahmed, Mr. M. Ishfaq, Mr. M. Salim and Mr M Azhar for their friendship over the past years, their company made me feel at home.

I would like to thank Miss N. Karapanagioti, a nice friend and colleague, for proof reading the thesis and for making useful remarks.

Every body at the spectroscopy group has been very nice to me and I am thankful to all of them. To mention some, I am thankful to my friends

and colleagues Miss J.A. Warry, Mr. G. Droungas, Dr B.K. Sarpal (now at U.C.L.), Dr. D Headings, Ms P. Eeles (the group secretary) and Mr A Kazmi (at physics store) for their friendship and general support.

I am also thankful to Mr B. Willey, chief technician at the workshop, for making a thermionic detector for me. Thanks are also due to Mr. G. Busby, group electrician, for making a power supply for my experiment.

The ministry of education—Islamabad, Pakistan—is gratefully acknowledged for providing me a scholarship and all the financial support for this work and for the M.Sc course work at the Georgia Institute of Technology, U.S.A.

Finally I would like to thank my family in Pakistan, especially my father, for their support and understanding over the many years I have been away for my studies.

Contents

1	Introduction	18
2	Spectral line profiles	21
2.1	Introduction	21
2.2	Natural Broadening	22
2.3	Doppler Broadening	24
2.4	Pressure Broadening	27
2.4.1	Resonance Broadening	27
2.4.2	Collision Broadening	27
2.5	Optical Depth	28

3	General properties of interacting resonances	32
3.1	Introduction	32
3.2	Autoionisation	33
3.3	Quantum mechanical treatment—Fano formula	36
3.3.1	Isolated resonance interacting with many continua . .	47
3.4	K-matrix Formalism—another approach	48
3.4.1	Perturbation by a broad intruder level and its effects on the shapes and widths of the Rydberg levels	54
4	Approximate solutions to the many-body problem	61
4.1	Introduction	61
4.2	The Hydrogen atom	62
4.3	Two electron atom	64
4.3.1	Independent particle model	65
4.3.2	Central field approximation	65
4.4	Many electron atom	67

	3
4.4.1 Hartree-Fock equation	68
4.4.2 Many-body perturbation theory (MBPT)	70
4.4.3 R-matrix theory	75
4.4.4 Quantum defect theory	77
4.4.5 Semi-empirical approach	84
4.4.6 <i>ab initio</i> calculations	85
5 The Case of Calcium	86
5.1 Introduction	86
5.2 Previous Experimental Investigations	88
5.3 Theoretical Survey	97
6 The Case of Barium and Strontium	115
6.1 Introduction	115
6.2 Barium Review	116
6.3 Review of strontium	120

7	Thermionic Diode Detector	123
7.1	Introduction	123
7.2	Early History	124
7.3	Working Principle	125
7.4	The Diode as an Ion Detector	125
7.4.1	Choice of Cathode	129
7.4.2	Directly Heated Cathode	130
7.5	Thermionic Diode as an Oven	131
7.6	The Gain	131
7.7	Design and Construction	132
7.8	Diode Circuit	133
7.9	Optimization and Operation	135
7.9.1	Operational Procedure	137
7.10	Noise and Sensitivity	138
7.11	Linearity	139

8	Data Acquisition System	141
8.1	Introduction	141
8.2	Lock-in Technique	142
8.3	Laser Beam Monitoring	144
8.3.1	Working Principle of PMT	144
8.4	Box-car Technique	147
9	Tunable VUV Generation	149
9.1	Introduction	149
9.2	Early Background	150
9.3	Four wave frequency mixing (sum-difference) theory	151
9.3.1	Third Order Processes	153
9.3.2	Gaussian beams	157
9.4	Experimental Setup For the VUV Generation	160
9.4.1	Nonlinear Medium Used	160
9.4.2	Laser system	162

9.5	Experimental setup for VUV generation	173
-----	---	-----

10 Synchrotron Experiment 177

10.1	Introduction	177
------	------------------------	-----

10.2	Synchrotron Radiation Source (SRS)	178
------	--	-----

10.2.1	Undulators and Wigglers	182
--------	-----------------------------------	-----

10.2.2	General Characteristics Of SRS	183
--------	--	-----

10.2.3	5 Meter Normal Incidence Monochromator at the Dares- bury Laboratory SRS	184
--------	---	-----

10.3	Experiment	189
------	----------------------	-----

10.4	Results and Discussion	191
------	----------------------------------	-----

11 Laser Based Experiments 194

11.1	Calcium Experiment	194
------	------------------------------	-----

11.2	Strontium Experiment	197
------	--------------------------------	-----

11.3	Barium Experiment	202
------	-----------------------------	-----

12 Data Handling	205
12.1 Wavelength Calibration	210
12.2 Cross-section calibration.	211
13 Results and Discussion	213
13.1 Calcium	213
13.1.1 The 3dnp 1P_1 series	221
13.1.2 The 3dnp 3P_1 series	226
13.1.3 The 3dnp $^3D_1^o$ series	238
13.1.4 The 3dnf series	238
13.2 Barium experiment	241
13.2.1 Conclusion	249
13.3 Strontium experiment	249
13.3.1 Conclusion	254
13.4 Suggestions for further work	254
References	257

List of Figures

2.1	Lorentzian profile of the naturally broadened line	24
2.2	Doppler broadened line	26
3.1	Energy level diagram of neutral calcium; most of the doubly excited levels converging to the 3d or 4p threshold lie in the first continuum.	35
3.2	Resonance shape of an autoionising level at energy E_0	40
3.3	a: Total absorption strength from a lower level to the continuum plus two discrete levels that do not interact with the continuum. The strength of the higher frequency discrete line is assumed to be zero (shown by dotted line). b: The situation when discrete levels interact with the continuum. A Beutler-Fano profile is observed for the finite width discrete level and a hole at the position of the zero strength discrete line.	44

3.4 Form of the coefficients, in the final mixed eigenfunction, of the discrete basis function (symmetrical curve) and of the continuum basis functions (asymmetrical curve). 45

3.5 Beutler-Fano profiles 46

4.1 Diagrams associated with matrix elements: (a) $\langle pq | v | mn \rangle$. Particles in the excited states ϕ_m and the unexcited state ϕ_n interact through v and scatter into excited states ϕ_p and ϕ_q leaving a hole in ϕ_n . (b) $\langle q | V | p \rangle$. A particle in an excited state ϕ_p is scattered by the potential V to the excited state ϕ_q . (c) $\langle pq | v | pq \rangle$. (d) $\langle pq | v | qp \rangle$. Diagrams (c) and (d) represent interactions of passive unexcited particles. 73

4.2 variation of phase shift with respect to the coefficients 80

5.1 The atomic absorption cross-section against wavelength. The peak absorption of the first two lines (3d5p & 3d6p 1P_1) is 30 and 70 Mb respectively 89

5.2 Photoelectric measurement of the absorption cross-section as a function of wavelength. (Newsom experiment) 93

5.3 Resonance diagrams involving doubly excited states of 4s electrons. Solid dot indicates matrix elements of z . Other dashed lines represent Coulomb interaction. A horizontal line in diagram (d) indicates that the denominator is treated according to $-i\pi\delta(D)$ 100

5.4 A comparison of Altun’s calculations with Carter experiment. Dashed curve is the experiment 101

5.5 A comparison of Altun results with Newsom experiment. Dashed curve is the experiment 102

5.6 Ca I spectrum calculated by Scott *et al*: —, length form;···, velocity form. 104

5.7 A comparison of the Scott results with the MBPT calculations: —, Scott *et al* , ···, MBPT results 106

5.8 A comparison of Scott results with the experimental outcome of Newsom 108

5.9 A comparison of the R-matrix calculation with Newsom results 110

5.10 Radial sp and pd components of the $^1P^o$ probability density are shown as a function of (r_1, r_2) . From Ref. 32 a 112

5.11	Cross-section for photoionisation of calcium for incident photon wavelengths between 1586 and 1790 Å (. . . the geometric mean of length and velocity calculation)	114
6.1	Absorption spectrum of Ba I below the 6p $^2P_{1/2}$ ionisation threshold (in the VUV), as recorded by Brown and Ginter ⁹⁰	118
6.2	Photoabsorption spectrum of the doubly excited autoionising resonances in Sr I, below 5p $^o_{1/2}$ threshold (as recorded by Brown <i>et al</i>). The lower spectrum is the eigenchannel R-matrix calculations performed by Aymar (1987)	121
7.1	A plot of β^2 as a function of R/a	127
7.2	Dependence of V on radial distance between the cathode and anode	127
7.3	Diode current signal as a function of time	128
7.4	The diode tube assembly	134
7.5	Complete layout of the thermionic diode detector system	136
8.1	Data acquisition system used in the present experiments	143
8.2	Lock-in amplifier circuit diagram	144

8.3	Circuit diagram of the PMT	147
9.1	Phase-matching factor as a function of optical depth	156
9.2	Partial energy level scheme for Kr, showing resonance enhanced sum-difference mixing to generate VUV radiation. . .	161
9.3	Littrow grating configuration	165
9.4	Grazing incidence design	166
9.5	General layout of the dye laser FL 3002	168
9.6	Dye laser setup	171
9.7	The VUV generation setup.	174
10.1	Main components of a synchrotron radiation source assembly	179
10.2	Emission of the synchrotron radiation from moving electrons round bending magnet	180
10.3	Beam line setup at the Daresbury Synchrotron Lab.	186
10.4	Photon flux output curves for the gratings used in the Daresbury Synchrotron	188
10.5	Setup for the synchrotron experiment	190

10.6 Calcium spectrum recorded by new thermionic diode detector at the Daresbury Synchrotron Laboratory	193
11.1 Absorption spectrum of the doubly excited autoionising series in Ca I	198
11.2 Absorption spectrum of the doubly excited series in Ca I . . .	199
11.3 Absorption spectrum of the doubly excited autoionising series in Sr I, below the $5p_{1/2}$ limit	201
11.4 Ba I spectrum investigated by using the VUV light source . .	204
12.1 A normalised data file in which the background base line has shifted	207
13.1 High resolution absorption spectrum of the 3dnp series in calcium near the series limit	217
13.2 Absorption spectrum of the 3d4f levels near the low energy end	218
13.3 Absorption spectrum of the 3d6p 1P_1 level showing vanish- ing particle width effect. The dashed curve is the calculated spectrum by Greene	220
13.4 A comparison of Greene's calculations with the present experiment	223

13.5 A comparison of : . Greene’s calculations with the experi-
ment at high energy values 224

13.6 A plot of n^*3f Vs n for the $3dnp\ ^1P_1^o$ series in calcium 227

13.7 A theoretical fit of the Fano formula to the first four members
($n=6-9$) of the $3dnp\ ^1P_1^o$ series in calcium 228

13.8 Absorption spectrum of the doubly excited series in Ca I be-
low the 3d threshold 229

13.9 Absorption spectrum of the autoionising series in Ca I below
the 3d threshold 230

13.10Absorption spectrum of the autoionising series in Ca I below
the 3d threshold 231

13.11Absorption spectrum of the autoionising series in Ca I below
the 3d threshold 232

13.12Absorption spectrum of the doubly excited series in Ca I be-
low the 3d threshold 233

13.13Absorption spectrum of the doubly excited series in Ca I be-
low the 3d threshold 234

13.14Absorption spectrum of the doubly excited series in Ca I be-
low the 3d threshold 235

13.15 Absorption spectrum of the doubly excited series in Ca I below the 3d threshold 236

13.16 The schematic diagram of the J=1 odd-parity spectrum of barium 242

13.17 Absorption spectrum of Ba I below the 6p_{1/2} threshold, showing the vanishing of fluctuations. 245

13.18 High energy end of the absorption spectrum of Ba I 246

13.19 Absorption spectrum of Sr I below the 5p_{1/2} limit 250

13.20 Absorption spectrum of Sr I just below the 5p_{1/2} limit 251

13.21 Theoretically predicted absorption cross-sections of Sr I below the 5p_{1/2} limit 253

List of Tables

2.1 Percentage errors due to the opacity effects (After Shen-1988) 31

8.1 General characteristics of the PMT employed to detect VUV
radiation 146

9.1 Excimer laser output wavelengths attainable with different
gas combinations 164

9.2 General characteristics of the VUV radiation generated by
sum-difference frequency mixing in Kr 176

Chapter 1

Introduction

The subject of interacting resonances in atomic spectra has been the focus of attention of both experimenters and theorists over many years. When there are more than one autoionising series present in a given energy range, especially, when an autoionising Rydberg series is perturbed by a very broad intruder level which may belong to another series, their mutual interaction and the interactions with the underlying continua give rise to many distinct effects. It turns out that the shapes of resonances—their line profiles and symmetries—are markedly affected by such overlaps and interactions.

During past decades many attempts have been made to understand these phenomena. Alkaline-earth elements are good candidates for such studies, as they have only two valence electrons outside a filled core, which makes theoretical study of the doubly excited autoionising series much simpler as compared to the other elements. Theoretically, the problem has been anal-

ysed numerically by many approximate models like the many-body perturbation theory (MBPT), *ab initio* calculations using the R-matrix technique, and semi-empirical methods (e.g. Quantum defect theory) which incorporate experimental data to make predictions. In fact, the combination of an eigenchannel R-matrix approach with multichannel quantum defect theory (MQDT) has described experimental spectra to a reasonable accuracy. While the R-matrix is convenient for numerical applications, it does not lend itself to a general discussion of the properties of the observed resonances. Analytically, the line profiles are better explained with the help of K-matrix formalism. The main advantage of the K-matrix is its simple pole structure. It therefore provides a suitable framework within which to discuss the general properties of the overlapping resonances. The analytical study of the lineshapes in perturbed autoionising series is very useful when the number of channels is small enough for simple expressions to be obtained. One can then pinpoint novel effects and determine the most favorable conditions for their observation. When many channels are present, it is of course necessary to resort to numerical techniques. Even in such cases, the parameters of K-matrix theory (electron and photon widths for each channel, and interchannel coupling strength) are physically significant. Most important is the fact that since Wigner's scattering theory finds application in a wide range of different areas of physics, the motivation for applying it to atomic structure is also one of unity in the description of observations.

Although there are many experimental data awaiting theoretical explanation, there is also a definite need of more experimental data to verify the theory, especially when most of the available data were obtained either by

employing a nonlinear detector or a radiation probe which was not of a narrow bandwidth. Absorption (or emission) spectroscopy using photographic detection is the most traditional method and is still competitive in terms of resolution with other experimental techniques. But it cannot give reliable quantitative data on high intensities because of the small linear range of photographic plate (or film). A more fundamental difficulty with traditional absorption (or emission) spectroscopy to obtain line intensities is that a large optical depth is necessary for a reasonable signal-to-noise ratio, but introduces errors due to the opacity effect.

Generation of coherent, narrow bandwidth, tunable vacuum ultraviolet (VUV) radiation by sum-difference frequency mixing in nonlinear medium coupled with a thermionic diode detector, which is linear over many decades of intensity and offers a very high signal-to-noise ratio, has provided an excellent opportunity to investigate atomic structure in much better detail.

The present work is a laser based study of interacting autoionising resonances in the spectra of Ca I, Ba I and Sr I, aiming at more reliable data for critical examination of the theoretical models. These spectra have a common feature that they are perturbed by one or more intruder levels belonging to different channels. The analytical treatment is based on the K-matrix formalism, which is very useful to study the cases of Rydberg series of interacting resonances in which an intruder resonance appears.

Chapter 2

Spectral line profiles

2.1 Introduction

If an atom exists in an excited state of energy E_2 , it may spontaneously decay to some other state of lower energy E_1 , the energy difference appearing as a photon of energy $E_2 - E_1$. This photon corresponds to emitted radiation of frequency ν , vacuum wavelength λ , and wavenumber given by

$$E_2 - E_1 = h\nu = \frac{hc}{\lambda} = hc\sigma \quad (2.1)$$

or if energy levels are given in the pseudo-energy units E/hc

$$\frac{E_2}{hc} - \frac{E_1}{hc} = \frac{1}{\lambda} = \sigma \quad (2.2)$$

Similarly, if the atom exists in the state 1 and lies in a radiation field that include radiation of wavenumber σ given by Equation 2.2, it may be excited to the state 2 by absorption of a photon of energy $E_2 - E_1$.

For many purposes one may make the approximation that the energy of each level of an atom is perfectly definite in value, i.e., has zero energy width. The wavenumber or wavelength given by Equation 2.2 is then also definite, and each spectrum line is monochromatic, with zero wavenumber width.

In reality, spectrum lines are never monochromatic, but show intensity distributed over a finite wavenumber range. This intensity distribution may arise from a number of different causes, which will be discussed in this chapter in a more general way. However, due to the importance of the autoionisation in the work presented in this thesis, it will be dealt with in detail in the next chapter.

2.2 Natural Broadening

As stated before, up to now the stationary states of atoms have been assumed to be infinitely sharp so that transitions between them have an infinitely narrow frequency spread. However, the uncertainty principle in the form $\Delta E \Delta t \approx \hbar$ requires an energy spread inversely proportional to the uncertainty in time associated with finding the atom in that particular state. Taking the mean life time τ of state (the fact that an atom in an excited state may spontaneously decay to a lower state implies that the former has a finite natural life time) as a measure of Δt , we have for the frequency spread of state j

$$\delta\nu_j \cong \frac{1}{2\pi\tau_j} \quad (2.3)$$

where $\delta\nu_j$ is negligible for the ground or metastable state ($\tau_j \rightarrow \infty$). Upper states of allowed optical transitions have lifetimes in the range of 10^{-6} - 10^{-9} sec. Any spectral line starting or ending on such a level must have a corresponding frequency spread, of the order 0.1—100 MHz, or 10^{-5} — 10^{-12} cm^{-1} . If both levels are broadened, then the width of the line is given by

$$\delta\nu_{12} = \delta\nu_1 + \delta\nu_2 \quad (2.4)$$

The life time of an excited state is the inverse of the spontaneous emission probability (assuming no collisional quenching) $\tau_2 = 1/A_{21}$. If more than one transition from level 2 are possible, this expression is generalized to

$$\tau_2 = \frac{1}{\sum_i A_{2i}} \quad (2.5)$$

Since the Einstein A coefficient is proportional to ν^3

$$A_{21} = \frac{8\pi h\nu_{12}^3}{c^3} B_{21} = \frac{g_1}{g_2} \frac{8\pi h\nu_{12}^3}{c^3} B_{12},$$

the natural line width decreases rapidly in the infra-red and microwave regions, but it may be appreciable in the far ultra-violet. In the visible region it is normally a couple of orders of magnitude smaller than Doppler broadening, but is still possible for it to make a significant contribution to the wings of the line because the two effects have different lineshapes. The autoionising levels (which are the theme of this thesis) constitute an important exception to the rule of small natural width: the high probability of a radiationless transition results in very short lifetimes, often of the order of 10^{-13} sec, and correspondingly broad lines.

The shapes of the broadened lines depend on the shape of the energy distribution. This can be derived from Dirac's quantum theory of radiation,

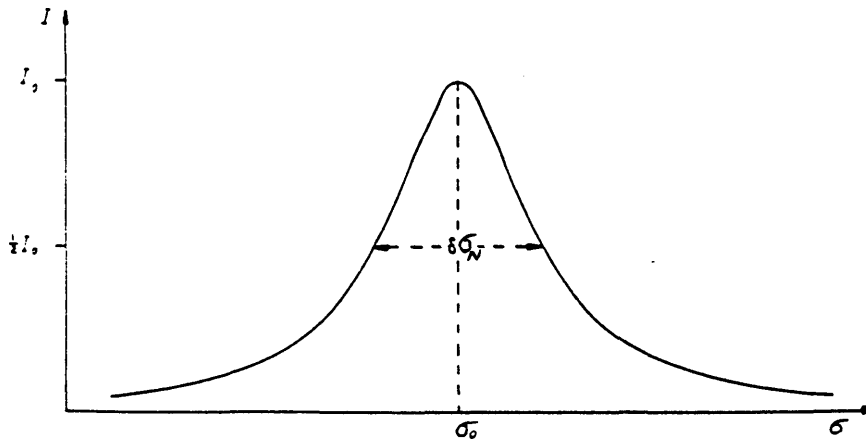


Figure 2.1: Lorentzian profile of the naturally broadened line

but in fact exactly the same line shape is obtained classically. The resulting intensity distribution has a resonance form as shown in fig 2.1.

$$I(\sigma) = \frac{\Gamma/\pi}{(\sigma - \sigma_0)^2 + \Gamma^2} \quad (2.6)$$

where σ_0 is the wavenumber at the center of the spectrum line, and Γ is the half width of the line at half maximum amplitude. This is the well known Lorentzian distribution.

2.3 Doppler Broadening

Doppler broadening is a result of the well-known "Doppler Effect", which is the apparent shift in wavelength of the signal from a source moving towards

or away from the observer. In a laboratory source, the shifts arise from the thermal motion of the emitting atoms or molecules. If the radiating atom has a translational motion with a component parallel to the observer's line of sight, the observer sees a spread of shifts corresponding to the spread of velocities, and this is tantamount to broadening the line.

The Doppler broadened lineshape follows the velocity distribution of atoms and can be derived for a gas with a Maxwellian velocity distribution. For an emitter approaching the observer with a velocity $v_{\parallel}$, the Doppler shift is given by

$$-\frac{\Delta\lambda}{\lambda_0} = \frac{\Delta\nu}{\nu_0} = \frac{v_{\parallel}}{c} \quad (2.7)$$

and thus

$$\sigma - \sigma_0 = \sigma_0 \frac{v_{\parallel}}{c} \quad (v_{\parallel} \ll c) \quad (2.8)$$

If the atoms have a continuous distribution of translational velocities, the result is a continuous distribution of wavenumbers σ and a corresponding apparent broadening of the spectral line. In the absence of other line width effects, a Maxwellian velocity distribution at absolute temperature T would produce a Doppler line shape

$$I(\sigma) = \left(\frac{\ln 2}{\pi\Gamma^2}\right)^{1/2} e^{-(\ln 2)\frac{(\sigma-\sigma_0)^2}{\Gamma^2}} \quad (2.9)$$

The half-width at half-maximum is given by

$$\Gamma = [2KT(\ln 2)/Mc^2]^{1/2} \sigma_0 = 3.581 \times 10^{-7} \left(\frac{T}{A}\right)^{1/2} \sigma_0 \quad (2.10)$$

and

$$FWHM = 7.16 \times 10^{-7} \left(\frac{T}{A}\right)^{1/2} \sigma_0 \quad (2.11)$$

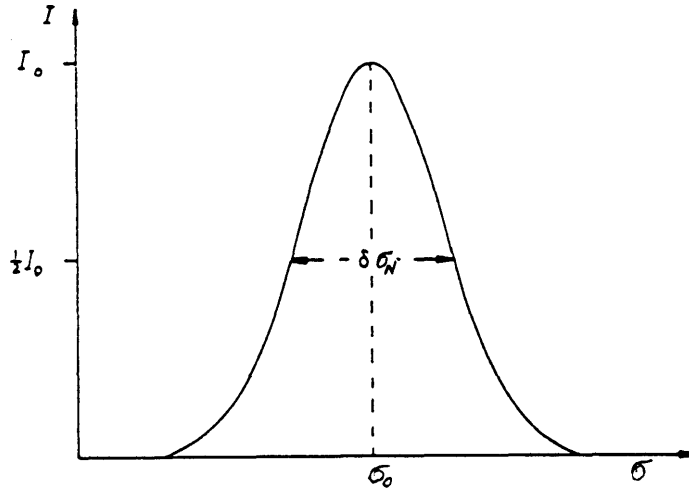


Figure 2.2: Doppler broadened line

where M is the mass of the atom and A is its atomic weight, K is Boltzmann constant and T is absolute temperature..

The line profile is as shown in fig 2.2. Intensity falls off much more rapidly in the wings than it does in fig 2.1. The range of the Doppler width can easily be found by putting specimen figures into Equation 2.10. For atoms and diatomic molecules and for most laboratory sources A and T are, respectively, in the range of 1—200 and 300—10000, so that the extreme values for the R.H.S. of the equation are roughly 7×10^{-5} — 7×10^{-7} . In the visible region the corresponding widths are 0.1 — 0.001 cm^{-1} . The instrumental resolving power required to match the Doppler width is found from equation 2.11 simply by taking reciprocals, and with above figures it ranges from 15000 to 1.5×10^6 .

2.4 Pressure Broadening

It is a well-known experimental fact that spectral lines are broadened and in many cases are also shifted by increasing gas pressure and by the presence of ions and electrons. Sometimes additional lines from the 'forbidden' transitions also appear. These perturbations—widening, shifting and mixing of energy levels—are due to interactions between the emitting or absorbing atoms or molecules and the other particles (usually atoms of some inert gas). Although the importance of the subject requires a detailed study, due to limited scope of this work, the discussion will be confined to resonance and collision broadenings.

2.4.1 Resonance Broadening

In any real case, atoms are not isolated but are coupled together by the radiation field: a photon emitted by one atom may be absorbed by some other atom lying in the appropriate lower level, or it may induce the emission of a similar photon by another atom in the appropriate upper level. This induced absorption and emission decreases the life time of atoms below the natural life times, causing resonance broadening of the spectral lines.

2.4.2 Collision Broadening

Collisional excitations and de-excitations by electrons or by other atoms in the source may also greatly reduce the life time of each state, leading to a

further broadening of the energy levels and spectrum lines. From a classical point of view, the collisions may be considered as interrupting the radiation wave train, thereby resulting in a broadening of the Fourier spectrum.

Both the resonance and collision broadenings leave the resonance line profile (equation 2.6) essentially unchanged in form, merely increasing the half-width Γ by one or two (or even more) orders of magnitude over the natural half-width.

2.5 Optical Depth

In experimental physics, an important cause of the line shape distortion is the opacity effect. This is quite significant when the light absorbed by a medium becomes comparable to the incident light. It introduces errors in the measurement of the spectral line strengths regardless of the measuring technique used. Table 2.1 gives errors at different absorption levels. In the classical absorption experiments a strong peak may absorb up to 50 % of the incoming radiation and hence gives a large error. In the *hot-wire* diode detector, by contrast, a few percent of the incident photons are absorbed and the errors are expected to be less than 5%.

When a collimated beam of light passes through an absorbing medium, the power absorbed in a distance δx is proportional to both δx and the incident flux. The constant of proportionality is defined as the absorption coefficient κ_ν , which is the fractional decrease in flux density per unit path

length. Thus

$$- \delta I_\nu = \kappa_\nu I_\nu \delta x \quad W m^{-2} Hz^{-1} \quad (2.12)$$

I_ν is the spectral flux density or irradiance, and units of κ_ν are m^{-1} . For a thickness l of the absorbing medium, a relation between the incident and emerging power is found by integrating this equation

$$I_\nu(l) = I_\nu(0) e^{-\int_0^l \kappa_\nu dx} \quad (2.13)$$

where $\int_0^l \kappa_\nu dx$ is the optical depth of medium. For a homogeneous medium κ_ν is independent of x , the optical depth is simply $\kappa_\nu l$ and

$$I_\nu(l) = I_\nu(0) e^{-\kappa_\nu l}, \quad (2.14)$$

κ_ν is then a decay constant in the exponential decrease of flux, and $1/\kappa_\nu$ can be thought of as the mean free path of photons in the medium.

If all the emitted radiation reaches the detector without re-absorption, the source is said to be optically thin for which $\kappa_\nu l \ll 1$, Equation 2.14 then becomes

$$I_\nu(l) = I_\nu(0)(1 - \kappa_\nu l) \quad (2.15)$$

let $x = \frac{I_\nu(0) - I_\nu(l)}{I_\nu(0)}$ then equation 2.14 can be written as

$$\kappa_\nu l = \ln\left(\frac{1}{1 - x}\right) \quad (2.16)$$

and equation 2.15 is then the approximate value of equation 2.14 and is given as $\kappa_\nu l = x$. Since the number of photons absorbed is proportional to κ_ν , it is possible to obtain the cross-section or the oscillator-strength, because in the case of Rydberg lines the oscillator-strength f is related to the κ_ν as

$$\int_{line} \kappa_{\nu} d\nu = \frac{e^2}{4\epsilon_0 m_e c} N f \quad (2.17)$$

where N is the number density.

The errors are estimated by assuming that the light source has negligible width. Then the percentage error in the measurement of the absorption coefficient is

$$1 - \frac{\kappa'_{\nu}}{\kappa_{\nu}} = 1 - \frac{x}{\ln \frac{1}{1-x}} \quad (2.18)$$

The line profile integration is performed in the measurement of the f values for the discrete levels, and the errors can be calculated for a given line shape. Since in practice the line shapes cannot be exactly known and the light source has a certain width, it is only possible to compute errors numerically by assuming certain experimental conditions.

Peak absorption C (%)	Absorption coefficient (%)	Gaussian profile integration (%)
1.0	0.50	0.18
2.5	1.25	0.44
5.0	2.52	0.89
10.0	5.1	1.8
15.0	7.7	2.7
20.0	10.4	3.7
50.0	27.9	10.2

Table 2.1: Percentage errors due to the opacity effects (After Shen-1988)

Chapter 3

General properties of interacting resonances

3.1 Introduction

This chapter presents a general study of the interacting resonances in atomic spectra. Autoionisation is the starting point of this discussion, and hence it completes the review of line profiles presented in the previous chapter. The study of the phenomenon of autoionisation is based on the Fano formula for an isolated resonance embedded in a smooth background continuum. The situation is considered in which the discrete level interacts with more than one continuum and it is then extended to the study of interaction of a Rydberg manifold of levels with a smooth background continuum. This treatment points to the importance of the shape parameter q , and the dependence of absorption cross-section on an energy variable. In a separate

section the same phenomenon is addressed by the K-matrix approach. This presentation complements the Fano approach (as it is also parametric in nature), and provides a simple formalism to understand various effects caused by interacting resonances, e.g., the q-reversal effect and vanishing width phenomenon caused mainly by a broad intruder level in the energy range of an autoionising series.

3.2 Autoionisation

The processes of autoionisation was first observed by Shenstone⁴⁵ and then White⁴⁶ extended these observations into the alkaline-earths and inert gases.

Above the series limit of any series lies a continuum of possible energy states. This continuum is characterised by the same quantum numbers as the series of discrete levels below the limit, i.e., the same L, S, J, and parity. An atom excited to a discrete energy level above the first ionisation threshold and into a region accompanied by a continuum characterized by the same L, S, J, and parity is in a condition of autoionisation. In order to understand the physics of the process, one has to consider the phenomenon of configuration-interaction. Electronic states of atoms and molecules are usually classified as belonging to a single well defined configuration, according to the independent particle model. Hence, a definite value of n and l can be allocated to each electron. A comparison of the theoretical values of the energy for levels with the experimental values and the transition probabilities shows that this assumption is not always justified. The system may

better be described by a different set of basis functions, formed by mixing into the original function contributions from one or more other configurations by "configuration-interaction", i.e., by terms of Hamiltonian which are disregarded in the independent-particle approximation.

For neutral and weakly ionised atoms, there usually exist important configuration-interaction effects between states belonging either to the same or to different Rydberg series of levels ("channels"). The interaction may produce either localized (resonance) distortion in the cross-section or wide spread redistribution of oscillator-strength from one spectral region to the other.⁴⁷ Of particular interest is the configuration mixing between a bound state and an adjacent ionisation continuum that gives rise to autoionisation. In a simple term diagram only one valence electron is excited and all terms converge to the series limit. However, there exist bound states equal in energy to the continuum states, due either to the simultaneous excitation of two electrons or to the excitation of an electron from an inner shell—e.g. one of the p electrons from the p^6 shell in an alkali atom. Fig 3.1 shows an example of the first case. Almost all of the bound states converging to either 3d or 4p limits have greater energy than the normal ionisation energy and can mix with the continuum states of the same parity and energy. The bound state becomes to some extent part of the continuum and is thereby broadened. One can also think in terms of the mixing representing a certain probability of finding the system in the ionised state—in other words, of undergoing a radiation-less transition. This process is known as autoionisation. Its probability may be as high as $10^{13} s^{-1}$, compared with a typical value of $10^8 s^{-1}$ for an allowed radiative transition.

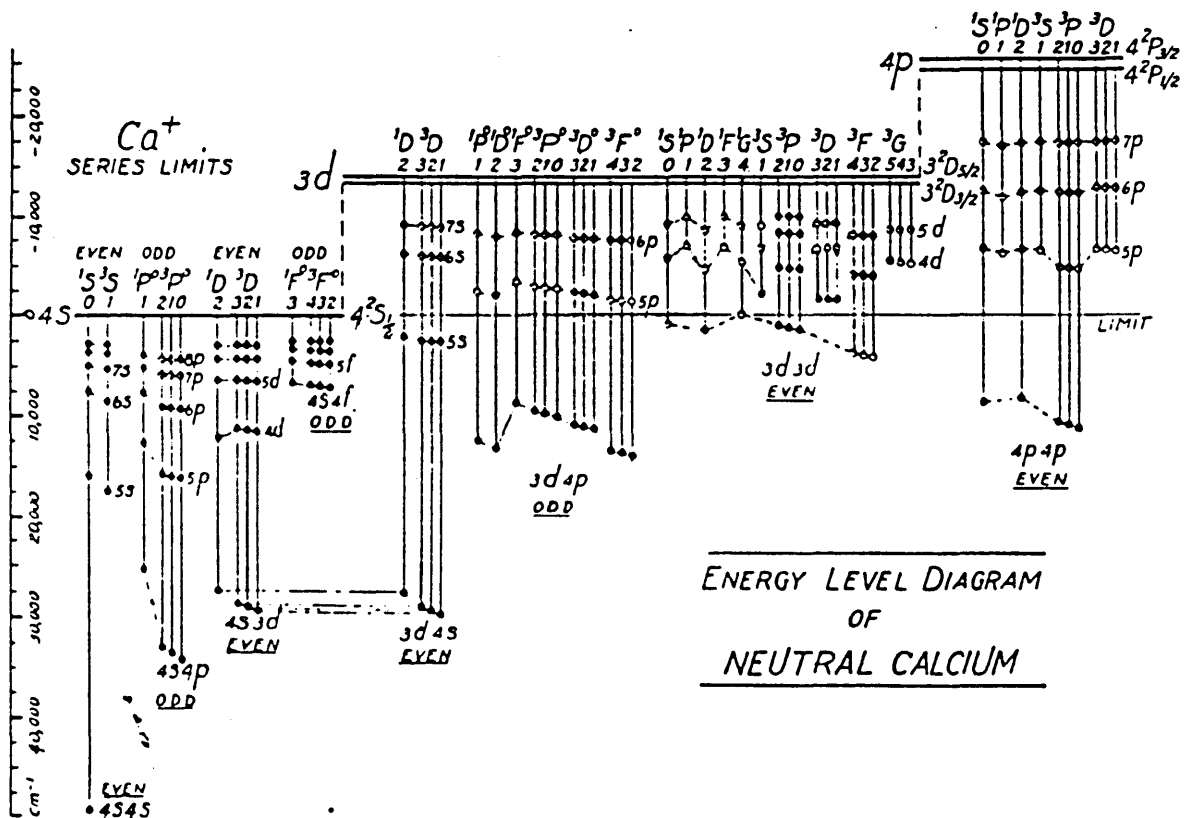


Figure 3.1: Energy level diagram of neutral calcium; most of the doubly excited levels converging to the 3d or 4p threshold lie in the first continuum.

3.3 Quantum mechanical treatment—Fano formula

As an example of configuration-interaction effects in the continuum, consider the case of a single (or, at least, an isolated) discrete state that lies within the energy range of the continuum states E_l . If transitions are possible from some initial state to both the discrete state and the continuum, and if these final states do not interact with each other, then a discrete absorption line appears superimposed upon the continuum, the total absorption strength at any given energy E is simply the sum of the discrete and continuum absorption strengths at that energy. If on the other hand the discrete state interacts with the continuum, then the wave functions for any given energy E are a linear combination of the unperturbed discrete and continuum functions. It is the amplitudes that are added and the total absorption strength shows pronounced interference effects. In addition, the "discrete" state acquires some of the properties of the continuum, and the discrete state may autoionise as discussed. If the interaction between the discrete and continuum states is not too strong, then the energy range over which the interaction is appreciable is small and does not include other discrete states. The problem has been treated analytically by Fano⁴⁸. Here we will present this treatment with more emphasis on understanding physics rather than putting detailed mathematical equations.

Consider an atomic system with a number of zero approximate states, let the unperturbed state be described by φ —calculated, in general as a linear combination of discrete basis states (to ensure maximum accuracy in the

calculation of the energy values and the eigen vectors of discrete states, the basis function expansion $\Psi_j^k = \sum_{\beta} Y_{\beta j}^k \Psi_{\beta j}$ must usually include basis functions from more than one configuration⁴⁹) with coefficients determined by diagonalization of the discrete-basis-state portion of the energy matrix. The coefficients $Y_{\beta j}^k$ are the components of Ψ_j^k in that basis. Also consider a mutually orthogonal set of continuum wave functions $\psi_{E'}$, constructed such that the continuum-state portion of the energy matrix is diagonal. Each of these states is nondegenerate; all degeneracy is removed by specification of an adequate set of quantum numbers. If all the energies are measured relative to the ionisation limit, then the continuum-continuum matrix elements are

$$\langle \psi_{E''} | H | \psi_{E'} \rangle = E' \langle \psi_{E''} | \psi_{E'} \rangle = E' \delta(E'' - E') \quad (3.1)$$

For the lone discrete state of interest we have the diagonal element

$$\langle \varphi | H | \varphi \rangle = E_{\varphi} \quad (3.2)$$

Where E_{φ} is the eigenvalue of φ relative to the ionisation limit. Let the configuration-interaction matrix element be abbreviated by $V_{E'}$:

$$\langle \varphi | H | \psi_{E'} \rangle = V_{E'} \quad (3.3)$$

It is understood that the discrete energy level E_{φ} lies within the continuous range of values of E' . The required eigenfunction of the Hamiltonian matrix for eigenvalue E has form

$$\Psi_E = a\varphi + \int dE' b_{E'} \psi_{E'} \quad (3.4)$$

The coefficients a and $b_{E'}$ are determined as solutions of the system of equations pertaining to the matrix Eq 3.1—Eq 3.3. This is done by solving the simple eigenvalue equation

$$H\Psi_E = E\Psi_E, \quad (3.5)$$

and

$$E_\varphi a + \int dE' V_{E'} * b_{E'} = Ea \quad (3.6)$$

$$V_{E'} a + E' b_{E'} = E b_{E'} \quad (3.7)$$

Solution of the problem can be obtained by expressing $b_{E'}$ in terms of a , but this involves division by $E - E'$ which can be zero. To avoid this Fano adopted the Dirac procedure of introducing the formal solution of Eq 3.7

$$b_{E'} = \left[\frac{1}{E - E'} + z(E)\delta(E - E') \right] V_{E'} a \quad (3.8)$$

The result of this configuration-interaction (of continuum states with a discrete state) is a phase shift Δ in the continuum states wave function. This can be verified if ψ_E is represented by a wave function with asymptotic behavior $\propto \sin(k(E')r + \delta)$, where δ is the phase shift of the unperturbed continuum. Now using this wave function along with the value of b (Eq 3.8) in the expression $\int dE' \psi_{E'} b_{E'}$, and after integration

$$\int dE' \psi_{E'} b_{E'} \propto [-\pi \cos(k(E)r + \delta) + z(E) \sin(k(E)r + \delta)] V_E a \quad (3.9)$$

Now if $-\frac{\pi}{\sqrt{\pi^2+z^2}} = \sin \Delta$ and $\frac{z(E)}{\sqrt{\pi^2+z^2}} = \cos \Delta$ then the above expression becomes $\propto \sin(k(E) + \delta + \Delta)$ and

$$\Delta = -\arctan[\pi/z(E)] \quad (3.10)$$

is the phase shift due to configuration interaction of ψ_E with φ .

$z(E)$ is determined by substituting the expression Eq 3.8 into Eq 3.6, and Eq 3.6 reduces to

$$E_\varphi + F(E) + z(E) |V_E|^2 = E \quad (3.11)$$

where

$$F(E) = P \int dE' \frac{|V_{E'}|^2}{E - E'} \quad (3.12)$$

P indicates "principal part of". Then

$$z(E) = \frac{E - E_\varphi - F(E)}{|V_E|^2} \quad (3.13)$$

$|V_E|^2$ which is an index of the strength of the configuration-interaction has the dimension of energy since $\psi_{E'}$ is normalised "per unit energy" according to Eq 3.3. The phase shift changes swiftly by $\sim \pi$ as E traverses an interval $\sim \pi |V_E|^2$ about the resonance at $E = E_\varphi + F$. The quantity F represents thus a shift of the resonance position with respect to E_φ . The value of $F(E_\varphi)$ is the perturbation of the discrete state by the entire continuum. $F(E)$ is the value that the perturbation would assume if the unperturbed level were

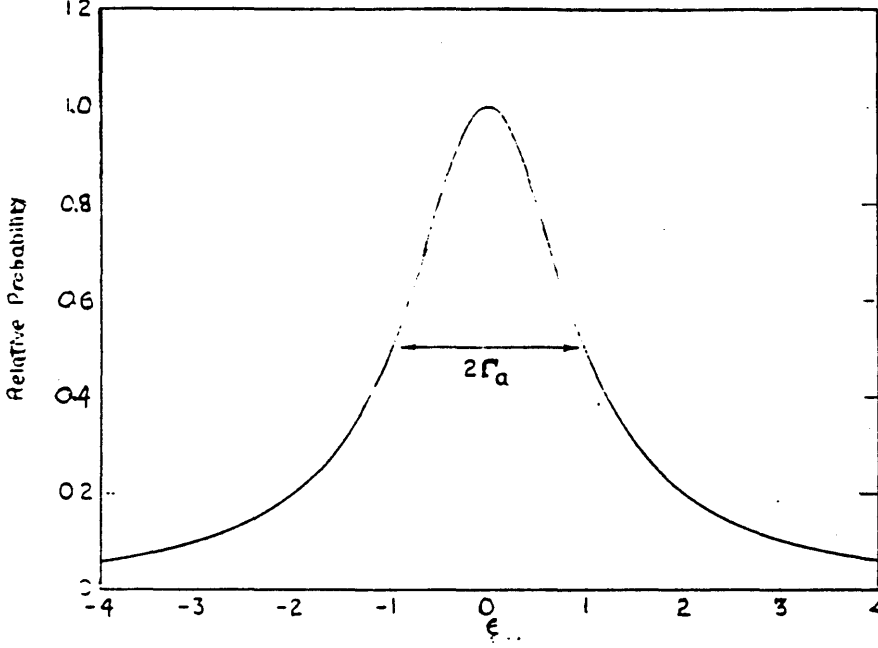


Figure 3.2: Resonance shape of an autoionising level at energy E_0

located at E instead of E_φ , and (like V_E) is usually a very slowly varying function of E . $z(E)$ is essentially the energy displacement from the perturbed position of the discrete level measured in units of $\pi |V_E|^2$. The coefficient a is determined by normalisation and is given as^{23,49}

$$|a(E)|^2 = \frac{|V_E|^2}{[E - E_\varphi - F(E)]^2 + \pi^2 |V_E|^2} \quad (3.14)$$

Together with the expression Eq 3.12 for $F(E)$, this provides a complete analytical result for the eigenfunctions Ψ_E for the mixed discrete state plus continuum. This result shows that the configuration-interaction "dilutes" the discrete state φ throughout a band of actual stationary states whose profile is represented by resonance curve with half width at half maximum as $\Gamma_a = \pi |V_E|^2$ as shown in Fig 3.2. Defining the energy variable ϵ as

$$\epsilon = \frac{E - E_\varphi - F}{\pi |V_E|^2} \quad (3.15)$$

and with the help of Eq 3.10, one can write both a and b as

$$a = \frac{\sin \Delta}{\pi V_E} = \frac{1}{\pi V_E} \frac{1}{(\epsilon^2 + 1)^{1/2}} \quad (3.16)$$

$$b_{E'} = \frac{V_{E'}}{\pi V_E} \frac{\sin \Delta}{E - E'} - \cos \Delta \delta(E - E') \quad (3.17)$$

The half life τ_a with which an atom prepared initially in the discrete state autoionises into the continuum state $\psi_E(E \cong E_0 = E_\varphi + F)$ can be inferred from the uncertainty principle $(\Delta E)(\Delta t) = \hbar$. Thus the half life and the corresponding transition probability rate are given by

$$A^a = \frac{1}{\tau_a} = 2 \frac{\Gamma_a}{\hbar} = \frac{2\pi |V_E|^2}{\hbar} = 1.2988 \cdot 10^{17} V_E^2 \text{ s}^{-1} \quad (3.18)$$

The above description explains how the wave function is evaluated due the configuration interaction. The variation of the probability of excitation of the stationary state Ψ_E can take place in three different ways, i.e., the transition from an initial level i can be only possible to the discrete state φ or only to the continuum or to the both. If T is any transition operator, then the matrix element of the transition from state i to the state Ψ_E can be expressed as

$$\langle \Psi_E | T | i \rangle = a \langle \varphi | T | i \rangle + \int dE' \langle \psi_{E'} | T | i \rangle b_{E'} \quad (3.19)$$

After substitution of the values of a and b

$$\begin{aligned}
 \langle \Psi_E | T | i \rangle &= \frac{1}{\pi V_E} \langle \varphi | T | i \rangle \sin \Delta \\
 &+ \frac{1}{\pi V_E} P \int dE' \frac{V_{E'} \langle \psi_{E'} | T | i \rangle}{E - E'} \sin \Delta \\
 &- \langle \psi_E | T | i \rangle \cos \Delta
 \end{aligned} \tag{3.20}$$

$$= \frac{1}{\pi V_E} \langle \Phi | T | i \rangle \sin \Delta - \langle \psi_E | T | i \rangle \cos \Delta, \tag{3.21}$$

or

$$= \frac{1}{\pi V_E} \frac{1}{(\epsilon^2 + 1)^{1/2}} \langle \Phi | T | i \rangle + \frac{\epsilon}{(\epsilon^2 + 1)^{1/2}} \langle \psi_E | T | i \rangle \tag{3.22}$$

where

$$\Phi = \varphi + P \int dE' \frac{V_{E'} \psi_{E'}}{E - E'} \tag{3.23}$$

is the modified discrete state at the energy $E = E_\varphi + F$, which is accessed by the experiment. Thus it is not possible to probe the unperturbed level φ in the vicinity of a resonance. This modification of the discrete state is due to the admixture of states of the continuum.

Now the three different situations are:

1. When transition from the initial state i is only possible to the discrete state i.e. $\langle \psi_E | T | i \rangle = 0$ for all E , then the wavenumber dependence of the line strength is proportional to $a^2 = \frac{1}{(\pi V_E)^2} \frac{1}{\epsilon^2 + 1}$, and one observes a discrete absorption line with center displaced by an energy F and broadened into a resonance shape with HWHM of Γ , as shown in Fig 3.2.

2. When transition from i is only possible to the continuum i.e. $\langle \Phi | T | i \rangle = 0$, then the line strength is proportional to $\frac{\epsilon^2}{\epsilon^2+1}$, and one sees the absorption continuum, except with a transparent window centered at a wavenumber corresponding to the perturbed position of the discrete line, as shown in Fig 3.3 (see lower left of the figure). This hole is created due to the interference effects. The continuum states are not perturbed so much in energy as in radial position, as shown in Fig. 3.4; the unperturbed continuum states (near $\epsilon = 0$) are mixed together with opposite phases in such a way as to nearly cancel each other out at those radii that contribute to the multipole matrix elements in Eq. 3.22, and they interfere constructively only at large r where they cannot contribute to radiative absorption.

3. If absorption is possible to both the discrete state and the continuum, then neither term in Eq 3.21 is zero. The sharp variation of Δ as E passes through the resonance at $E = E_\varphi + F$ causes a sharp variation of the $\langle \Phi_E | T | i \rangle$. Since $\sin \Delta$ is an odd function of energy variable ϵ and $\cos \Delta$ is an even function of this variable, the terms interfere constructively on one side of $\epsilon = 0$ and destructively on the other. There exists a value of E at which the destructive interference is complete—namely, that value of E which is equal to the negative of

$$q = \frac{\langle \Phi | T | i \rangle}{\pi V_E \langle \psi_E | T | i \rangle} \quad (3.24)$$

Since $\Gamma_a = \pi |V_E|^2$ is the half width at half maximum (HWHM) of the autoionised state, the q^2 represents approximately the ratio of the line strength for the unperturbed discrete state to the line strength for a bandwidth

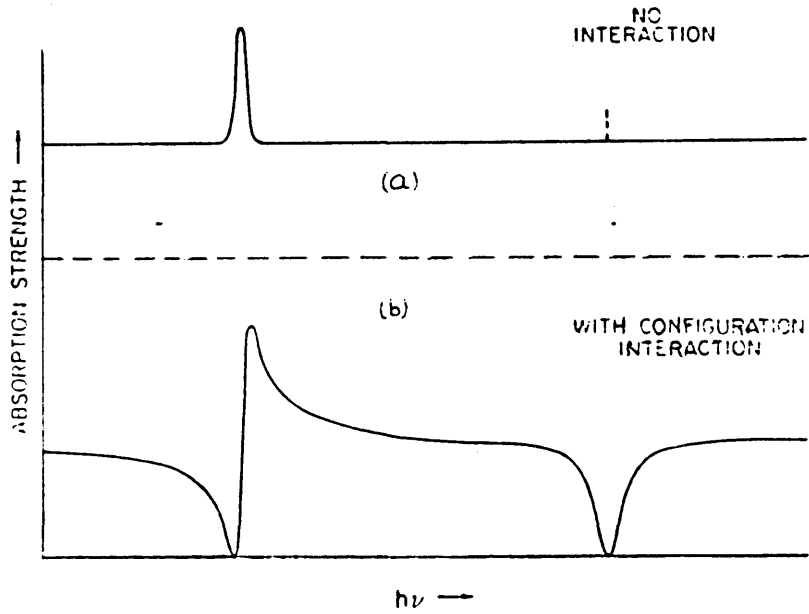


Figure 3.3: a: Total absorption strength from a lower level to the continuum plus two discrete levels that do not interact with the continuum. The strength of the higher frequency discrete line is assumed to be zero (shown by dotted line). b: The situation when discrete levels interact with the continuum. A Beutler-Fano profile is observed for the finite width discrete level and a hole at the position of the zero strength discrete line.

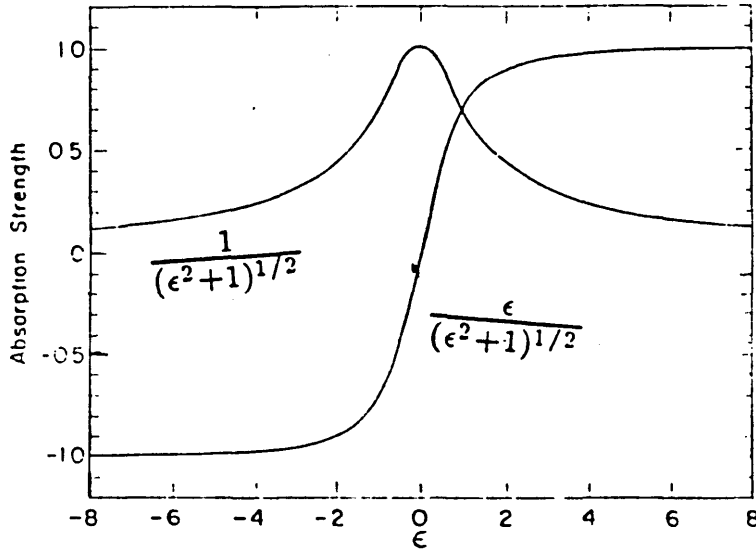


Figure 3.4: Form of the coefficients, in the final mixed eigenfunction, of the discrete basis function (symmetrical curve) and of the continuum basis functions (asymmetrical curve).

$\pi\Gamma_a$ of the unperturbed continuum. The ratio of the transition probability $|\langle \Psi_E | T | i \rangle|^2$ to the probability $|\langle \psi_E | T | i \rangle|^2$ of transition to the unperturbed continuum is

$$\frac{|\langle \Psi_E | T | i \rangle|^2}{|\langle \psi_E | T | i \rangle|^2} = \frac{(q + \epsilon)^2}{(1 + \epsilon^2)} \quad (3.25)$$

This ratio is represented by a family of curves in Fig 3.5. Thus we see that in terms of energy variable ϵ , the line shape has a simple form that depends only on the q parameter. This simple but powerful expression explains the three different situations outlined above. The line shape is asymmetric except for $q = 0$ or ∞ . This asymmetry is due to interference between the discrete state and the continuum. The direction of the asymmetry depends on the sign of q , which in turn depends on the sign of the two dipole matrix elements and

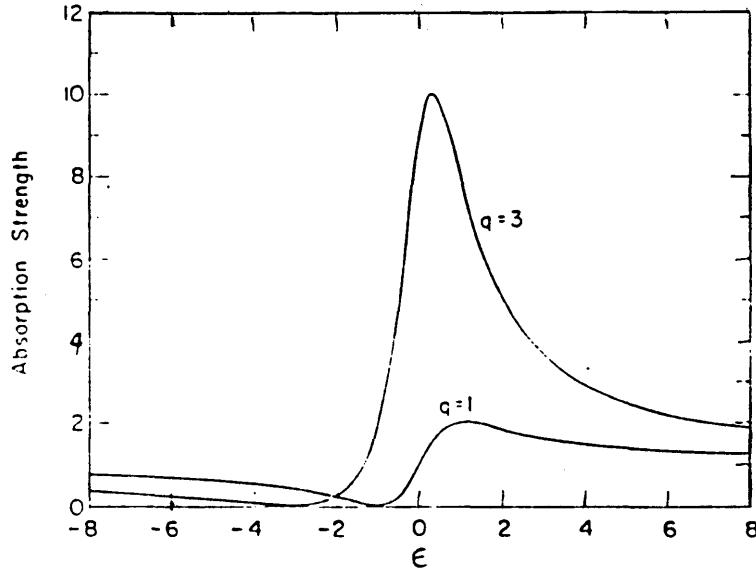


Figure 3.5: Beutler-Fano profiles

the configuration-interaction matrix element V_E . The situation when $q = 0$ is the same when there is excitation only possible to the continuum states, and $q = \infty$ corresponds to the situation when excitation is only possible to the discrete state, thus in this case the profile is a Lorentzian. These family of curves are called Beutler-Fano profiles.

3.3.1 Isolated resonance interacting with many continua

The situation becomes more complicated when an isolated resonance interacts with more than one continuum, $\psi_{E'}, \chi_{E'}, \dots$, e.g., the resonance may lie above the second ionisation threshold and so on. The procedure adopted by Fano and then Fano and Cooper is quite straight forward. Additional matrix elements of interaction similar to V (let say U, W , etc), corresponding to the interaction of discrete level with different continua, are added to the expressions like Eq 3.3, 3.4 etc. The total wave function then becomes

$$\Psi_{hE} = a\varphi + \int dE' [b_{E'}\psi_{E'} + c_{E'}\chi_{E'} + \dots], \quad (3.26)$$

where h indicates a set of $n - 1$ parameters required to specify Ψ , since each value of E is an n -fold degenerate eigenvalue. The coefficients $a, b_{E'}, c_{E'}$ are functions of E and h .

Total phase shift is given as

$$\bar{\Delta} = -\arctan \frac{\pi(|V_E|^2 + |W_E|^2 + \dots)}{E - E_\varphi - G(E)}, \quad (3.27)$$

$$G(E) = P \int dE' \frac{|V_E'|^2 + |W_E'|^2 + \dots}{E - E'} \quad (3.28)$$

The probability of transition from an initial state i to all the stationary states of energy E is

$$|\langle \Psi_{1E} | T | i \rangle|^2 + |\langle \Psi_{2E} | T | i \rangle|^2 + \dots \quad (3.29)$$

The first term in this sum varies as a function of energy in the proximity of the resonance at $E_\varphi + G$ according to the pattern discussed. The remaining terms are wholly unaffected by the resonance. Therefore in the presence of two or more continua, one should expect an excitation spectrum of the type shown in Fig 3.5 superposed on a smooth background, which is zero only if all the terms in Eq 3.29 are zero except first, i.e., the states $\Psi_{2E}, \dots$ can not be excited.

3.4 K-matrix Formalism—another approach

The previous section described autoionisation by the Fano formalism. The Fano formula is well celebrated and is widely used to understand the process of autoionisation. However, there is a fundamental problem which arises in the description of even the simplest, isolated resonance in the parametric approach followed by Fano (1961), that the atom can not be deperturbed, i.e. access to the discrete state is not possible, as autoionisation is an intrinsic property of an atom.

This section describes the same phenomenon with an alternate formalism, which also follows the parametric approach. This not only explains the phenomenon of autoionisation and interacting resonances, but also describes in detail the phenomena like q-reversal and vanishing of particle and radiative widths in a channel. This all is done with a few parameters like width of the levels. By this approach it is also very simple to explain pole structures. It is based on the K-matrix theory, which has previously been used in

nuclear physics⁹. K-matrix, like R-matrix has been derived from Wigner's scattering matrix¹⁰ or S-matrix. The theory of resonances is well explained in 'Quantum Mechanics' by Landau and Lifshitz, and the S-matrix and concept of photoionisation as a 'half scattering' has been extensively discussed by Shore⁸⁶. Recently Connerade and Lane^{96,101} have studied the relation between K-matrix and MQDT approach and have worked out a simple development of K-matrix through Wigner's scattering or S-matrix. The main advantages enjoyed by K-matrix over S, and R-matrix can be summarized as following:

1. The S-matrix is the one most directly related to the scattering amplitude, but not easily connected to the specific target states since it is independent of a and b (Wigner's scattering theory is developed by the consideration of a sphere of certain radius ' a ' round the target (see chapter 4), and b is a free parameter, obtained by matching the logarithmic derivatives at the boundary a). Moreover it does not have a simple pole structure especially when resonances overlap (see Ref.94).

2. The R-matrix is convenient for numerical applications precisely because it depends on b (and thus related to the internal states of the target during interaction). However, because it depends on both a and b , it is not suitable to analyse the analytic pole structure near overlapping resonances, although with appropriate choices of a & b it should reproduce the spectra correctly.

3. The K-matrix is both independent of a and b (as we will see below it is directly derived from S, and S is independent of a , b) and simple in pole

structure (because it is meromorphic)¹. It therefore provides a suitable framework within which to discuss the general properties of overlapping resonances, without the need of any specialised knowledge of the target.

In its simplest form the K-matrix can be derived from the S-matrix by the relation

$$S = \frac{1 + iK}{1 - iK} \quad (3.30)$$

K is real and in its very simple form is given as

$$K = \tan \delta \quad (3.31)$$

where δ is the phase shift of the continuum wave function in the absence of any resonance. However, if there is any variation in the phase shift, due either to the presence of a resonance or of any perturber in that region, then this additional phase shift is added to the δ to get the expression for K. The essential part of the cross-section (when there is only one open channel) is given as⁹⁴

$$\sigma_{aa} = \frac{4K_{aa}^2}{1 + K_{aa}^2} \quad (3.32)$$

In the case of an isolated resonance in a 'flat' continuum (which means that the phase shift δ of the continuum states is regarded as constant within the range of the resonance), if Δ_0 is the phase shift due to this resonance, then

¹A function $F(z)$ is said to be meromorphic as a function of the complex variable z in some domain if $F(z)$ is analytic in that domain apart from isolated poles of finite order (see Pearson⁹⁵)

$$\mathbf{K} = \tan(\delta + \Delta_0) \quad (3.33)$$

Now if Γ is the width of the resonance and E_0 is the resonance energy, then there exists (see, e.g., Landau and Lifshitz 1965) a simple relation

$$\tan \Delta_0 = \frac{\Gamma}{2(E_0 - E)} \quad (3.34)$$

By using this expression for $\mathbf{K}$ in Eq 3.32,

$$\sigma(E) = \frac{4\mathbf{K}^2}{1 + \mathbf{K}^2} = 4 \sin^2 \delta \frac{[(E_0 - E) + \frac{1}{2}\Gamma \cot \delta]^2}{[(E_0 - E)^2 + (\frac{1}{2}\Gamma)^2]} \quad (3.35)$$

For $q = \cot \delta$ and $|\tilde{D}|^2 = 4 \sin^2 \delta$, Eq. 3.35 yields the standard Fano formula for an isolated autoionising resonance line (see Eq 3.25)

$$\sigma(\epsilon) = |\tilde{D}|^2 \frac{(q + \epsilon)^2}{1 + \epsilon^2} \quad (3.36)$$

where $\epsilon = 2(E - E_0)/\Gamma$.

One can, without loss of generality, easily extend this treatment to the case of two overlapping resonances in a flat continuum. If Γ_1 and Γ_2 are the widths and E_1 and E_2 resonance energies of the two overlapping resonances then

$$\tan \Delta_0 = \frac{\Gamma_1}{2(E_1 - E)} + \frac{\Gamma_2}{2(E_2 - E)} \quad (3.37)$$

Then using the expression for cross-section (Eq 3.32)

$$\sigma(E) = \frac{4\mathbf{K}^2}{1 + \mathbf{K}^2} = 4 \sin^2 \delta \frac{(1 + \frac{q\Gamma_1}{2(E_1 - E)} + \frac{q\Gamma_2}{2(E_2 - E)})^2}{[1 + (\frac{\Gamma_1}{2(E_1 - E)} + \frac{\Gamma_2}{2(E_2 - E)})^2]} \quad (3.38)$$

Now if two resonances happen to be in two different channels, then two different values q_1 and q_2 should be introduced⁹⁴. This argument can easily be extended to the case of N overlapping resonances with one flat continuum (see Ref.94), thus one gets

$$\sigma(E) = \frac{4K^2}{1 + K^2} = 4 \sin^2 \delta \frac{(1 + q \sum_n \frac{\Gamma_n}{2(E_n - E)})^2}{[1 + (\sum_n \frac{\Gamma_n}{2(E_n - E)})^2]} \quad (3.39)$$

Now one can make contact with quantum defect theory through substitution

$$\sum_n \frac{\Gamma_n}{2(E_n - E)} \equiv x \cot \pi(\nu + \mu) \equiv x \cot \theta \quad (3.40)$$

where ν is the energy variable defined by $E_\infty - E = R/\nu^2$ and μ is the quantum defect. Thus

$$\sigma(\theta) = \frac{4K^2}{1 + K^2} = 4 \sin^2 \delta \frac{(1 + qx \cot \theta)^2}{1 + (x \cot \theta)^2} \quad (3.41)$$

and with simple algebra one can show that

$$\sigma(\nu) = |\tilde{D}|^2 \frac{\tan^2 \pi \nu + 2B \tan \pi \nu + B^2}{\tan^2 \pi \nu + 2C \tan \pi \nu + D^2} \quad (3.42)$$

The three shape parameters B , C and D are given as

$$B = \frac{qx + \tan \pi \mu}{1 - qx \tan \pi \mu}, \quad C = \frac{(1 - x^2) \tan \pi \mu}{1 + x^2 \tan^2 \pi \mu}, \quad D = \frac{x^2 \tan^2 \pi \mu}{1 + x^2 \tan^2 \pi \mu} \quad (3.43)$$

Of these only B depends on q , and from the expression for B

$$q = \frac{1}{x} \tan \pi(\beta - \mu) \quad (3.44)$$

where $B = \tan \pi\beta$.

For an isolated or Beutler-Fano resonance, $q=0$ implies a symmetric window. In the present case, when $B = \tan \pi\mu$, the transmission maxima also coincide with the resonance energies.

This formula for $\sigma(\nu)$ (Eq 3.42) is identical to the formulae given by Dubau and Seaton⁹⁷(1984) and independently by Giusti-Suzor and Fano⁹⁸. It provides a simple expression for a complete and unperturbed (i.e. a flat continuum) Rydberg series of autoionising resonances in terms of just three shape parameters, which are constant over the whole series. The structure of the formula reveals that the cross-section goes to zero for $\tan \pi\nu = -B$, which corresponds to the transmission window in Fano formula. Similarly a peak occurs for $\tan \pi\nu = (D^2 - BC)/(B - C)$. There are bounds on C set by choosing D positive (as the cross-section is a positive definite), thus $-D < C < D$.

Connerade and Lane in their review paper on interacting resonances⁹⁴ have studied the various shapes of the overlapping profiles in a Rydberg series of autoionising resonances by varying the shape parameters. They divide the profiles in two distinct categories of type 1 and type 2. Type 1 contains all those resonances whose linewidth is much smaller than the separation between the successive members of the series, and type 2 comprises of all those profiles whose width is much larger than (or comparable with)

the separation between successive members of the series. In the isolated line limit, the type 1 profiles tend to the typical Fano shape.

3.4.1 Perturbation by a broad intruder level and its effects on the shapes and widths of the Rydberg levels

Until now the discussion was confined to the cases where the phase shift of the background continuum is almost constant i.e., flat continuum. However, the situation may arise when the phase shift is no longer the same everywhere, rather it varies. This can happen e.g., if a perturber is present in the range of interest. The situation has been dealt with detail in a letter to the J.Phys. B, by Connerade and Lane^{101a}, and has been elaborated by real experimental examples in their review paper⁹⁴. Reference 101a, is mainly concerned with the shape or giant resonance (for details about the shape or giant resonances see, e.g., review by Connerade *et al*¹⁰²) interacting with a Rydberg series. Connerade and Lane^{101a} suggest that there are two possible theoretical approaches, depending on whether the giant resonance is subsumed in the continuum, or whether it is treated as an additional very broad spectral feature. It has been shown that both approaches lead to the same conclusion. Here both the approaches are followed, but the discussion is based on the second one i.e, giant resonance treated explicitly as an intruder, because in the present context, a giant resonance is simply a special case of an intruder which happens to be very broad. Thus, if there is a perturber (in this case some intruder of large linewidth Γ_B with resonance energy E_B), in a Rydberg series of autoionising levels with a

smooth background, then the resonant part of the phase shift, in the weak coupling condition (between the Rydberg series and the perturber), is the sum of the individual phase shifts of all the resonances, plus a mixed term which represents the coupling of n to B (where n are the individual members of the Rydberg series and B is the perturber level)

$$\tan \Delta_0 \approx \frac{\Gamma_B}{2(E_B - E)} + [1 - \frac{\mu^{-1}\Gamma_B^{1/2}}{E_B - E}]^2 \sum_n \frac{\Gamma_n}{2(E_n - E)} \quad (3.45)$$

where Γ_n is the profile width of the Rydberg member, $\mu = \frac{\Gamma_n^{1/2}}{H_n}$ and H_n is the coupling between n and B . It is a property of the Coulomb potential that μ is independent of n for a Rydberg series.

Similar to Eq 3.40, one can make a connection to the quantum defect theory, and Δ_0 can be written as

$$\tan \Delta_0 \approx \bar{\Delta} + x_1 x_2 \cot \theta \quad (3.46)$$

where

$$\bar{\Delta} \equiv \frac{\Gamma_B}{2(E_B - E)}, \quad x_1 \equiv 1 - \frac{\mu^{-1}\Gamma_B^{1/2}}{E_B - E}, \quad x_2 \cot \theta \equiv \sum_n \frac{\Gamma_n}{2(E_n - E)} \quad (3.47)$$

Now, once again if the cross-section is expressed in terms of $\mathbf{K}$ -matrix (see Eq 3.32) and the definition of $\mathbf{K}$ as in Eq 3.33 is used, then

$$\sigma(\theta) = \frac{(\bar{\Delta} + \bar{\delta})^2}{(1 + \bar{\Delta}^2)(1 + \bar{\delta}^2)} \frac{\tan^2 \theta + 2B \tan \theta + B^2}{\tan^2 \theta + 2C \tan \theta + D^2} \quad (3.48)$$

where

$$B \equiv \frac{x_1 x_2}{\bar{\Delta} + \bar{\delta}}, \quad C \equiv \frac{x_1 x_2 \bar{\Delta}}{1 + \bar{\Delta}^2}, \quad D^2 \equiv \frac{x_1^2 x_2^2}{1 + \bar{\Delta}^2}, \quad \bar{\delta} \equiv \tan \delta \quad (3.49)$$

The second factor in this expression (Eq 3.48) is the same as in Eq 3.42 for N overlapping resonances, with the exception that, now, the three shape parameters B, C, and D are energy dependent. This energy dependence is mainly through $\bar{\Delta}$, which is a function of detuning ($E_B - E$) from the centre of the perturber. Thus, the second factor in Eq 3.48 represents a Rydberg series of autoionising lines, whose shape (and in particular the profile index q) vary with energy in a manner which reveals the influence of the perturber on the individual Rydberg members.

The first factor in (Eq 3.48) is an amplitude term. It only depends on $\bar{\Delta}, \bar{\delta}$, and thus gives information only about the perturber and the background continuum, and contains no information about the Rydberg series. Rather it is the profile of the perturber in the absence of any autoionising series.

The q-reversal effect

According to the above discussion when there is a perturbation by a broad intruder level, in general, the shape parameters of the series (B, C, and D) are not constant, and their variation with energy expresses the influence of the intruder (or giant) resonance on the shapes of the individual Rydberg

members. This variation can be studied through the Fano profile index q , which is readily related to the shape parameter (Connerade and Baig)¹⁰⁹:

$$q = \frac{(B - C)}{(D^2 - C^2)^{1/2}} = \frac{1 - \bar{\delta}\bar{\Delta}}{\bar{\delta} + \bar{\Delta}} \quad (3.50)$$

In the weak-coupling limit, q is determined entirely by the perturber (or shape) resonance and the background phase shift. Note that $q = 0$ when $\bar{\Delta} = 1/\bar{\delta}$, which is also the condition for a maximum in the first factor of Eq 3.48, i.e., when:

$$E = E_B - \frac{\Gamma_B}{2} \tan \delta \quad (3.51)$$

Again, for small $\bar{\delta}$, this lies close to $E = E_B$. In general $q \rightarrow 0$ (window resonance) at the peak intensity of the giant resonance. At about this value, $\bar{\Delta}$, and therefore q , changes sign.

This change in symmetry of the profiles in a Rydberg manifold (change in sign of q between two successive members) is called the *q-reversal effect*.¹⁰³ The appearance of q -reversals in perturbed series of autoionising profiles is frequent, but not universal, and the conditions under which q reversal may occur, as well as the number of q reversals, are of interest because they reveal the nature and strength of the coupling between the intruder level and the perturbed Rydberg manifold. The q -reversal effect was discovered experimentally by Connerade¹⁰³ in Tl I, and since then a number of examples have been found¹⁰⁴. In the original theory, it was implicit that the point about which q -reversal occurs should coincide in energy with the peak of the giant resonance (or the intruder level); however, the experimental observations

in Tl I do not support this idea, and Connerade^{103a} remarked ' it must be borne in mind that the energy of maximum coupling does not necessarily coincide in energy with a peak in the absorption cross-section, as the matrix elements involved are not the same in both cases ' .

A study was made to solve the problem of Rydberg autoionising series perturbed by a very broad intruder. This work was intended to show the consistency of the results from the previous studies where the giant resonance was regarded as a special kind of intruder. This study was based on the formal K-matrix theory for a Rydberg manifold perturbed by a broad intruder, set up by Lane¹⁰⁵ and the results were related to the q-reversal problem by Connerade¹⁰⁴. For a Rydberg series (represented by n) and a very broad intruder level B , the full problem is solved involving two open channels, a strongly coupled particle channel a and a weakly coupled radiative channel γ . If the radiative widths $\Gamma_{B\gamma}^{1/2}$ and μ_γ are very small and the background constant is neglected, then the formula for cross-section is simplified to the following expression

$$\sigma(\epsilon) = \frac{(\epsilon + \frac{1}{2}q\Gamma_B)^2}{(\epsilon + \sum)^2 + [(\mu_a\Gamma_B^{1/2} + \frac{1}{2}\mu_a^2\epsilon)\sum - \frac{1}{2}\Gamma_B]^2} \quad (3.52)$$

which is closely related to the standard Fano formula for an isolated resonance. In fact, the numerator is the same as in Fano formula for the resonance E_B, Γ_B , while an additional Rydberg series of resonances is introduced through the presence of $\sum$ in the denominator. A good review of this work is included in Ref. 94.

Connerade *et al* have also done some numerical studies¹⁰⁴, and an im-

portant conclusion was that q reversals are a hallmark of *weak* coupling, i.e. they tend to disappear as the coupling strength H_n is increased. A question which therefore arises is how many q reversals one expects to find in a Rydberg series and the condition under which they may occur. A study was made by Connerade and Lane^{101a,b,c}, and an expression for q variation as a function of the detuning from the energy of the intruder, was derived within the K-matrix approach. Their predictions show that as many as six q reversals can occur in the general case in photoionisation but that, in elastic scattering, there are at most two.

Vanishing width effect

The conclusion of the above discussion is that with the help of K-matrix theory, Connerade *et al* have established that the q -reversal effect is a consequence of the perturbation of a Rydberg autoionising series by a very broad intruder level. Not only this, the theory also explains the vanishing of the width (both radiative and particle) in a channel in terms of perturbation by a broad intruder level, and thus both the q -reversal and the vanishing width phenomena are related to each other—as they have a common cause. For a general intruder, two quantities are of interest in defining the level sequence, namely the shape parameter, and the strength function. As has been shown by Connerade and Lane^{101a}, the shape parameter is given as

$$-q^{-1} = \tan \tilde{\Delta} \quad (3.53)$$

where $\tilde{\Delta}$ is the total phase shift including the giant resonance. Thus Eq 3.53 is equivalent to Eq 3.50). The strength function is given by

$$\frac{\pi\Gamma}{2D} = \frac{\frac{1}{2}\pi t(\Gamma_B^{1/2} + \epsilon\mu)^2}{\sum_{\infty}^2 + (\overline{K_{aa}}\epsilon - \frac{1}{2}\Gamma_B)^2} \quad (3.54)$$

where D is the average level spacing. Thus the strength function has a vanishing point at $\epsilon = -\mu^{-1}\Gamma_B^{1/2}$, which implies that the particle width vanishes.

The vanishing of particle width of a resonance as a result of an intruder state disturbing the sequence of levels is a well known phenomenon in nuclear physics¹⁰⁵. In atomic physics, under suitable conditions, either the radiative width (Garton 1965)¹⁰⁶ or the particle width (Rinneberg *et al* 1985)¹⁰⁷ may go to zero.

Chapter 4

Approximate solutions to the many-body problem

4.1 Introduction

This chapter describes different theoretical models developed so far to study many-body problem in atomic physics. This starts with the general discussion of the two-body problem i.e. the hydrogen atom. Neglecting the fine structure effects, the general solution of the nonrelativistic Schrödinger wave equation and the effect of a pure coulomb potential are discussed. This is followed by the case of a two electron atom and the problems arising due to a non-Coulomb but central potential are discussed. A birds eye view of different models developed to solve the two-electron problem is presented and later the models are extended to the many-body case ending with the discussion of models especially appropriate for alkaline-earths, including dis-

cussion at some length of the many-body perturbation theory (MBPT), the multi-channel quantum defect theory (MQDT), and the R-matrix theory, all of which have been applied by various authors to the alkaline-earth spectra reported in the present thesis.

4.2 The Hydrogen atom

In the hydrogen atom the single electron experiences a pure Coulomb force due to the positively charged nucleus. The energy eigenvalues and eigenfunctions are obtained by solving the Schrödinger wave equation in the non-relativistic approximation. It does not, therefore, account for the fine structure effects. In the center of mass system, the total Hamiltonian in a.u is

$$H = \frac{p^2}{2\mu} - \frac{Z}{r} \quad (4.1)$$

where μ is the reduced mass, and p is the relative momentum. The wave equation is

$$H\psi = E\psi \quad (4.2)$$

E is the energy eigenvalue. Because the interaction potential is central, the wave function may be separated in spherical polar coordinates. Let $u_{E,l}(r) = rR_{E,l}(r)$, where $R_{E,l}$ is the radial solution of the wave function, then

$$\frac{d^2 u_{E,l}}{dr^2} + 2(E - V_{eff}(r))u_{E,l} = 0 \quad (4.3)$$

Where V_{eff} is the effective potential

$$V_{eff} = -\frac{Z}{r} + \frac{l(l+1)}{2r^2} \quad (4.4)$$

made up of the coulomb potential and the centrifugal barrier potential $\frac{l(l+1)}{2r^2}$. For $E > 0$, the solution $u_{E,l}(r)$ will have an oscillatory behavior at infinity and a continuous spectrum is observed. However, for $E < 0$, a solution is obtained by imposing restrictions on $u_{E,l}(r)$ to vanish at both $r = 0$ and $r \rightarrow \infty$. Energy eigenvalues for bound states are given by

$$E_n = -\frac{Z^2}{2n^2} \quad (4.5)$$

n can take any discrete value from $1 \rightarrow \infty$. The energy spectrum corresponding to the Coulomb potential contains an infinite number of discrete levels—this is due to the fact that the magnitude of the Coulomb potential falls off slowly at large r . Also levels are degenerate with respect to l and m (orbital angular momentum quantum number and magnetic quantum number respectively); the total degeneracy is n^2 . Degeneracy with respect to m is present for any central potential. On the other hand, the l degeneracy is a characteristic of a pure Coulomb potential. This degeneracy is removed when the potential—though central—is no longer pure Coulomb.

The nonrelativistic Schrödinger equation does not include the spin of the electron. The spin effects are obvious when relativistic corrections are made. This is done by solving the Dirac equation. For small relativistic corrections it is convenient to use perturbation theory. The unperturbed

wave functions are modified (two-component) Schrödinger wave functions. Since the Hamiltonian considered above (unperturbed Hamiltonian in this case) does not act on the spin variable, the two-component wave functions are separable in space and spin variables. Each Schrödinger energy level E_n is now $2n^2$ degenerate. The spin degeneracy is removed by the spin-orbit term (L.S) in the total Hamiltonian.

4.3 Two electron atom

A two electron atom presents a three body problem in which not only the two electrons interact with the nucleus, but they also experience a mutual repulsive force. In the case of the hydrogen atom, the electron spin only affects the fine and hyperfine structures. On the contrary, for two electron atoms spin effects directly influence the spectrum, because of the Pauli's exclusion principle. The spatial part of the two-electron wave function can be space-symmetric (i.e. its spatial part does not change sign on interchanging the spatial coordinates of the two electrons) or space-antisymmetric. Also, the spin wave function can be symmetric or antisymmetric. The total wave function now consists of spatial and spin eigenfunctions. To satisfy the antisymmetry requirement for the total wave function (condition imposed by the Pauli principle) either the spatial or the spin wavefunction in the combination has to be antisymmetric—this gives rise to singlet and triplet states.

4.3.1 Independent particle model

This model in its very crude form does not take into account the mutual interaction of two electrons, i.e. the screening of nuclear charge due to the other electron is completely ignored. Thus, each electron experiences a pure coulomb potential, and the 1 degeneracy remains intact. Since the total wave function is the product of the two independent electron wave functions—or rather a linear combination under coordinate exchange of the two electrons—singlet and triplets are also degenerate in energy. This degeneracy of the singlet (para) and triplet (ortho) states is removed if the $\frac{1}{r_{12}}$ term—representing the mutual interaction of two electrons—is considered.

4.3.2 Central field approximation

The rough independent-particle model is refined by the central field approximation. In this method—while remaining within the convenient framework of the independent particle model—the Hamiltonian is split as

$$H = H_0 + H_1 \tag{4.6}$$

such that H_1 is now a small perturbation. The expression for H_0 and H_1 is

$$H_0 = -\frac{1}{2}\nabla_{r_1}^2 + V(r_1) - \frac{1}{2}\nabla_{r_2}^2 + V(r_2) \tag{4.7}$$

$$H_1 = \frac{1}{r_{12}} - \frac{Z}{r_1} - V(r_1) - \frac{Z}{r_2} - V(r_2), \quad (4.8)$$

where $V(r)$ is the central potential. The net effect of each electron on the motion of the other one is to screen a portion of nuclear charge.

$$V(r) = \frac{Z - S(r)}{r} \quad (4.9)$$

$S(r)$ is the screening constant which varies with r . $S(r)$ has a value between 0 & 1 for $r \rightarrow 0$ and $r \rightarrow \infty$ respectively. At short distances ($r \rightarrow 0$) the electron feels the full Coulomb potential $-\frac{Z}{r}$ due to the nucleus. At large distances ($r \rightarrow \infty$) the electron experiences a potential mainly due to the Coulomb field $-\frac{Z-1}{r}$. Since S is a function of r , the potential is no longer a Coulomb potential, and l degeneracy—which is a characteristic of Coulomb potential—is removed. If the perturbation term in the total Hamiltonian is still ignored, then the para (spin singlet) and ortho (spin triplet) levels will remain degenerate. The energy eigenvalue is now a function of both n and l . For a fixed value of n , the algebraic value of E_{nl} is an increasing function of l . Indeed, for small l , the electron has more chance to penetrate the centrifugal barrier (see Eq 4.4) and hence to feel fully unscreened Coulomb attraction of the nucleus. Thus according to the central field approximation, each electron moves independently of the other one in a net central potential $V(r)$ which represents the attraction of the nucleus plus some average repulsive potential due to other electrons. This basic idea was first expressed by Hartree in 1928. As discussed earlier, introduction of the perturbation term in the Hamiltonian removes the exchange degeneracy (due to the presence of the $-\frac{1}{r_{12}}$ term). The $(-\frac{1}{r_{12}})$ term is not very effective in the case of ortho states

as the two electrons stay at larger distance from each other. However, it does contribute much in the case of para states, in which the two electrons come close to each other at certain times and thus experience strong repulsion. Thus the para levels are raised and the degeneracy is removed. Introduction of the central potential leads to variational methods to find an appropriate value for $V(r)$.

4.4 Many electron atom

It has been noticed that the Schrödinger wave equation cannot be solved exactly for the two electron atom and variational methods are applied to reach an approximate solution. This remains true if the number of electrons in an atom is increased. However, the variational methods like the Rayleigh-Ritz type—which provide very accurate results for helium-like atoms—cannot help much when the number of atomic electrons increases. The reason is obvious; in contrast to the two electron atom where the term $\frac{1}{r_{12}}$ can be treated by perturbation theory, in the many-electron atoms this term is generally too large to be treated as a perturbation, also, the number of variables involved is increased. Thus, one has to look for some other more general methods to deal with the situation. The starting point to solve the many electron atom is the central field approximation. However, the expression for the screening constant $S(r)$ has to be slightly modified for $r \rightarrow \infty$. Thus for the many electron atom

$$V(r) = -\frac{Z}{r} \quad r \rightarrow 0$$

$$V(r) = -\frac{Z - N + 1}{r} \quad r \longrightarrow \infty \quad (4.10)$$

where N is the total number of electrons. Determination of the effective potential at intermediate distances is a much more difficult problem. At the intermediate distances the central potential $V(r)$ —which represents the attraction of the nucleus plus the average repulsion of the electrons—must depend on the details of the charge distribution of electrons.

Many models are developed to solve the many-electron atoms. Following is a brief discussion of a few of these models.

4.4.1 Hartree-Fock equation

The Hartree-Fock method or self-consistent field method is the refined version of the idea initially proposed by Hartree in 1928. This idea was based on the "independent particle model", according to which each electron moves in an effective potential which takes into account the attraction of the nucleus and the average effect of the repulsive interactions due to the other electrons. Each electron in the multielectron system is then described by its own wave function. Hartree also proposed an iterative procedure, based on the requirement of self-consistency, to solve the individual electron equations. The Hartree total wave function for the atom is not antisymmetric in electron coordinates—a requirement imposed by the Pauli exclusion principle. A modification in the original Hartree method was proposed in 1930 by Fock and independently by Slater, and achieved an antisymmetric total wave function.

In the Hartree-Fock method, the N-electron wave function is a Slater determinant, or in other words an antisymmetric product of individual electron spin-orbitals. The optimum Slater determinant is then obtained by using the variational method, in which the trial function for the N-electron atom is the Slater determinant whose individual spin-orbitals are optimized. To solve the Hartree-Fock integro-differential equations, one proceeds by iterations. The algorithm is like this: Starting from approximate individual spin-orbitals, one first calculates, by Gauss's theorem, approximate expression for the Hartree-Fock potential. The Hartree-Fock equations (N-one electron Schrödinger equations) are then solved with this potential to obtain new spin-orbitals, which in turn yield a new potential. If the new potential is identical to the previous value i.e. if it converges, then the iteration is terminated, otherwise it continues until convergence is attained. The Hartree-Fock potential obtained in this way is known as the self-consistent field of the atom.

The Hartree-Fock approach is a variational method, in which the trial function for the N-electron atom is a Slater determinant, whose individual spin-orbitals are optimized. Thus the energy of a given state $E_{H.F.}$ and the corresponding Hartree-Fock wave function are only approximations to the exact energy E_{exact} and the exact wave function. The difference

$$E_{corr} = E_{exact} - E_{H.F.} \quad (4.11)$$

is known as the correlation energy. E_{exact} is the exact energy of the non-relativistic Hamiltonian. Although a certain amount of correlation is already included in the Hartree-Fock function because of the fact that it is totally

antisymmetric, one has to consider *correlation effects*—the effects not included in the Hartree-Fock wave function, and which are responsible for the correlation energy. Correlation effects can be studied by using *perturbation theory*, starting with the Hartree-Fock energies and wave functions as the 'Zero-order' approximations. Alternatively, correlation effects can be studied by an approach known as the *configuration-interaction method*. This approach uses a trial function which is a linear combination of Slater determinants,

$$\phi = \sum_i c_i \phi_i \quad (4.12)$$

where the coefficients c_i are variational parameters. The various Slater determinants ϕ_i differ in the choice of the spin-orbitals occupied by the electrons, and correspond therefore to different electronic configurations.

4.4.2 Many-body perturbation theory (MBPT)

As stated previously, the Hartree-Fock (H.F.) approach does not take into account correlation effects. Errors in the H.F. wave function arise due to smearing out or averaging of electronic wave functions in H.F. equation. As a result the repulsion between electrons is not accounted for properly. Another approach—diagrammatic many-body perturbation theory (MBPT)—was presented in 1953 by Bruckener. This theory was initially proposed to solve the many-body problem in nuclear physics. The principal formal difficulty, divergences in the structure of the perturbation expansion in higher order terms for large number of particles, was analysed by Bruckener⁴, who introduced for their elimination the "linked cluster expansion." The theory

was later developed by Goldstone in 1957⁵. Kelly⁶, in 1963 applied this theory to solve the many-body problem in atoms. In order to understand how this theory works, Goldstone's work is briefly discussed, followed by application of the theory to the atomic physics problems.

The Total Hamiltonian for the N electron atom is

$$H = \sum_i^N T_i + \sum_{i<j}^N v_{ij} \quad (4.13)$$

where T_i is the K.E. energy of the i th electron and v_{ij} is the interaction potential between i th and j th electrons. Remaining in the independent particle frame, one-body potential V is introduced, and the total Hamiltonian is divided into two parts—unperturbed H_0 , perturbation H_1 where

$$H_0 = \sum_i (T_i + V_i) \quad (4.14)$$

$$H_1 = \sum_{i<j} v_{ij} - \sum_i V_i \quad (4.15)$$

The potential V is required to be Hermitian so that the single-particle wave functions ϕ_n , which are the solutions of

$$(T + V)\phi_n = \epsilon_n \phi_n, \quad (4.16)$$

constitute an orthonormal set. The state ϕ_0 is a determinant formed from the N solutions of Eq 4.16 that are lowest in energy. It is assumed that

this state is nondegenerate. The states occupied in ϕ_0 are called unexcited states. An unoccupied unexcited state is called a hole, and an occupied excited state is called a particle. The true ground state is

$$\Psi_0 = \lim_{\alpha \rightarrow 0} \frac{U_\alpha(0)\phi_0}{\langle \phi_0 | U_\alpha(0) | \phi_0 \rangle}, \quad (4.17)$$

with

$$\Delta E = \langle \phi_0 | H_1 | \Psi_0 \rangle \quad (4.18)$$

where

$$U_\alpha(t) = \sum_{n=0}^{\infty} (-1)^n \int_{t > t_1 > t_2 \dots > t_n} H_1(t_1) \dots H_1(t_n) dt_1 \dots dt_n \quad (4.19)$$

and

$$H_1(t) = e^{iH_0 t} H_1 e^{-iH_0 t} e^{\alpha t} \quad (4.20)$$

By use of Wick theorem¹¹⁰, $U_\alpha(0)\phi_0$ becomes a sum of terms that may be represented by Feynman diagrams or graphs. A particle in an excited state is represented by a line directed upwards, and a hole in an unexcited state is represented by a line directed downwards. The direction of increasing time is upwards (See fig 4.1). The rules can be summarized as:

1. Draw all distinct diagrams with no free lines at the bottom.
2. For each diagram multiply the v and V matrix elements and appropriate e^{iEt} and $e^{\alpha t}$ factors and

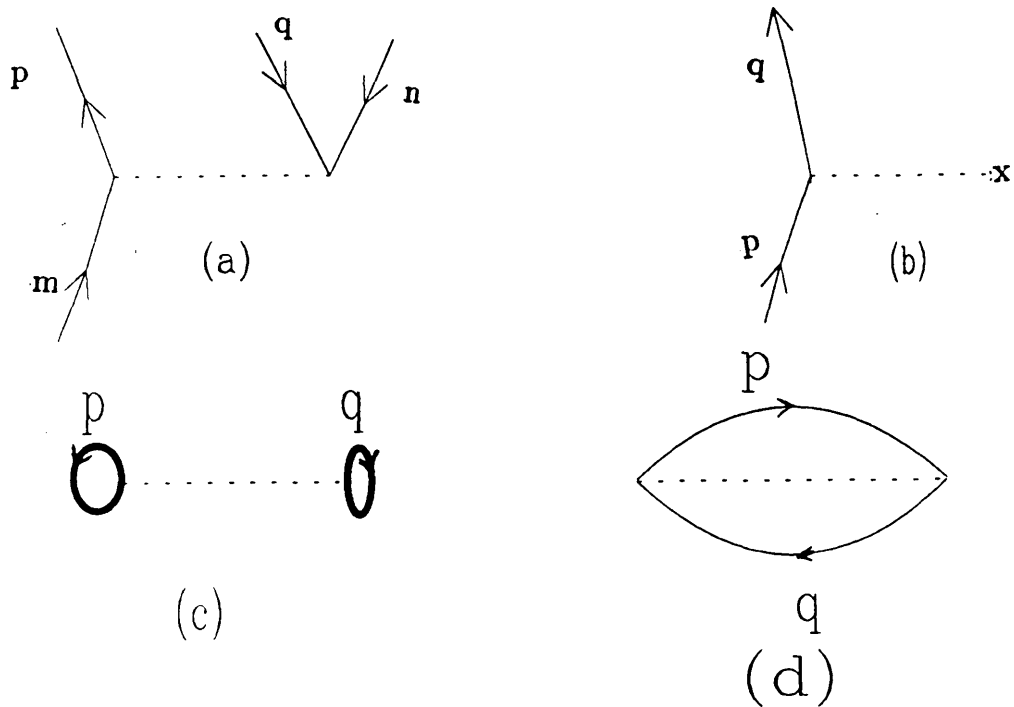


Figure 4.1: Diagrams associated with matrix elements: (a) $\langle pq | v | mn \rangle$. Particles in the excited states ϕ_m and the unexcited state ϕ_n interact through v and scatter into excited states ϕ_p and ϕ_q leaving a hole in ϕ_n . (b) $-\langle q | V | p \rangle$. A particle in an excited state ϕ_p is scattered by the potential V to the excited state ϕ_q . (c) $\langle pq | v | pq \rangle$. (d) $\langle pq | v | qp \rangle$. Diagrams (c) and (d) represent interactions of passive unexcited particles.

- include a factor $(-1)^{h+l}$, where h is the number of inter hole lines and l is the number of closed loops.
3. Note that each V has a minus sign with it.
 4. Attach a pair of creation and destruction operators corresponding to the free lines (external) of each loop.
 5. Carry out the time integration and note that the diagrams are time ordered.

Kelly's calculations are an application of the Bruckener-Goldstone diagrammatic many-body perturbation theory. He has not used very complicated methods of quantum field theory and of Green's function. The convergence of the perturbation expansion is strongly dependent on the choice of the basis set of the single particle states. Kelly pointed out that it is desirable to choose the potential in such a way that the excited states correspond essentially to the physical single-particle excitations. This approach is a departure from the choice of the H.F. potential, because the H.F. potential, though a good starting point for the ground state calculations, where it gives zero diagonal matrix elements of H_1 , is a poor choice for the excited states. In the study of the correlation energies for the 2s electrons, Kelly⁶ observed that the perturbation expansion converged slowly; this was due to large effects from certain hole-particle interactions referred to as second-type EPV (exclusion-principle-violating) diagrams. They were shown to arise from the fact that interactions of excited particles with the occupied unexcited states do not cancel the interaction with V_{HF} . Kelly suggested that the obvious modification to make in the single particle potential is to omit the self-interaction terms. This modification presents an added complication,

particularly in the loss of Hermiticity of the single-particle Hamiltonian and hence wave function orthogonality. Kelly showed that a reasonable compromise for each angular momentum (or symmetry) state was to omit in the filled-state sum the last filled state and to use this potential for all states. The potential then becomes l (or symmetry)-dependent but remains Hermitian. The wave functions of the last filled states then are still the original H.F. ones, the excited states are correctly a positive ion, but the lower filled states are now incorrect. This adds a small correction term to the energy expansion. The remaining problem of inclusion of high excited states and continuum can be approximately solved by replacing the integrals by sums, as is required in the numerical computation.

4.4.3 R-matrix theory

The development of R-matrix theory is a result of the advances made in the theoretical study of nuclear reactions during the first half of this century. To give a comprehensive background of this theory, the present review is mainly confined to the very earlier papers on this topic by Wigner and his co-workers. This is to understand basic principles of formalism of the theory which is now extensively used in atomic physics. In 1937 Bethe gave a quantitative discussion of nuclear reactions in terms of the compound nuclear mechanism, which was followed by a number of publications. These discussions were not based upon any general and rigorous theory of reactions but were constructed in an ad-hoc fashion around the assumption that reactions proceed by the compound nucleus mechanism. The first rigorous

theory of reactions was presented by Kapur and Peierls⁸ in 1938 which was not dependent upon any particular physical picture (such as compound nucleus mechanism) or upon any dubious mathematical approximation. Its essential feature is the occurrence of a complete set of formal states (of all particles) defined in a volume of nuclear size by the imposition of some fixed boundary condition on the surface of this volume. Since the paper by Kapur and Peierls in 1938, Wigner with co-workers has written papers on the same problem of providing a rigorous theory of nuclear reactions. Wigner in his work emphasized the occurrence of parameters (the interaction radii) in the theory and exploited the fact that particular choice of these parameters have physical significance and therefore, enables one to introduce physical information into the theory. This is especially true of the "R-matrix" theory, first expounded by Wigner and Eisenbud¹⁰. The main achievement of Wigner's particular formulation has been to make the energy dependence of all expressions as explicit as possible. The R-matrix theory is rigorous, and therefore its application is not confined to the reactions that proceed through compound nucleus mechanism; in principle, it can be used to describe all types of reaction phenomena. Although, the essential basis of the R-matrix theory is quite straight-forward, the full development is lengthy and involves considerable algebraic manipulation. Unless one is made familiar in advance with the essential ideas and objectives, one tends to lose track of the main arguments because of distraction by details.

The essential idea of the method is that configuration space describing the scattered particle and the target is divided into two regions. In the internal region ($r < a$ where r is the relativistic coordinate of the colliding

particles) the interaction is many-body and strong and the collision process is difficult to calculate. In the external region, on the other hand, the interaction is weak and in many cases is exactly solvable in terms of plane waves or Coulomb waves. In the internal region a complete discrete set of states describing all the particles is defined by imposing logarithmic boundary conditions on the surface of this region. This R-matrix basis can then be used to expand the collision wave function at any energy and in particular to obtain the logarithmic derivatives of this wave function on the boundary. From this information and the known solution in the external region the S-matrix and the cross-sections can be calculated. So far the theory described is exact and is completely equivalent to solving the scattering problem exactly. In applications, however, only a finite number of eigenstates can be retained in the internal region. Indeed in some applications in nuclear physics only one state is retained, giving the so-called one-level formula which has been remarkably successful in describing reactions close to an isolated resonance. Over the last few years attention has been directed to using the R-matrix method as a scheme for calculating resonant and nonresonant processes over an extended energy range.

4.4.4 Quantum defect theory

An other powerful method of dealing with the many-body problem is the quantum defect theory (QDT) and multichannel quantum defect theory (MQDT), which is the extension of the QDT to many channels. The quantum defect theory was developed for hydrogen-like spectra, typically of the

alkali vapors. Its basic concept lies in treating the motion of one particle—or even of a few particles—outside a given atomic or molecular system separately from its motion at short radial distances within that system. Relevant properties of the separate motions are so parameterised as to facilitate the formulation of the analytical quantisation rules—which determine energy levels—of transition probabilities, angular distributions of photoelectrons, etc. This approach places hardly any restriction on the potential acting in the outer region. An early application to an electron escaping from a negative ion into a zero field dates from 1970, but explicit development of the theory with wide flexibility is rather recent. The quantum defect theory originates from the empirical representation of the energy levels of regular Rydberg series.

$$E_n = -\frac{I_H}{(n - \mu)^2} \quad (4.21)$$

where $I_H = 13.6\text{eV}$ is the ionisation potential of H atom; n is the running integer; and μ is called the quantum defect. This formula was understood from the outset as a variant of the H atom formula, where μ vanishes. Its structure reflects the circumstances that an excited electron moves primarily in the hydrogenic Coulomb field outside an ionic core. The insertion of the quantum defect represents the effect of the additional field strength that prevails within the core. With the help of quantum mechanics it was realized that the extra field within the ionic core modifies the radial wave function in the external region simply by shifting its nodes; μ represents this shift expressed in half-wavelengths (Figure 4.2). The formal development of these wave-mechanical concepts by Ham³⁴ and Seaton³⁵ followed only in 1950's. Its point of departure lies in the asymptotic expansion of the radial wave function $f(\epsilon, r)$ regular at $r = 0$, normalized per unit energy, for an electron

in the field of a H^+ ion. $\epsilon = E/2I_H$ is the electron energy in a.u. For $\epsilon < 0$ this function consists, at large r , of one exponentially decaying term and one rising term

$$f(\epsilon, r) \longrightarrow_{r \rightarrow \infty} e^{-r/\nu} r^\nu D \cos \pi\nu - e^{r/\nu} r^{-\nu} D^{-1} \sin \pi\nu \quad (4.22)$$

where $\nu = (-2/\epsilon)^{1/2}$. An acceptable bound-state wave function must reduce to its decaying term only. Thus

$$\sin \pi\nu = 0 \quad (4.23)$$

That is, ν is an integer, n , and the energy levels are

$$\epsilon_n = -1/2n^2 \quad (4.24)$$

Now consider an excited electron in the Coulomb field around a nonhydrogenic ion, the ground-state electrons are confined approximately within a radius $r < r_0$. At $r > r_0$ the wavefunction of the excited electron with energy ϵ is a solution $F(\epsilon, r)$ of the Coulomb field equation. This solution must also be regular at $r = 0$, but nevertheless does not coincide with $f(\epsilon, r)$ because, at $r < r_0$, it obeys a different equation that takes into account the excited electron's full interaction within the ion's structure. *ab initio* calculations of $F(\epsilon, r)$ must solve this equation, but the key point is that the process of solving at $r < r_0$ influences the solution outside the core only by determining the phase of $F(\epsilon, r)$ at the ion's boundary $r = r_0$, e.g., its logarithmic slope $[d \ln F(\epsilon, r)/dr]_{r=r_0}$. Semi-empirical procedures determine this boundary phase alternatively by fitting experimental data, thus bypassing the solution at $r < r_0$ for immediate purposes. Thus, $F(\epsilon, r)$ can be represented as superposition of $f(\epsilon, r)$ and of a second independent solution

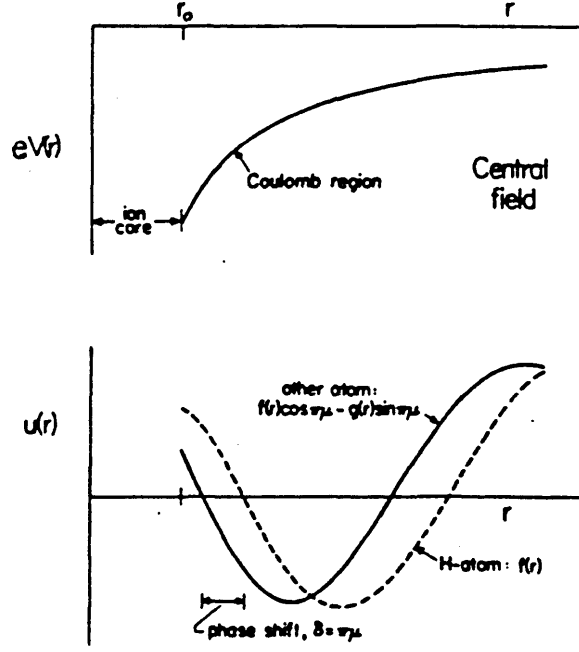


Figure 4.2: variation of phase shift with respect to the coefficients

$g(\epsilon, r)$, irregular at $r = 0$, which is taken to lag in phase by 90° with respect to $f(\epsilon, r)$ and to be normalized per unit energy. The coefficients of the superposition are chosen to match the boundary condition at $r = r_0$.

$$F(\epsilon, r) = f(\epsilon, r) \cos \pi\mu - g(\epsilon, r) \sin \pi\mu \quad (4.25)$$

Fig. 4.2 shows how the phase difference of $F(\epsilon, r)$ and $f(\epsilon, r)$ at $r = r_0$ is incorporated in the coefficients of Eq 4.25 through the parameter μ . Thus

$$F(\epsilon, r)_{r \rightarrow \infty} \longrightarrow e^{-r/\nu} r^\nu D \cos \pi(\nu + \mu) - e^{r/\nu} r^{-\nu} D^{-1} \sin \pi(\nu + \mu) \quad (4.26)$$

The quantisation condition is then

$$\sin \pi(\nu + \mu) = 0. \quad (4.27)$$

That is, $\nu + \mu$ is now an integer, n , and

$$\epsilon_n = -1/2(n - \mu)^2, \quad (4.28)$$

which establishes the theoretical basis of the empirical Eq 4.21. This derivation provides a somewhat more specific interpretation of the quantum defect μ , expressed in radians as $\pi\mu$: it represents the accumulation of the phase difference of $F(\epsilon, r)$ and of the hydrogenic $f(\epsilon, r)$, over the range $0 \leq r \leq r_0$. The original Rydberg formula Eq 4.21 owes its simplicity to the analytic properties of the hydrogenic field. Nevertheless the separation of the integral number of half-waves of the radial function $F(\epsilon, r)$ into contributions ν and μ of outer and inner ranges of r does not hinge on the analytic form of the outer field. Separation of the two contributions is appropriate, because they are controlled by different circumstances. The outer contribution depends on a well defined potential field, but may diverge at threshold and is anyhow often a sensitive function of ϵ . The inner contribution hinges generally on multiparticle interactions but is restricted to a finite volume of space, within which the wave function of the entire atom can be expanded in a discrete set. This wave function can in fact be calculated *ab initio* for any given energy ϵ by treating the boundary parameter of the excited electron, $[d \ln F(\epsilon, r)/dr]_{r=r_0}$, as a variational eigenvalue. The main task thus involved for the outer fields is to determine the energy dependence of the radial phase accumulation at $r > r_0$. Greene *et al* ³⁶ have treated outer fields $1/r^p$, with $p = 0, 1, 2$, stressing that the phase accumulation diverges at $\epsilon = 0$ only for $p \leq 2$. Greene *et al.* designate the phase accumulation of the radial function over the entire range $0 \leq r < \infty$ by $\beta_l(\epsilon)$ rather than $\pi\nu$, for $\epsilon < 0$, irrespective of the potential field $V(r)$ prevailing in the outer region, and regarding this field as extrapolated into the core region $r < r_0$. The index l indicates here the usual orbital quantum number. The radial-quantization condition analogous to Eq4.27 requires the value of $\beta_l(\epsilon)$, expressed in radian for a

level $\epsilon = \epsilon_n$, to satisfy

$$\beta_l(\epsilon_n) = \pi(n - \mu), \quad (4.29)$$

Where $\pi\mu$ indicates the excess phase accumulated in the core.

MQDT

A channel of excitation of an atom (or molecule) is specified by internal states and angular momenta of an ion core and an electron (or of any fragments) and by orbital momentum of their joint motion about the center of mass. The fragment can generally pass from one channel to another exchanging energy and/or angular momentum. Probability amplitudes for transitions between channels have been expressed by Seaton in terms of a reaction matrix of the core fragment R_{ij} in the representation of the radial functions (f_i, g_i) of the long range field of each channel. For a single channel R_{ij} reduces to a single element $\tan \pi\mu$, where μ indicates a quantum defect. The single-channel quantisation condition for the bound states of an hydrogen atom, $\epsilon_n = -\frac{1}{2}n^2$ a.u. has been modified by Seaton in terms of R_{ij} as follows. At energies insufficient for an electron to escape from an atom in any channel, i.e. , $\epsilon_i = -\frac{1}{2}\nu_i^2 < 0$, the energy parameter ν_i obeys the determinant equation

$$| \delta_{ij} \tan \pi\nu_i + R_{ij} | = 0 \quad (4.30)$$

For a single channel this equation reduces to

$$\tan \pi\nu + \tan \pi\mu = 0 \quad (4.31)$$

or equivalently to $\sin \pi(\nu + \mu) = 0$ which amounts to $\nu = n - \mu$ and hence to $\epsilon_n = -\frac{1}{2}(n - \mu)^2$. Fragmentation in the non-Coulomb field is treated

by replacing $\pi\nu_i$ with $\beta(\epsilon_i)$ and Coulomb wave functions with appropriate pairs (f_i, g_i) . The connection of Eq 4.30 to its single channel prototype Eq 4.31 extends to multichannel systems by an orthogonal transformation that diagonalizes R_{ij} :

$$\sum_{ij} \hat{U}_{\alpha i} R_{ij} U_{j\beta} = \delta_{\alpha\beta} \tan \pi\mu_{\alpha} \quad (4.32)$$

Each quantum defect μ_{α} represents the effect of short range forces in an eigenchannel of the fragments' interaction. An eigenchannel is the superposition of i-channel wave functions with coefficients $U_{i\alpha}$ insensitive to the short range forces. In the case of rare gases where the eigenchannels are represented approximately by LS-coupled wavefunctions, the $U_{i\alpha}$ are then the elements of the transformation from LS to jj coupling. Thus for a multichannel system, a general solution is

$$F = \sum_i \phi_i (f_i \sum_{\alpha} U_{i\alpha} \cos(\pi\mu_{\alpha}) N_{\alpha} - g_i \sum_{\alpha} U_{i\alpha} \sin(\pi\mu_{\alpha}) N_{\alpha}) \quad (4.33)$$

where ϕ_i are the wave functions of the ionic core. The matrix U satisfies the relation derived from the boundary condition on the bound states that $F \longrightarrow 0$ as $r \longrightarrow 0$

$$\det | U_{i\alpha} \sin \pi(\nu_i + \mu_{\alpha}) | = 0 \quad (4.34)$$

For the region $r \leq r_0$, again it is only possible to find the numerical solutions which are joined smoothly to F.

4.4.5 Semi-empirical approach

The theory can be used in a semi-empirical parameterised form in which the values of certain theoretical parameters are determined by least-square fitting of empirically determined energy levels. This is the time-honored method in which the quantitative theory has been mainly employed since the nineteen thirties. This procedure can of course be utilized only after a number of levels have been found by empirical spectrum analysis, but it is then very useful for identifying the nature of the corresponding quantum states and for predicting approximate energies of unknown levels. These predictions may then make it possible to find missing levels by means of more detailed wavenumber searches.

In a one-channel problem, because μ is just the spectroscopic quantum defect appearing in the Rydberg formula, it can be obtained by fitting the discrete energy level data. The usefulness of finding μ relies on the fact that μ is a very slowly varying function of energy and can often be taken as a constant over the range of interest in spectroscopy.

A multi-channel problem is conveniently dealt with by the eigenchannel method. For each channel i corresponding to a series limit I_i , ν_i satisfies the Rydberg formula

$$E = I_i - \frac{1}{\nu_i^2} \quad (4.35)$$

where E is an energy level found experimentally. The task is then to solve eqs (4.34) and (4.35) simultaneously with the application of appropriate

boundary conditions. Having found μ_α and the matrix U the wave functions (4.33) can be obtained and then various atomic properties can be calculated.

4.4.6 *ab initio* calculations

The theory can also be used in a completely *ab initio* fashion by computing theoretical values for the parameters mentioned in the previous section. The accuracy of the computed results is limited, especially for very complex neutral atoms, but the predicted energy level structures can still provide a very helpful guide for getting started to an empirical spectrum analysis. Particularly, for not too complex spectra of multiply ionised atoms, *ab initio* calculations may be adequate in accuracy to clarify dubious points of an analysis or even to identify the transitions producing spectrum lines when empirical information alone is quite inadequate. In the *ab initio* form of the theory (and to a certain extent in the semi-empirical form also), one obtains not only level energies but also the wave functions of the corresponding quantum states. From these wave functions one can (at least in principle) compute any desired properties of the atom—of which most important are the strengths of the spectral lines.

Chapter 5

The Case of Calcium

5.1 Introduction

This chapter presents a review of the work done so far, both experimentally and theoretically, on the calcium spectrum in the range 1586 Å to 1789 Å corresponding to the region between 4s and 3d thresholds. This range is dominated by the doubly excited autoionising series converging to the 3d threshold. It contains 3dnp ($^1,^3P_1, ^3D_1$) series and 3dnf ($^1,^3P_1, ^3D_1$) series and a perturber level 4p5s. This spectrum was originally studied by Kaiser⁸³ in 1960, though in literature⁶² it is credited to Garton and Codling. In fact, after Kaiser this series was investigated by Ditchburn and Hudson¹⁹ in 1960. Garton and Codling⁸² published their work in 1965. It was subsequently followed by Newsom¹⁸ in 1966, Brown *et al*¹⁶, Karamatskos *et al*⁸³, and finally by Griesmann *et al*⁶² in 1988. The first three of these and Brown

et al used a photographic detection technique. A photoionisation technique was employed in the work of Newsom and Karamatskos *et al* and the last experiment (Griesman 1988) was done with the *hot-wire* detector. However, it was Garton and Codling who, with their high resolution 3 m vacuum spectrograph, classified the levels into six different series. Thus, there is a large distribution of experiments in this energy range. This chapter describes each one of these in detail and it also points out reasons which made other experiments necessary and finally led to the present investigation of this spectrum.

Theoretical activity on this spectrum has also been intense. From the present standpoint, interest attaches to the 3dnp series because of the 'q-reversal' effect (see chapter 3) and the related 'vanishing width' phenomenon. There has been some dispute over the origin of the q variation in the 3dnp series and of the narrow width of the 3d6p 1P_1 resonance. According to the many-body calculations of Altun *et al* ¹⁴, this would be due to interchannel interference. However, Scott *et al* ²⁰, in an ab-initio R-matrix calculation proposed that the q variations and line narrowing could be due to the presence of a Seaton-Cooper minimum in the continuum, which can also lead to phase cancellation in the matrix elements responsible for autoionisation. In recent calculations Greene and Kim^{32a}, using the R-matrix theory with a semi-empirical potential, showed that the vanishing of the width within the 3dnp series is due to perturbation by an intruder level (4p5s). This chapter examines each one of these works in detail and compares them with the previous experimental investigations. Their predictions are compared with the present experimental findings in chapter 13.

5.2 Previous Experimental Investigations

As stated earlier in the introduction, the 3dnp series in calcium was discovered by Kaiser⁸³; although the series was mentioned in the Moore table (1949) and the process of autoionisation in calcium was described by White¹⁹³¹, it was the first experimental work on this series. Kaiser, in fact, was trying to study the 4snp series, by absorption measurement in the vacuum ultraviolet (2000 Å to 1500 Å), previously investigated by Justum⁸⁴. He also recorded a number of intense autoionising lines. Kaiser divided them into two categories—broad series and narrow series—according to their widths: broad series corresponding to the 3dnp 1P_1 levels, converging on the 3d $^2D_{5/2}$ level of the excited ion, and narrow series corresponding to the 3dnp 3P_1 levels and converging on the 3d $^2D_{3/2}$ level of the excited ion. He identified them with the help of the Moore tables (1949). However, he was unable to observe any of the 3dnp 3D_1 levels, which are highly forbidden in the L.S. coupling. Kaiser discovered seventeen new lines altogether. His experiments were done with a fluorite spectrograph at the university of Reading.

This experiment was followed by another one by Ditchburn and Hudson¹⁹ on essentially the same experimental setup. Ditchburn and Hudson extended the observation of 3dnp levels to $n = 16$, they measured the oscillator strength of most of these two-electron transition lines and also recognised an interloper level from another configuration (4p4d 1P_1 level of 4pnd configuration at 57465 cm^{-1}). Fig 5.1 shows the spectrum recorded by Ditchburn and Hudson.

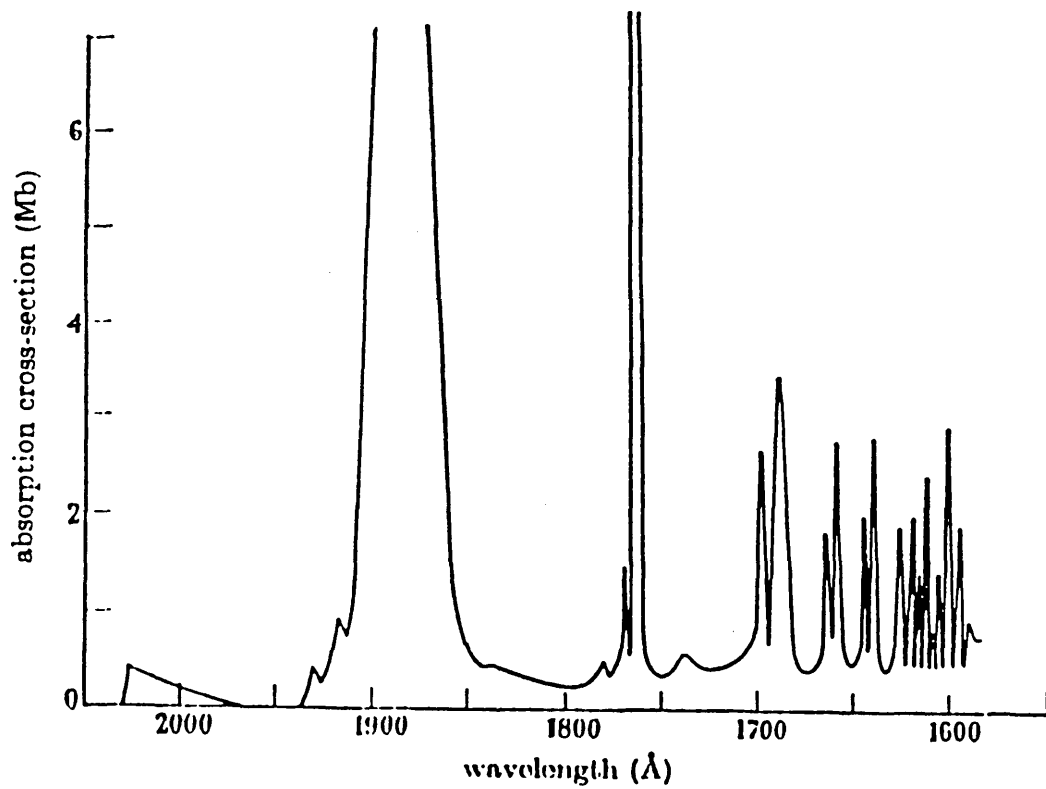


Figure 5.1: The atomic absorption cross-section against wavelength. The peak absorption of the first two lines ($3d5p$ & $3d6p \ ^1P_1$) is 30 and 70 Mb respectively

In 1965 Garton and Codling⁸² published their observations of the doubly excited 3dnp series in Ca I. They extended the number of observed lines to $n = 29$, and altogether, obtained 82 absorption lines above the $^2S_{1/2}$ limit. They classified them into six series ($4\ ^1S_0 \longrightarrow 3\text{dnp}, \text{nf } ^1,^3P_1, ^3D_1$).

Their experimental setup consisted of a King furnace for producing calcium vapors, a coaxial flash tube and a 3m concave grating (normal incidence) vacuum spectrograph. Exposures were made on Ilford Q-2 and Kodak SWR plates at a number of furnace temperatures up to 1000 °C. The plates were reduced by a Zeiss Abbe comparator and wavelengths of all sharp lines were measured to an estimated accuracy of 0.004 Å.

The spectrum recorded by Garton and Codling could be traced, fairly by inspection, up to $n = 13$, and thereafter it was not so obvious as the lines crowded together and higher resolution was required, so they identified them on the basis of the run of the quantum defect. They were, however, able to observe the Fano profiles (see chapter 3) on the low energy side of the spectrum with window in cross-sections on the short wavelength side. Although they observed a gross perturbation of 3dnp 1P_1 series between $n = 5$ and 7, as discussed by Ditchburn and Hudson¹⁹, they disagreed about the identity of the perturber. Ditchburn and Hudson had identified it as the 4p4d 1P_1 level, but according to Garton and Codling it was the 4p5s level. Another observation made in this paper was about the relative line strength of singlet and triplet P levels. They observed that in the low members of the series the singlet combinations are much stronger than the triplet, but the line strength ratio diminishes with increasing n , until at $n = 15$ the lines

of the two series are of about equal strength, after which the $16\ ^3P_1$ is strong and $16\ ^1P_1$ anomalously weak. They also observed that at this point $17\ ^3P_1$ level is nearly coincident with the $16\ ^1P_1$. The $n = 17$ members of both series are again of about equal strength and fairly strong, and thereafter $18\ ^3P_1$ becomes extremely weak ; similar switching of intensities was also observed near the high energy end of the spectrum. Garton and Codling describe this behavior in these words, '... as we proceed to high n , the $(n + 1)^3P_1$ line approaches the position of the $n\ ^1P_1$ from the short wavelength side and during this progress the $(n + 1)^3P_1$ combination gains in strength, at the expense of the $n\ ^1P_1$, and that the effect becomes extreme when the two levels are close together. At the next stage $(n + 1)^3P_1$ has passed below $n\ ^1P_1$ and the intensities switch back again. A similar sequence of changes occurs when $(n + 2)^3P_1$ approaches and crosses $n\ ^1P_1$...'

In their experiment, Garton and Codling, however, could not observe the $4s^2\ ^1S_0 \longrightarrow 3d5p\ ^3P_1$ transition, which was marked by Ditchburn *et al* at 1914.8 Å, and also some levels in the principal series, already detected by Ditchburn, were missing. So Newsom¹⁸ set up an experiment to discover transitions to the new energy levels in this doubly excited series in Ca I. His apparatus consisted of a Burrell furnace, a hydrogen positive-column discharge operated at approximately 400 mA, which provided the background continuum, and a McPherson scanning monochromator of the automatic focus normal-incidence type, with a gold-coated grating of 30,000 lines/inch. A photomultiplier tube recorded the spectral intensity, which was measured by Keithley 600 A electrometer and displayed on a speedomax chart recorder.

Newsom identified the $3d5p\ ^3P_1$ level at $1926.5\ \text{\AA}$, about $11.7\ \text{\AA}$ to the red of the position of Ditchburn and Hudson¹⁹. A comparison of the Newsom results (Fig 5.2) with a similar spectrum from Ditchburn and Hudson experiment (Fig 5.1) reveals major differences. The Ditchburn and Hudson curve gives a cross-section of greater than or equal to $0.3\ \text{Mb}$ for all wavelengths except the 'window' between the $1885.9\ \text{\AA}$ line and the series limit, while Fig 5.2 decreases to $0.18\ \text{Mb}$ at $1785\ \text{\AA}$ and $0.05\ \text{Mb}$ at $1706\ \text{\AA}$. Ditchburn and Hudson measured the absolute cross-section for transitions to the $3d5p\ ^1P_1$ and $3d6p\ ^1P_1$ levels as 30 and $70\ \text{Mb}$ respectively, while the photoelectric measurements gave 14 and $21\ \text{Mb}$. This great discrepancy cannot be blamed on the somewhat poor resolution from the fluorite spectrograph (used in the Ditchburn and Hudson experiment) as compared to the better resolution from the scanning monochromator (used in the Newsom experiment), because if it was limited by resolution then the cross-section value should be smaller for the Ditchburn and Hudson experiment, but this is not the case.

The use of photoelectric detection yields a large dynamic range and avoids errors which arise in calibration through the use of characteristic curves, thus one expects more accurate results from the photoelectric measurements. The Newsom experiment, however, suffered through a serious variation ($35\ \%$) in brightness during the experiment, for which he applied a somewhat arbitrary, time-dependent correction. This variation raises serious doubts about the accuracy of the Newsom's measurement of absolute cross-section.

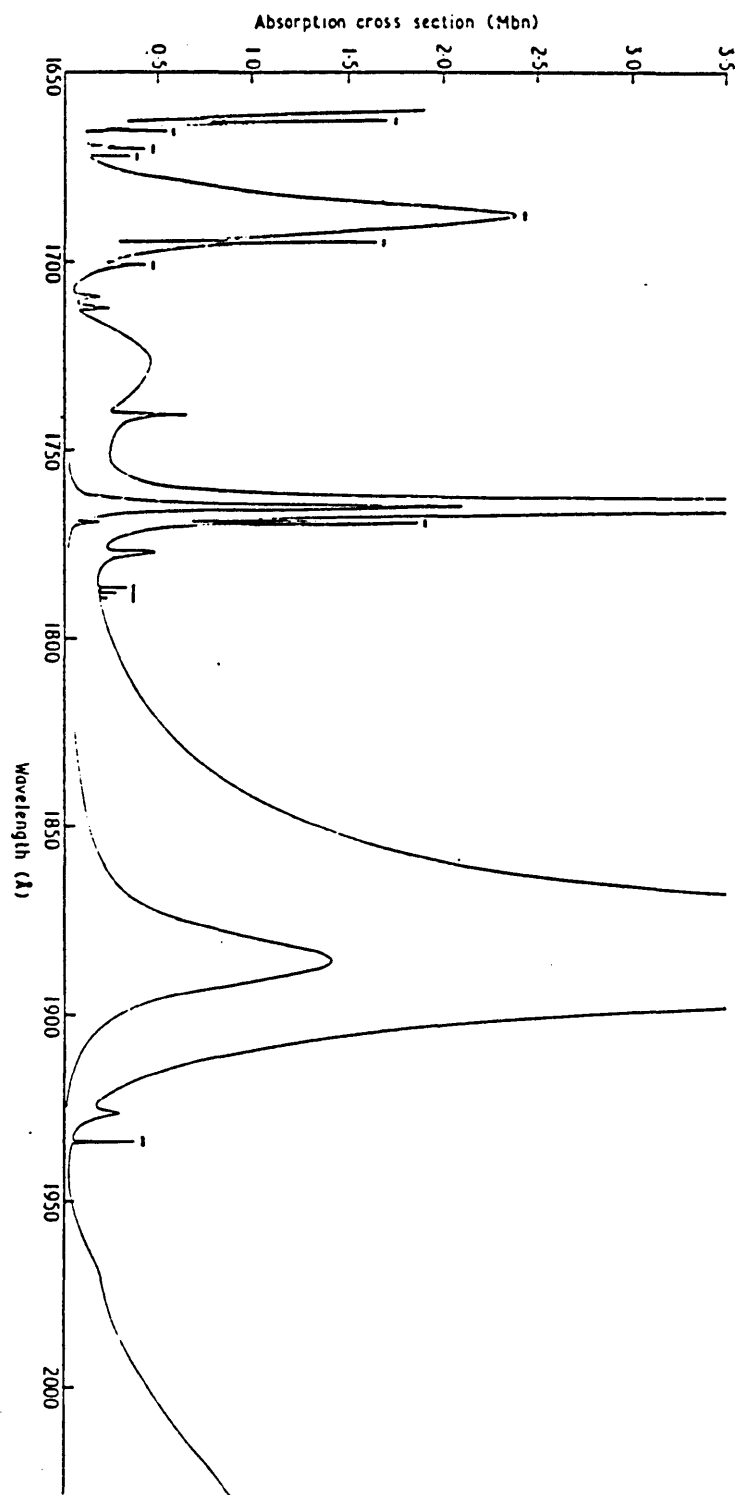


Figure 5.2: Photoelectric measurement of the absorption cross-section as a function of wavelength. (Newsom experiment)

This work was followed by the experiment by Carter *et al* in 1971¹⁷. Their apparatus consisted essentially of a 2.2-m normal-incidence monochromator using a 1200 lines/mm grating, behind the exit slit of which was a temperature-regulated furnace serving as an absorption chamber. The entrance and exit slits were set at 20 μm , giving an instrumental bandwidth of 0.075 Å; a molecular-hydrogen discharge lamp was used as the light source. Their results are shown in Fig 5.4. They conform the relative measurements of Newsom.

Brown *et al* ¹⁶ in 1973 published their observations on this spectrum. With their long absorption path, high resolution, and a continuum source with few impurity lines they were able to observe over 230 doubly excited levels in the wavelength range 1586-1769 Å. They had used a King furnace to produce calcium vapors, and experiments were performed using flowing argon with pressure in the range $\sim 0.1 - 0.5$ torr. The absorption spectrum was photographed on Kodak SWR plates in the third-order of a 6.6 m spectrograph (third-order reciprocal dispersion ≈ 0.31 Å/mm). A microwave-excited xenon lamp provided the background continuum. The uncertainty of absolute wavelength is reported to be within ± 0.005 Å.

Brown *et al* , like Garton and Codling⁸², also observed asymmetric profiles, but they also observed emission-like feature on the short wavelength side of most of these asymmetric profiles, with a few having this 'emission-like' feature on the longer wavelength side. According to their observation this 'emission-like' feature (a decrease in the absorption coefficient towards the continuum) occurs on the side of a line nearest a $3dnp\ ^1P_1$ absorption.

They thought it might be explained in terms of a general problem of several discrete states interacting with several continua. Thus a $3\text{dnp } ^3\text{P}_1$ level may interact not only with the continua but also with the nearby $3\text{dnp } ^1\text{P}_1$ level. The irregularities in the 3dnp series between $n=6$ and $n=7$, Brown *et al* assumed, were due to the $4\text{p}5\text{s } ^1, ^3\text{P}_1$. They observed that at higher n the two series bearing designations $3\text{dnp } ^3\text{P}_1$, and $3\text{dnf } ^3\text{P}_1$ exchange series limits, which results in two series from the 3dnp configurations converging on $^2\text{D}_{5/2}$ and the third one on $^2\text{D}_{3/2}$, whereas two series from 3dnf converge on $^2\text{D}_{3/2}$ and one to $^2\text{D}_{5/2}$. Brown *et al* argue that '... simple addition of angular momenta of an np or nf electron to that of the ^2D ionic core leads us to predict that the two of the three $J=1$ series arising from the 3dnp configurations converge to $^2\text{D}_{3/2}$ and one to $^2\text{D}_{5/2}$, whereas the 3dnf configuration should have two $J=1$ series converging to $^2\text{D}_{5/2}$ and one to $^2\text{D}_{3/2}$. This phenomena has the appearance of an avoided crossing, the $3\text{dnf } ^3\text{P}_1$ series being unable to reach $^2\text{D}_{5/2}$ limit without crossing the $3\text{dnp } ^3\text{P}_1$. An alternate interpretation is that the two series cross and continue to their predicted limits, with slight perturbation of the levels in the vicinity of the crossing ...'. Brown *et al* also observed irregularities in the assigned series near the series limit, which they suggested might be due to a perturber level found at $1598.5 \text{ \AA}$. They identified it as the doubly excited $4\text{p}4\text{d}$ level.

Brown *et al*, in fact, presented a very valuable high resolution spectrum in this energy range in calcium, and have identified levels to the end of the series. Their identification of the levels is taken as a reference in the present work—as no other photographic work is so rich in terms of number of levels. However, this work is neither suitable enough for the measurement of

the absolute cross-sections of transitions, nor does it help in studying interacting resonances. This is due to the nonlinear nature of the photographic detection scheme involved. However, any future work with a combination of a linear detector and a narrow band width radiation source will find their identification very helpful for analysis, and it is, indeed, the case in the present work.

The work of Brown *et al* was soon followed by a photoionisation study by Karamatskos *et al* ²⁸. They were interested in the measurement of the q values—a measure of the symmetry of the profiles. The experimental setup comprised of an atomic beam source and synchrotron radiation source (Berlin electron storage ring (BESSY)) behind a 1 m McPherson monochromator. The spectrum was detected against photon energies. The counting rate was normalized with respect to the incident photon flux. Experimental resolution of 0.08 nm was claimed.

The spectrum produced by this experiment was unable to show any of the 3dnf transitions previously observed by Garton and Codling⁸² and Brown *et al* ¹⁶. These transitions (as argued in the Ref. 32b) have a profound effect on the line shapes, and thus, any measurement of the q values from Karamatskos *et al* experiment is bound to have serious errors. This inability is due to the poor experimental resolution they had.

In 1988, Griesmann *et al* ⁶², for the first time, configured a *hot-wire* detector with a synchrotron radiation source to study this doubly excited spectrum in calcium. The experiment was conducted at the DORIS II electron accelerator at HASYLAB, Germany. The absolute calibration of the

spectrum was achieved by using information from the previous work^{87,88,89}, based on the Hook method. The experimental resolution was claimed to be 0.75 Å. This experiment, although it presented much better results as compared to the Karamatskos *et al*²⁸ work and was able to detect some of the 3dnf transitions, was also limited by resolution, and the results are not so detailed as to compare to the recent theoretical work (see Ref 32b). This work, however, established the usefulness of the hot-wire diode detector in such experiments.

5.3 Theoretical Survey

The calcium photoabsorption spectrum up to 10 eV has proved unexpectedly difficult to describe theoretically, and hence many attempts have been made to explain this spectrum by applying different theoretical models. The first case worth mentioning is a many-body perturbation theory (MBPT) (see chapter 4) calculation performed by Altun *et al*¹⁴. The Hamiltonian of the system is divided into two parts i.e.

$$H = H_0 + H_C \quad (5.1)$$

where

$$H_0 = \sum_{i=1}^N \left[-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + V_i \right] \quad (5.2)$$

and

$$H_c = \sum_{i,j=1, i < j}^N v_{ij} - \sum_{i=1}^N V_i \quad (5.3)$$

where V_{ij} is the Coulomb interaction between electron pairs in the atom. The effect of radiation field on the atom is treated by time-dependent perturbation theory. In the diagrams of Fig 5.3 the doubly excited bound configurations corresponding to two-electron excitations are represented. Diagrams 5.3(a)—(c) have a series of simple poles from energy denominators:

$$D_n = 2\epsilon_{4s} - \epsilon_{K'} - \epsilon_{K''} + \omega \quad (5.4)$$

where K' and K'' states represent resonant doubly excited states. These poles are broadened by summing higher-order contributions geometrically to all orders as indicated in diagram 5.3(d). That is, the segment shown above the horizontal line in diag 5.3(d) may be repeated in higher orders and summed geometrically to give a ratio

$$R = -i \sum_m \left[\sum_n \frac{\frac{1}{2}\Gamma_{mn}}{D_{mn}} + \frac{2}{K} R_m(K) \right], \quad (5.5)$$

where $R_m(K)$ is the contribution to the segment of Fig 5.3(d) when one of the states K''' or K^{iv} is in the continuum and the other is the bound state m . The term $\frac{1}{2}\Gamma_{mn}/D_{mn}$ is the contribution to the segment of Fig 5.3(d) when the states K''' and K^{iv} are bound states mn , and

$$\frac{1}{2}\Gamma_{mn} = 2/K \left| \langle \Phi_{mn} | v | \Phi_{4skp} \rangle \right|^2 \quad (5.6)$$

where D_{mn} is the energy denominator for pairs of bound states mn . In their calculations Altun *et al* included bound states $3dnp$ 1P ($n=4-9$), $4pns$ 1P ($n=5-10$), and $4pnd$ 1P ($n=4-8$). Except for $3d4p$ 1P , all of these

states lie above the first ionisation threshold and appear as autoionising resonances in the photo-ionisation cross-sections. These doubly excited states were obtained from self-consistent HF calculations, and for the doubly excited states they constructed relaxed HF V^{N-1} potentials from $3p^6 3dkp\ ^1P$ and $3p^6 4pkd\ ^1P$ couplings. Relaxed HF V^{N-2} ionic potentials were used for the 3d and 4p orbitals. According to Altun *et al* , by using a combination of V^{N-2} and V^{N-1} potentials¹⁵ for K'' and k''' in the diagram of Fig 5.3(a) and for K', K'', K''' in diagrams 5.3(b) and 5.3(c), the higher-order corrections can be substantially reduced in the final state [diagram 5.3(a)] and in the ground state [diagram 5.3(b)]¹⁴. In calculating the double electron resonances, they used experimental energy positions of Brown *et al* ¹⁶ for 3dnp resonances. Fig 5.4 represents a comparison of Altun's calculated spectrum with the experimental results of Carter *et al* ¹⁷. Fig 5.5 gives the comparison of Altun's results with the experimental measurements of Newsom¹⁸ between 6.11 and 7.45 eV. The magnitude of their calculated cross-section for $3d5p\ ^1P_1$ resonance is about 27 Mb, which is in reasonable agreement with the experimental measurements of Ditchburn and Hudson¹⁹, but shows a gross disagreement with Newsom. According to Altun *et al* , the narrowing of the $3d6p\ ^1P_1$ line was caused by interaction with $4pns\ ^1P$ and $4pnd\ ^1P$ resonances. MBPT results did a good job at describing the global oscillator strength distribution, considering the fact that channel interactions are so strong. Still its agreement with experiment deteriorates rapidly as the energy increases towards the 3d threshold, and shows very little resemblance to experiment.

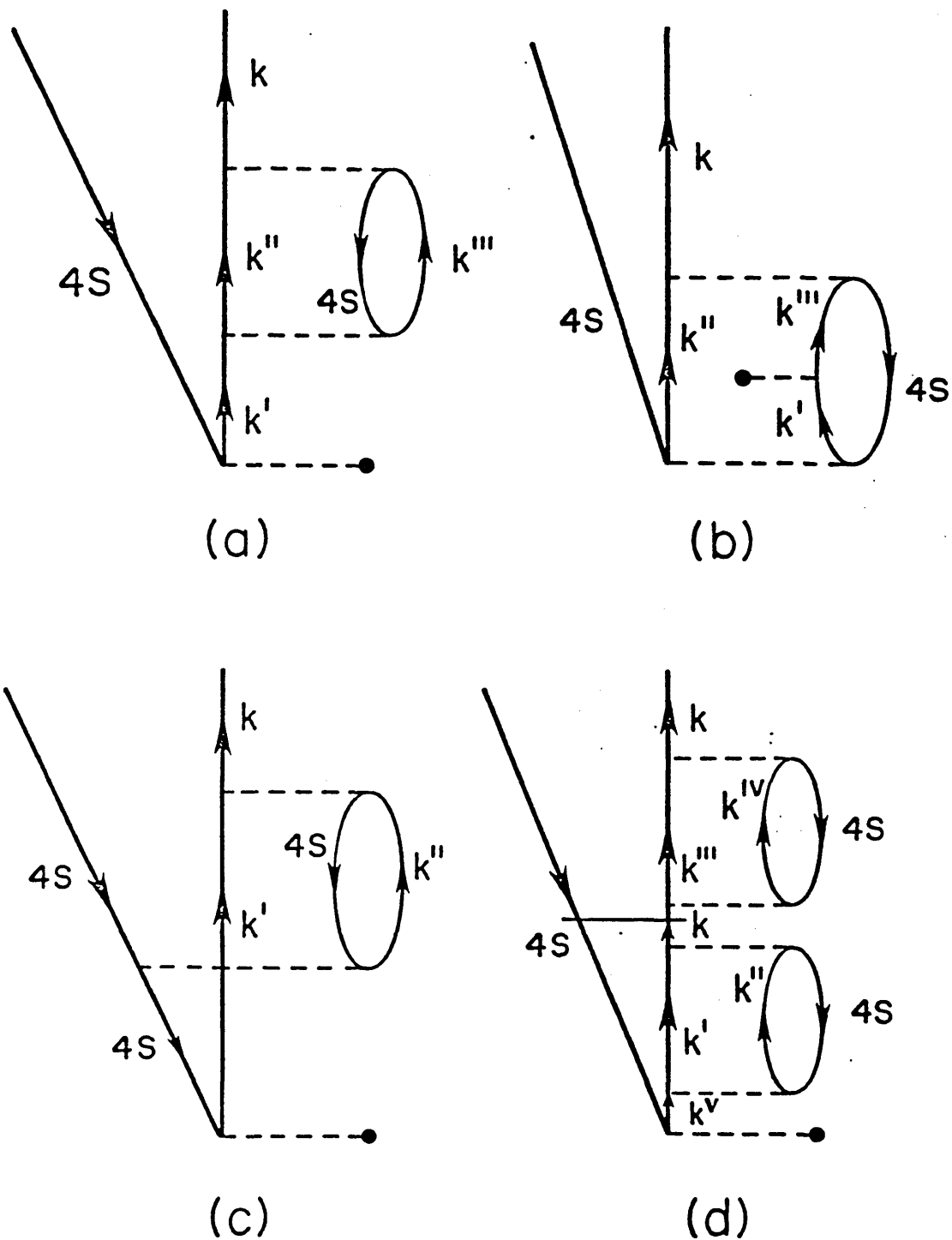


Figure 5.3: Resonance diagrams involving doubly excited states of 4s electrons. Solid dot indicates matrix elements of z . Other dashed lines represent Coulomb interaction. A horizontal line in diagram (d) indicates that the denominator is treated according to $-i\pi\delta(D)$.

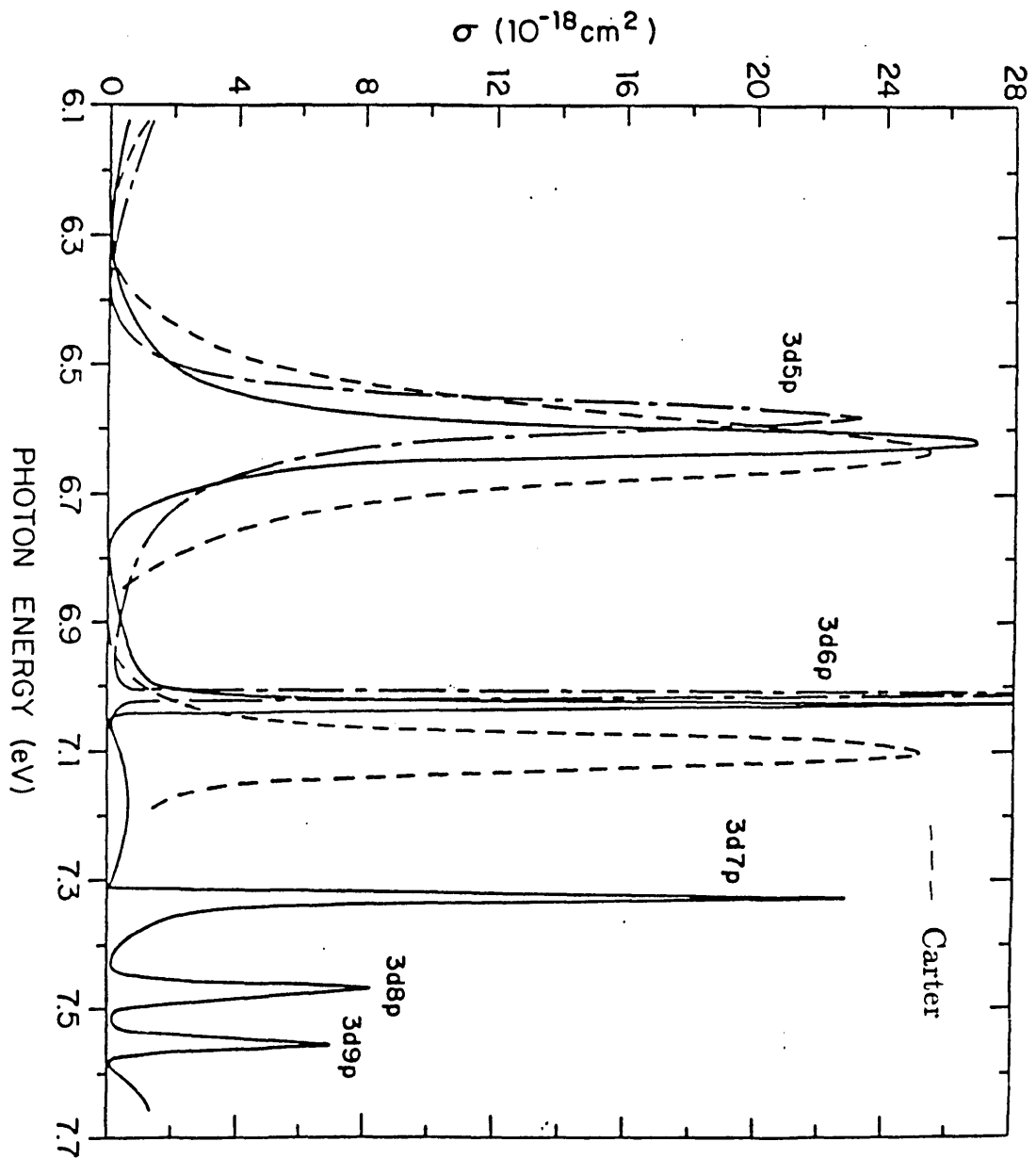


Figure 5.4: A comparison of Altun's calculations with Carter experiment. Dashed curve is the experiment

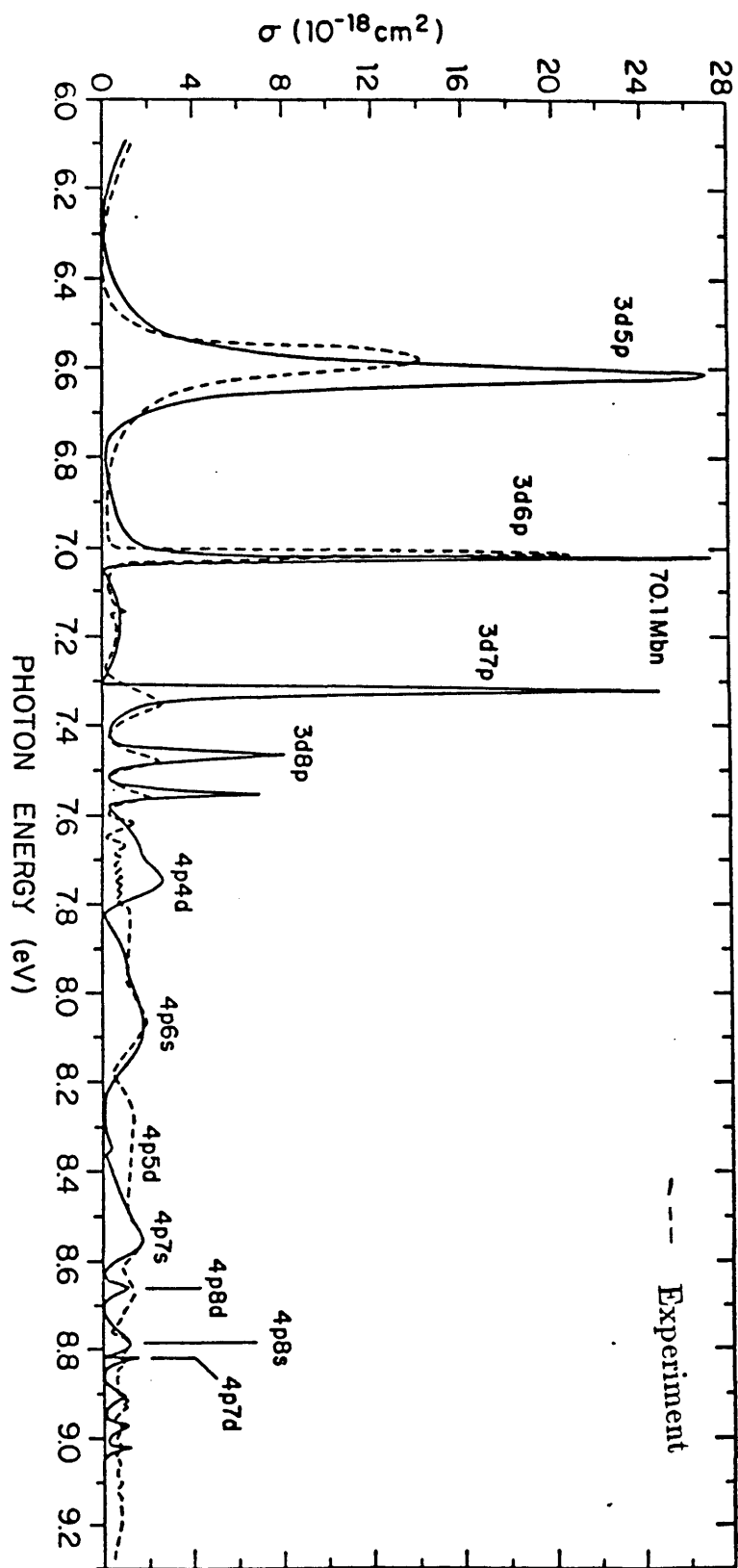


Figure 5.5: A comparison of Altun results with Newsom experiment. Dashed curve is the experiment

Scott's work

The first *ab initio* calculations were performed by Scott *et al*²⁰ using the R-matrix method as described by Burke and Taylor²¹. Configuration interaction wavefunctions were used to describe the initial ground Ca state and final Ca⁺ states. Total photoionisation cross-sections were calculated for photon energies in the range 6.11 eV (²S threshold of Ca⁺) to 9.25 eV (²P threshold of Ca⁺), and were compared with the experimental measurements of Brown *et al*¹⁶ and Connerade *et al*²². The three channel approximation used to study photoionisation process can be represented as:

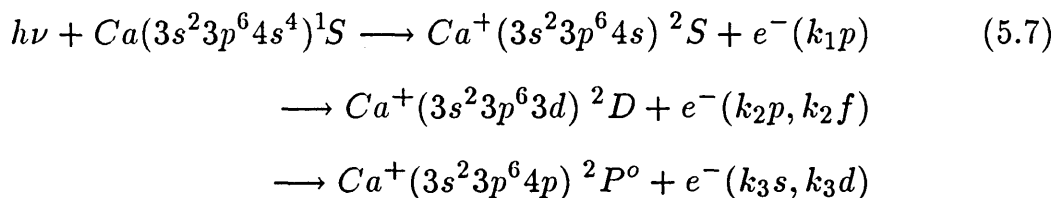


Fig 5.6 represents results for the total photoionisation cross-section in the energy range 6.11 to 7.807 eV in dipole length and velocity approximations. Scott *et al* predicted the existence of only one interloper resonance between ²S and ²D thresholds. However, the vanishing of width of the 3d6p ¹P₁ line was blamed on the presence of a Cooper minimum. The paper says, '... it is important to note the rapid change in the value of q between the $n = 6$ and $n = 7$ members of the 3dnp series. This is due to the presence of a minimum close to the ²S threshold, which is caused by the dipole matrix element passing through zero as it changes sign. Such minima have been discussed by Bates²⁵, Seaton²⁶ and Cooper²⁷. Fano and Cooper²⁴ give the

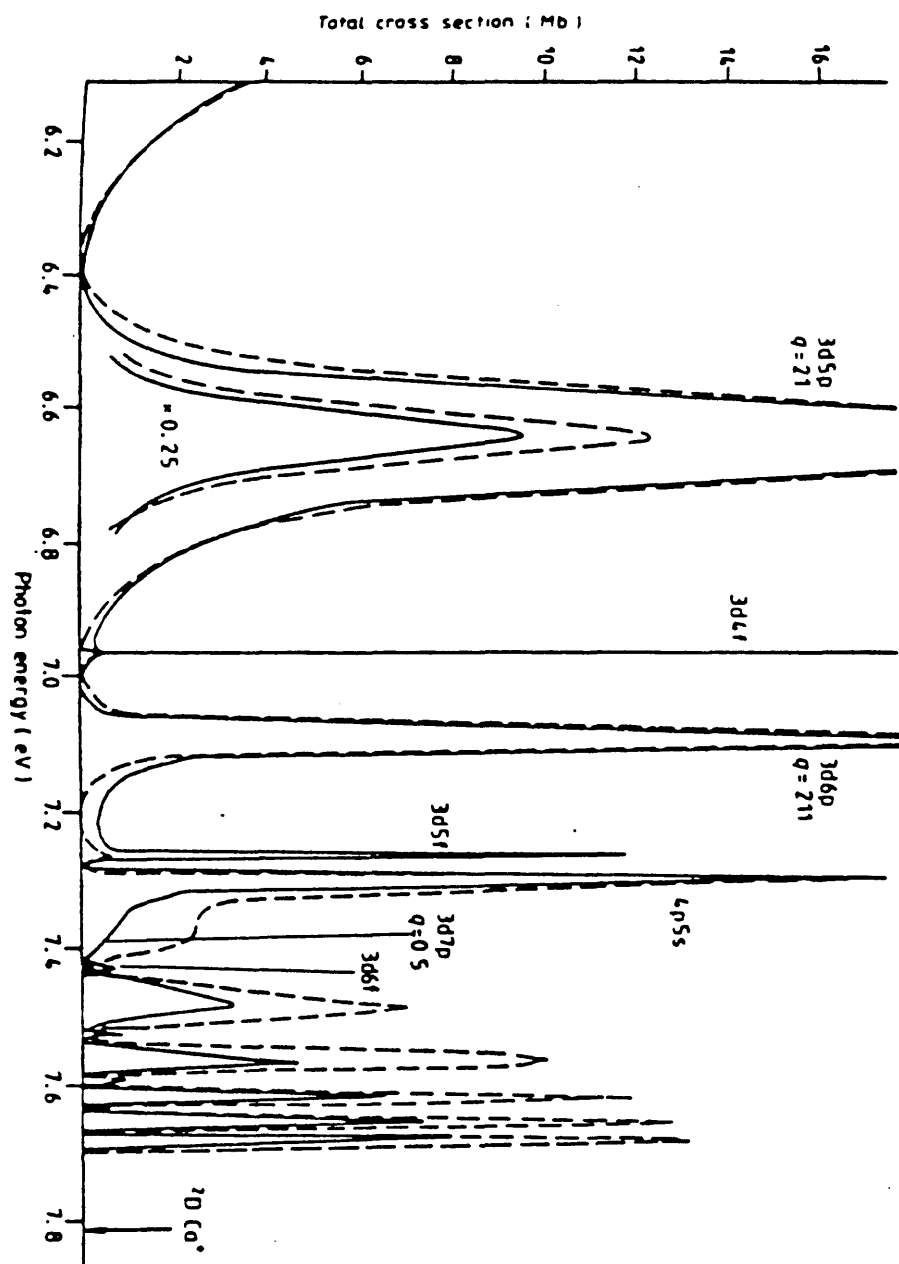


Figure 5.6: Ca I spectrum calculated by Scott *et al* : —, length form; ···, velocity form.

following expression for q :¹

$$q = \frac{(\phi | z | \psi_0) + p \int_0^\infty dE' (\phi | H | \psi_{E'}) (\psi_E | z | \psi_0) / (E - E')}{(\phi | H | \psi_E) (\psi_E | z | \psi_0)} \quad (5.8)$$

where ψ_0 is the initial state wave function, z is the dipole operator, and ϕ the discrete state which interacts with the continuum states ψ_E . This expression considers only one discrete state and would need extending where the resonances overlap, as in the present case. However, it is sufficiently accurate to show that as the dipole matrix element $(\psi_E | z | \psi_0)$ changes sign there is a rapid change in q due to the presence of this matrix element in both the numerator and denominator of Equation 5.8. This rapid change in q is illustrated in Fig 5.6 where the shape of the 3dnp resonances changes from the traditional Lorentz profile (characterized by high q value) before the Bates-Seaton-Cooper minimum, to that of the window resonance (characterized by q value close to zero) after the minimum.^{23 ...}

In Fig 5.7 these results are compared with the MBPT calculations¹⁴. One advantage of these calculations is that the resonances are generated automatically while in the MBPT method they must be included explicitly. In these calculations the 3dnf Rydberg series is therefore also included, while in the calculations by Altun *et al* . this series is omitted. However, the main difference is in the prediction of the position of the Cooper minimum. Scott *et al* found it at 7.4 eV and Altun *et al* predict it at 8.2 eV. The minimum reported by Altun will therefore lie above the 2D threshold and will not

¹In the paper by Scott *et al* , the first expression in the numerator has H as the operator, which is not correct. It is, in fact, z , the transition operator, also the first expression in the denominator is incorrect.

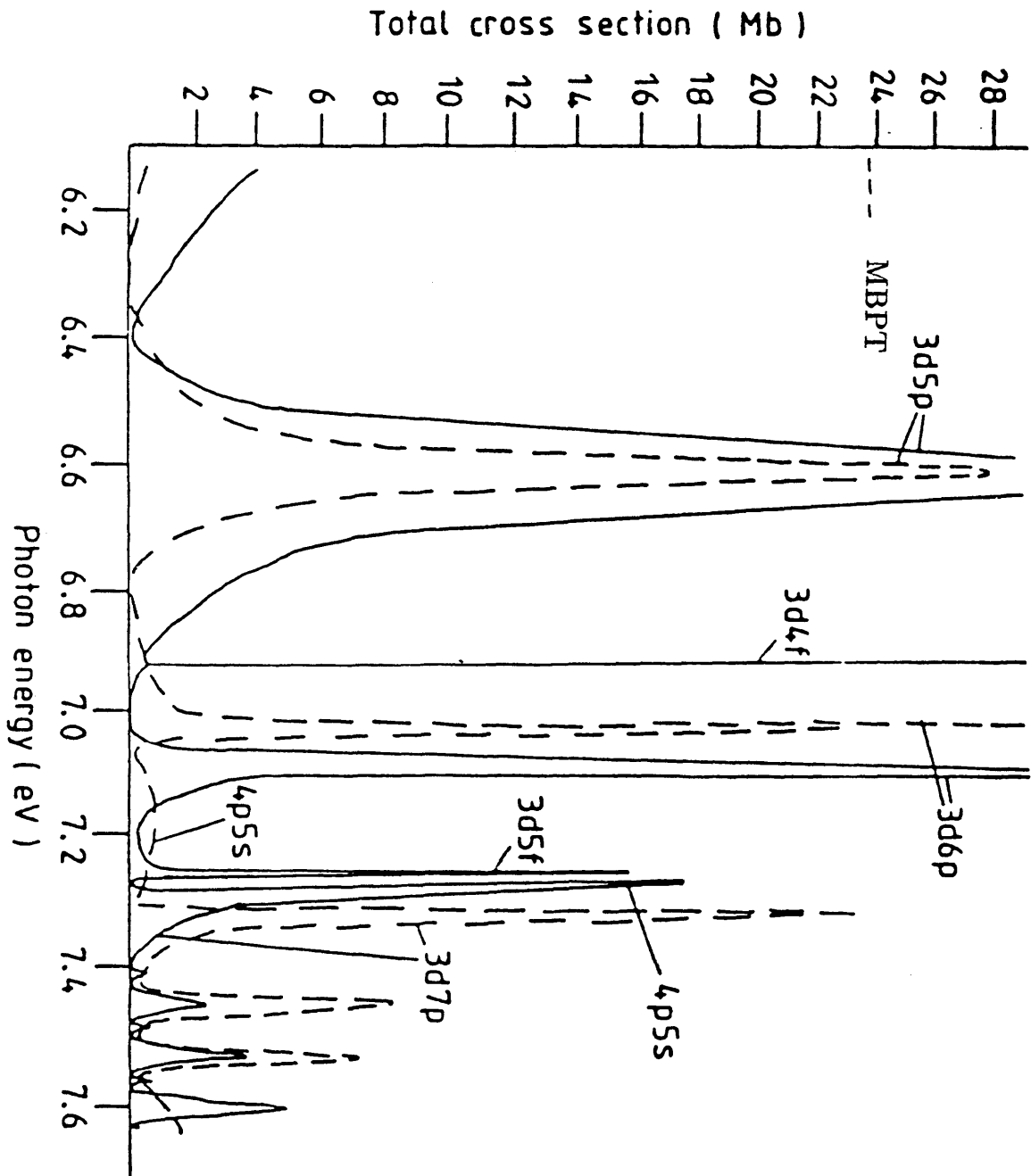


Figure 5.7: A comparison of Scott results with the MBPT calculations:
 —, Scott *et al.*, ..., MBPT results

cause a dramatic change in the line profile indices of the members of 3dnp ($n \geq 7$) series. Hence in Fig 5.7 these resonances in the MBPT curves will have the traditional Lorentz profiles. Fig 5.8 compares Scott's results with the experimental measurements of *Newsom*¹⁸.

Greene and Kim's Work

Greene and Kim^{32a} have examined the pattern of electron correlation for odd-parity $J = 1$ states of calcium over a wide range of energies from far below the 4s threshold up to the 4p threshold of Ca^+ , by using a combination of quantum-defect theory and a small-scale eigenchannel R-matrix calculations. The formulation adopted uses a variational expression for the eigenvalues of the R-matrix, i.e. for the (negative of the) normal logarithmic derivative on the surface of the finite reaction volume. When a linear combination of nonorthogonal Slater-determinantal orbitals is used as a trial function in the variational functional, good convergence is achieved with modest size basis set.

The theoretical description is achieved by considering the two electron Hamiltonian (in a.u.)

$$H = h(r_1) + h(r_2) + 1/r_{12} \quad (5.9)$$

The effective one electron Hamiltonian $h(r)$ includes the electron kinetic energy $-\frac{1}{2}\nabla^2$ and a radial l -dependent potential $v_l(r)$ which describes mainly

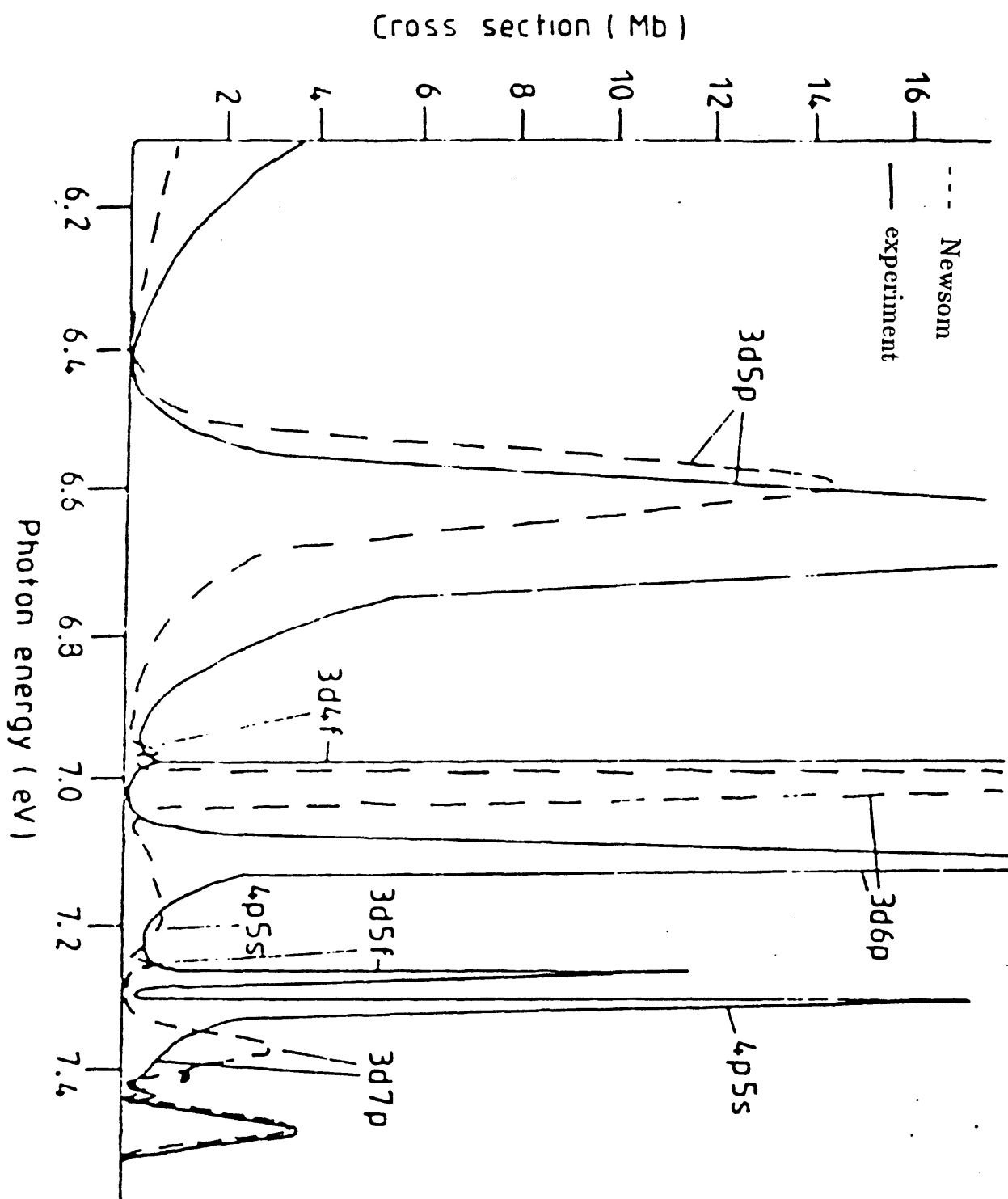


Figure 5.8: A comparison of Scott results with the experimental outcome of Newsom

the net screened nuclear potential experienced by a valence electron. However, no attempt is being made to find a highly accurate *ab initio* description of Ca^+ . Instead, a small empirical polarisation correction is made to a set of Hartree-Slater potentials $v_l(r)$ chosen such that the one-electron s, p, and d levels of Ca^+ are accurately reproduced.

$$v_l(r) = v_l^{HS}(r) - \frac{\alpha_{cp}}{2r^4} \{1 - \exp[-(r/r_{cl})^6]\} \quad (5.10)$$

The core polarization α_{cp} and the l-dependent "cut-off radius" r_{cl} are then adjusted crudely to give optimum agreement with the known spectrum of Ca^+ . The final values obtained are $\alpha_{cp} = 8.0$, $r_{c0} = 1.109$, $r_{c1} = 1.420$ and for $l \geq 2$, $r_{cl} = 1.089$.

The renormalised experimental results of Newsom¹⁸ are compared with these R-matrix calculations in Fig 5.9. The theoretical calculations shown in this figure include two channels below $\varepsilon_{4s} \sim 0.014$ a.u., and five channels (4s ε p, 3d ε p, 3d ε f, 4p ε s, 4p ε d) at all higher energies. According to Greene *et al*, the nonmonotonic variation of widths from one level to next in Fig 5.9 reflects the influence of the closed 4p ε s channel which is just becoming energetically accessible. The presence of this channel causes the energy dependence of two channel (4s ε p—3d ε p) MQDT parameters above $\varepsilon_{4s} = 0.02$ a.u. In particular the mixing angle vanishes at $\varepsilon_{4s} = 0.032$, implying that there is no mixing between 4s ε p and 3d ε p at this particular energy. If an autoionising level was present at exactly this energy, it would in fact be a true bound state (i.e. its decay width would vanish). The 3d6p resonance lies very close to the energy where the channel mixing disappears, the photoionisation cross-section in the vicinity of this state is then unusually sensitive to errors in its height and width, although its integrated width

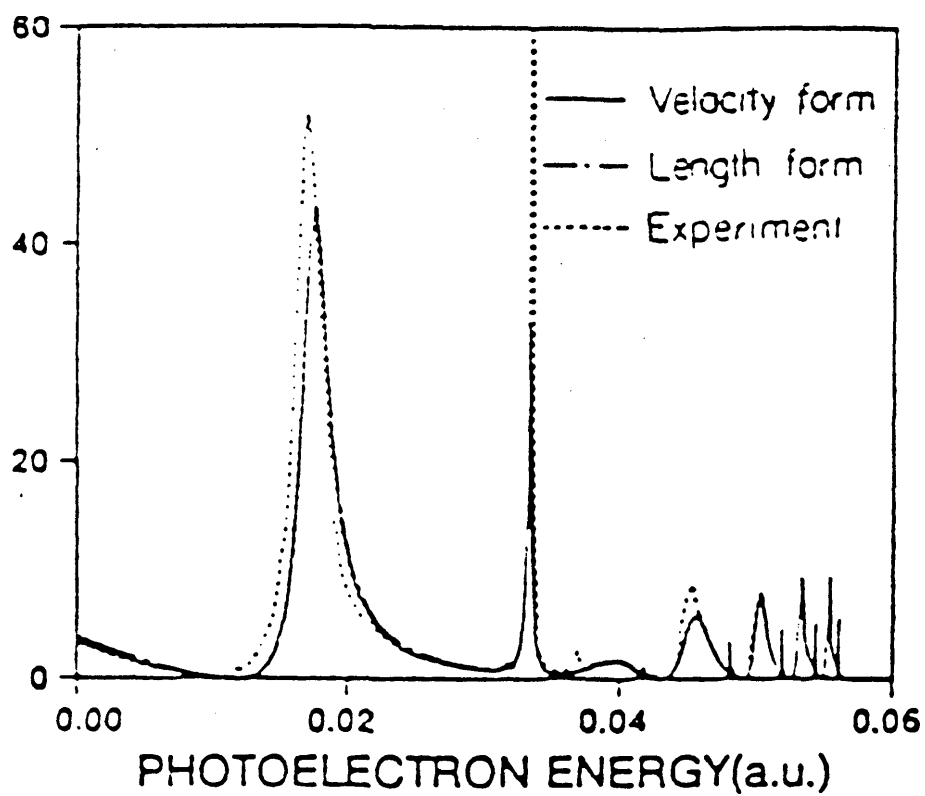


Figure 5.9: A comparison of the R-matrix calculation with Newsom results

is probably described correctly. The destructive interference occurring at $\varepsilon_{4s} = 0.032$ a.u. is a simple example of cancellation between amplitudes for two alternative and indistinguishable decay paths:

$$3dnp \longrightarrow 4s\varepsilon p \quad (5.11)$$

and

$$3dnp \longrightarrow 4pns \longrightarrow 4s\varepsilon p \quad (5.12)$$

This interpretation is further supported by the study of probability densities as shown in Fig 5.10(c). $\alpha = 1$ density shows no $3d\varepsilon p$ component, while the $\alpha = 2$ density shows no $4s\varepsilon p$ component. On the other hand, both $\alpha = 1$ and 2 show a dominant contribution from the closed $4pns$ channel. The energy is sufficiently high at this point to excite $4p5s$, the lowest quasi-bound state in the channel. It is the presence of this new excitation mode which permits a destructive interference to develop between the two decay paths shown in Equations 5.11 and 5.12, a phenomenon that requires at least three channels to be involved.

In this work, Greene and Kim had not taken into account the spin-orbit interaction term in the Hamiltonian, and were thus not able to calculate the ever present fine structure^{18,82}. This was not possible as long as LS coupling was considered. In their next paper^{32b}, they took into account the spin-orbit interaction by means of a geometrical frame transformation. Using Wigner 9-j coefficients, LS-coupled reaction matrices (calculated in the Ref. 32a) were transformed into a 13-channel reaction matrix in a jj-coupling scheme.

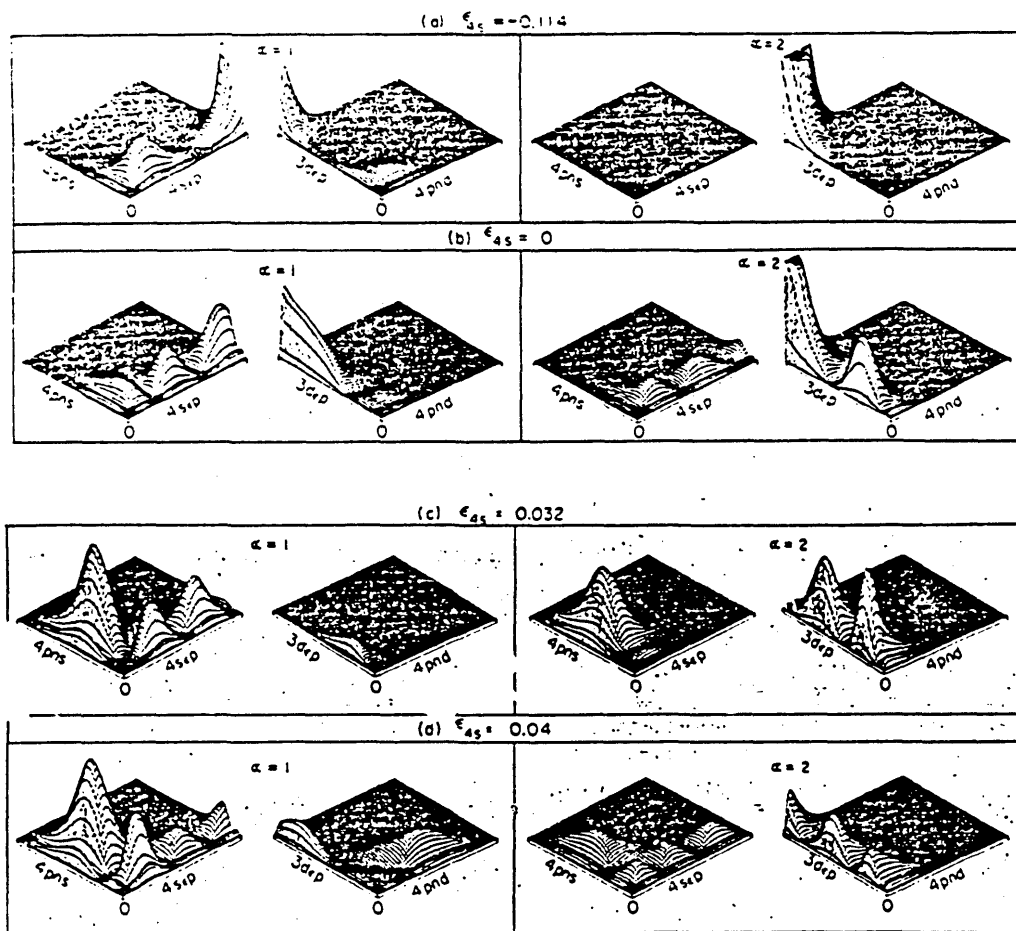


Figure 5.10: Radial sp and pd components of the $^1P^0$ probability density are shown as a function of (r_1, r_2) . From Ref. 32 a

Multichannel quantum-defect theory then predicted observables in the usual fashion.

Inclusion of fine-structure effects caused numerous additional resonances to appear between 4s and 3d thresholds which were not present in the previous work (Ref.32a). After the frame transformation, for each ionisation threshold $\text{Ca}^+(n_i, l_i)$ with $l_i > 0$, instead of one resonance series expected from an LS-coupling calculation, there are at least two separate resonance series with slightly different phases and energy intervals due to the energy splitting of the threshold. These two thresholds have two different values of total angular momentum, $j_i = l_i \pm \frac{1}{2}$. However, instead of calculating the energy splittings of these thresholds by including the spin-orbit interaction term explicitly in the Hamiltonian, they used the experimental value (it is similar to what they did in Ref.32a, for the first ionisation threshold value). The inclusion of this spin-orbit interaction has produced a remarkable spectrum, which compares reasonably well with the present experimental results. They are shown in Fig 5.11, and will be compared with the present results in chapter 13.

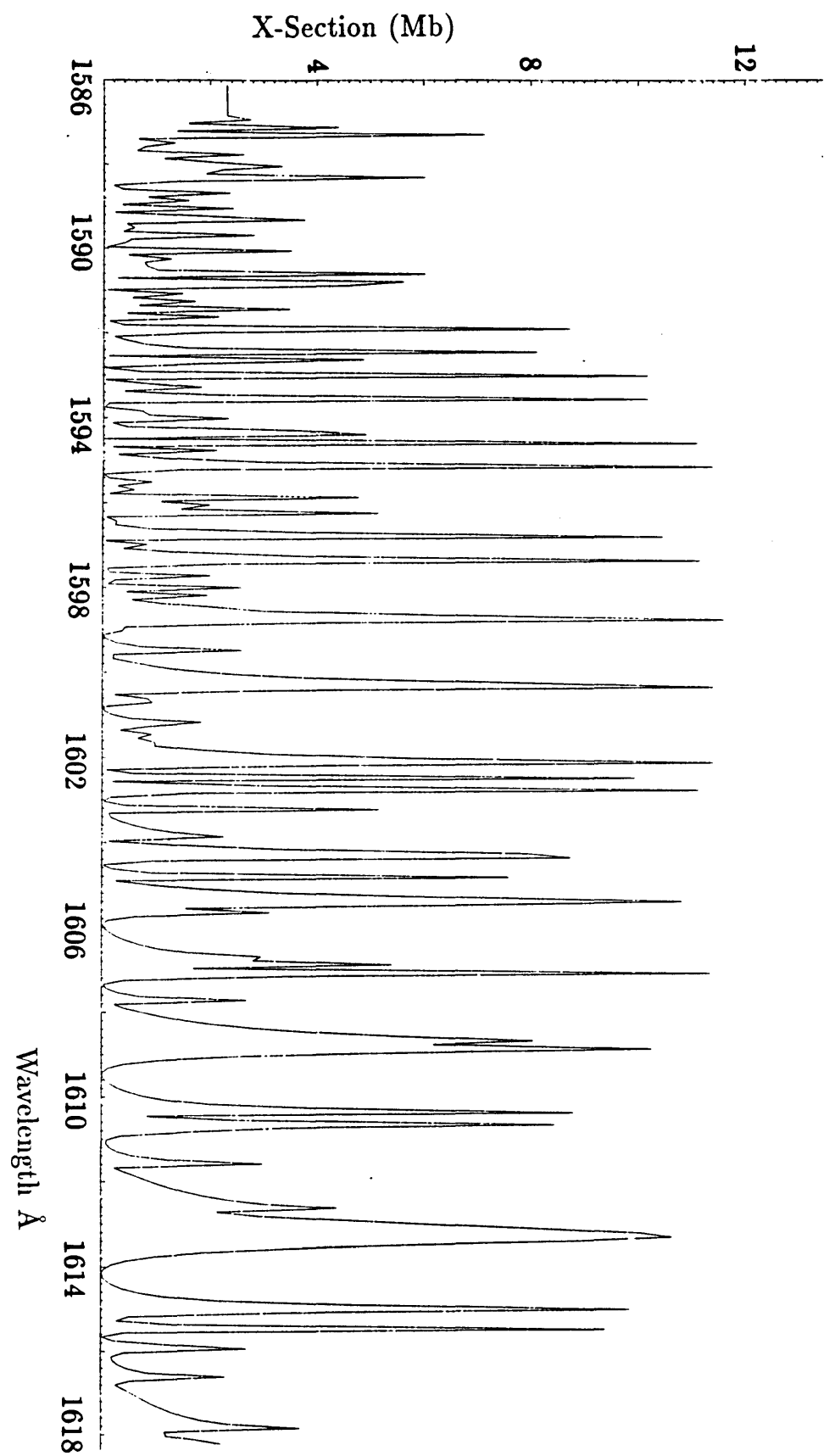


Figure 5.11: Cross-section for photoionisation of calcium for incident photon wavelengths between 1586 and 1790 Å (it is the geometric mean of length and velocity calculation)

Chapter 6

The Case of Barium and Strontium

6.1 Introduction

The previous chapter was based on a review (both experimental and theoretical) of the work done so far in calcium in the energy range of our interest. Apart from calcium, some interesting spectra of the interacting resonances in barium and strontium are also investigated in the present study, which exhibit some peculiar phenomena. Of theoretical interest is the phenomenon of vanishing fluctuations in the barium spectrum below the $6p\ ^2P_{1/2}^o$ threshold of Ba II. This chapter presents a brief review of the important work done so far on these spectra.

6.2 Barium Review

The absorption spectrum of Ba I under discussion consists of transitions from $6s^2\ ^1S_0$ to odd parity channels with $J = 1$ which are based on the $6p\ ^2P^\circ$ terms of Ba II. There are five such channels consistent with the addition of s or d electrons to the $6p\ ^2P^\circ$ core, two to the $^2P^\circ_{1/2}$ (lower) ion core level and three to the $^2P^\circ_{3/2}$ (upper) ion core level. The L-S ancestry of the $J=1^\circ$ channels under discussion would be $6pns\ ^1,^3P^\circ_1$, and $6pnd\ ^1,^3P^\circ_1, ^3D^\circ_1$. Since $6p\ ^2P^\circ$ term lies above both the $6s\ ^2S$ and $5d\ ^2D$ terms in Ba II, the continuous portions of all $J=1^\circ$ channels associated with the 2S and 2D cores will be present in the energy range under consideration. Eight such channels are of importance here: $6s\epsilon p_{1/2,3/2}, 5d_{3/2}\epsilon p_{1/2,3/2}, 5d_{3/2}\epsilon f_{5/2}, 5d_{5/2}\epsilon p_{3/2}, 5d_{5/2}\epsilon f_{5/2,7/2}$. All of these channels have the potential of interacting with the five channels based on $6p\ ^2P^\circ$ to produce the autoionisation related effects.

This review begins by considering the work of Brown *et al* ⁹⁰. Experimental investigations prior to this work are well cited in this paper and they do not reveal anything exciting as regards the main theme of the present study, thus the detail of those experiments is omitted here. Brown *et al* scanned in the VUV from 1770 Å to 1560 Å. Their experimental setup consisted of a King furnace system, in which Ba was evaporated. The furnace was heated to temperatures in the range ~ 900 -1100 °C. Absorption spectra were obtained from a single pass through the furnace using microwave-excited xenon and krypton lamps to provide background continua. Spectra were photographed on Kodak SWR plates using the third and fourth orders

of a 6.6 m spectrograph with reciprocal dispersions of 0.41 and 0.31 Å/mm, respectively. Most of the experiments were performed with flowing argon in the furnace at pressures in the range 1-10 Torr. The wavelength uncertainty in sharp, unblended lines is estimated to be ~ 0.003 Å, which corresponds to ± 0.11 cm $^{-1}$ at 1650 Å. The wavelengths of diffused or blended lines are more uncertain. The spectrum recorded is as shown in Fig 6.1. Brown *et al* used MQDT approach to analyse data. They found that instead of three series converging on the $6p\ ^2P_{3/2}^o$, only two are evident. Their analysis of the spectrum just below and above the $6p\ ^2P_{1/2}^o$ limit revealed strong mixing associated with both core levels, and they suggested that missing fifth series might be present here.

The feature of most interest is the systematic decrease in fluctuations which reach a minimum near 1609 Å (this cannot be mistaken for the usual decrease towards the series limit, as the series limit is at 1605.2 Å, and is obvious in their spectrum). This strange behavior was thought by Brown *et al* as possibly due to an instrumental interference effect which can occur amongst higher members of Rydberg series when spacing between the adjacent levels gradually approaches to the resolution limit of a classical grating spectrograph⁹¹.

To understand the physics of this vanishing of spectral fluctuations, Lane⁹² made a study of the magnitude of cross-section fluctuations caused by the Rydberg states as a function of energy. Regarding the above spectrum, he raised the following theoretical points: does one expect fluctuations to vary ? does one expect them to have a zero or simply a minimum ? does

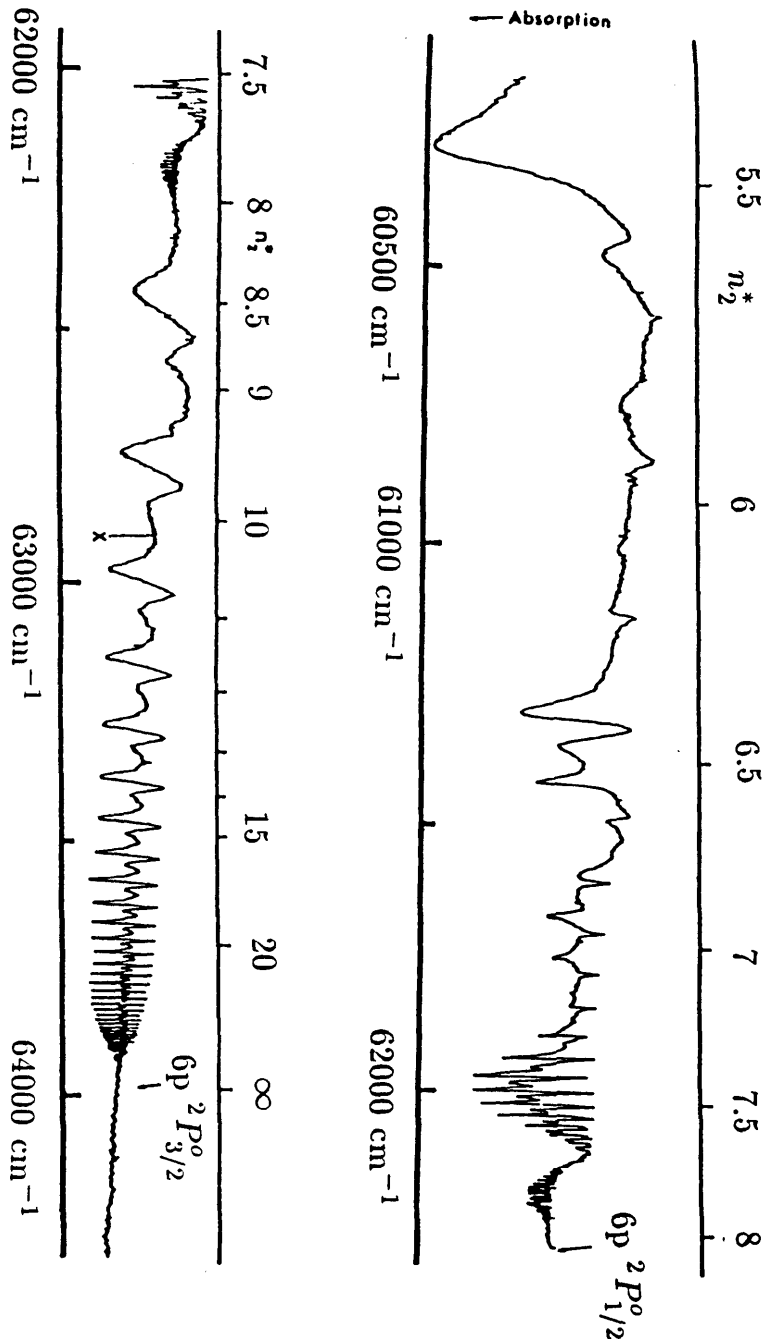


Figure 6.1: Absorption spectrum of Ba I below the $6p\ ^2P_{1/2}$ ionisation threshold (in the VUV), as recorded by Brown and Ginter⁹⁰.

the minimum necessarily coincide with the minimum of the gross structure ? As a result of his analysis, he concluded that the number of parameters needed in this example is large, so that a zero-point in the fluctuations might prove unlikely. In his own words '...the strong minimum in the fluctuations in figure 1 is an exception to general expectation. In view of this, it may be just as well that there is some doubt about the effect in figure 1 being genuine ...'

However, some recent R-matrix calculations^{92,93} (LS and jj-coupled respectively, but otherwise same approach) show that the minimum observed by Brown *et al* must be a real effect. The jj-coupled calculations⁹³ had a similar numerical energy resolution to the experiment of Brown *et al* , and differences between the predictions for the high members of the series are therefore hard to assess. This R-matrix calculation includes all the relevant open channels, and thus produces impressive agreement with the experimental data, but unfortunately does not provide much clue as to exactly which specific interaction is responsible for the fluctuation.

Also, it is clear by inspection of the published spectrum that the energy resolution is inadequate to reveal the true behavior of the resonances in the vicinity of the vanishing fluctuations. Keeping in view all this, this spectrum is reinvestigated with the present high resolution VUV setup and the hot-wire diode detector—linear over many decades of light intensity.

6.3 Review of strontium

The structure of the absorption spectrum of strontium observed in the present work (1430-1448 Å region below the $5p_{1/2}^o$ threshold) is due mainly to transitions from $5s^2\ ^1S_0$ to $J=1^o$ channels based on the $5p\ ^2P^o$ core term of Sr II. There are five such series consistent with the addition of nl ($l=0,2$) electrons to the $5p\ ^2P^o$ core, two of which are built on $5p\ ^2P_{1/2}^o$ and three on $5p\ ^2P_{3/2}^o$. The maximum number of dipole-allowed absorption series from $5s^2\ ^1S_0$ to $5pnl$ channels with s or d ancestry would be five, two converging near 1435 Å and three near 1419 Å.

Initially this spectrum was investigated by Connerade *et al*²² in their pursuance of the study of potential barrier effects on the double excitation series. Latter this was studied by Brown *et al*¹⁰⁸. Their experimental setup was similar to the one used in the study of doubly excited spectra in calcium and barium^{16,90}. The absorption spectrum was obtained from a single pass through the King furnace using microwave-excited xenon and krypton lamps to provide background continua. The spectrum was photographed on Kodak SWR plates using the third and fourth orders of a 6.6 m spectrograph at reciprocal dispersions of 0.41 and 0.31 Å/mm, respectively. The experiment was performed using flowing argon in the furnace at pressure in the ~ 0.5 -7 torr range. The furnace was heated to temperatures in the range ~ 700 -900 °C. The wavelength uncertainties in sharp, unblended lines are estimated to be ± 0.002 Å. The wavelengths of broadened or blended features are more uncertain. Their recorded spectrum is as shown in Fig 6.2 (upper portion).

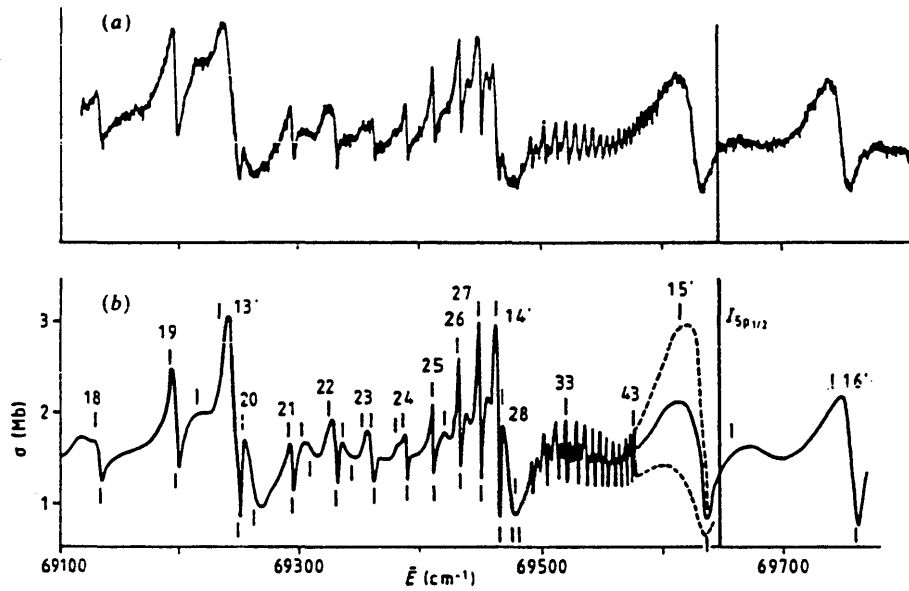


Figure 6.2: Photoabsorption spectrum of the doubly excited autoionising resonances in Sr I, below $5p_{1/2}^o$ threshold (as recorded by Brown *et al*). The lower spectrum is the eigenchannel R-matrix calculations performed by Aymar (1987)

Brown *et al* analysed their data by using a quasi-two-limit MQDT-based approach that treats the channel structures built on $4d\ ^2D_{3/2,5/2}$ and on $5p\ ^2P_{1/2,3/2}^o$ as two semi-independent two limit problems. Transitions in this region are to the bound (closed) $J=1^o$ channels associated with $5p\ ^2P_{1/2}^o$ that can couple (mix) with the continuous (open) $J=1^o$ channels built on $5s\ ^2S_{1/2}$, $4d\ ^2D_{3/2,5/2}$, and $5p\ ^2P_{3/2}$. If there were no interactions with the open $J=1^o$ channels built on $4d\ ^2D$ and (or) $5s\ ^2S$, the spectrum in Fig 6.2 to lower energies from the $5p\ ^2P_{1/2}$ limit would have consisted of sharp features rather than window resonances, although the general periodic intensity variations would remain. These variations are due to periodic crossing of levels belonging to different ionic core levels.

Eigenchannel R-matrix calculations of this spectrum were performed by

Aymar (1987) (lower portion of the Fig. 6.2). The results in general show an agreement with the experiment except near the $5p_{1/2}$ limit.

Chapter 7

Thermionic Diode Detector

7.1 Introduction

Photo-absorption spectroscopy has been revolutionised by the use of the thermionic diode detector—a detector capable of counting each single ion produced during the absorption process—thus, ideal for measurement of the intensity of the autoionising lines, as ions are produced in such transitions. However, it has been equally successful in the high Rydberg spectroscopy of the excited atoms under certain experimental conditions which help ionise these highly excited atoms. The diode detector is linear over many decades of light intensity, offers high signal to noise ratio, has dark background and simultaneous observation of opacity effects is possible.

7.2 Early History

The recognition of the thermionic diode as an ion detector can be traced back to the 1920's, when it was referred to as a space charge diode or Kingdon cage⁵⁸. The applicability of the diode in spectroscopy was suggested by Foote and Mohler^{59,60}. But it was in the late 1970's, after the development of the narrow band tunable dye lasers, that the popularity of the diode detector rapidly increased. First there were several investigations using pulsed tunable dye lasers mainly performed at Dallas, IBM Orsey, and at the York university (for detail see reference 53 and the references cited in it). A few years later, with the CW dye lasers it was used in Doppler free spectroscopy⁶¹. Today many spectroscopists are using this detector which allows one to study, in particular, the transitions to highly excited states with remarkable sensitivity.

In collaboration with the group at the university of Bonn, spectroscopists from the Blackett laboratory have successfully configured the thermionic detector for use with the synchrotron light source⁶². It has also been used in single photon absorption spectroscopy of the high Rydberg levels in Ba I⁵¹, and Mg I⁶³ using a frequency doubled tunable dye laser and VUV light source developed at the Blackett laboratory laser consortium. With the same VUV source a diode detector is used for the inner-shell spectroscopy of Yb I⁶⁴. Multi-photon absorption spectroscopy became very easy due to the two open ends of the thermionic tube. Light beams from two different lasers were focussed in the diode detector through the two ends of the tube to study the Hg I⁶⁵ inner-shell spectrum. Two photon spectroscopy of high Rydberg

states in Ca I has also been performed, and the influence of collisions in mixing them with doubly excited states has been investigated.

7.3 Working Principle

The thermionic diode detector like any other ordinary diode has two electrodes—an electron emitting cathode and an anode. The cathode, however, in this case, is a long stretched thin metal wire of low work function, and a concentric cylindrical tube of stainless steel acts as the anode. The cathode wire heated at a fairly high temperature emits electrons. A small bias voltage pushes these electrons towards the cylindrical anode. The electrons emitted from the cathode form a space-charge cloud which eventually stops the flow of electrons to the anode, and the detector is said to be in space-charge limited mode.

7.4 The Diode as an Ion Detector

The space-charge limited mode is key to the ion detection. In the space-charge limited mode, as described above, the electrons are held back from reaching the positive anode. The reason for this space-charge cloud formation is that the cathode emission current is high enough to develop a potential minimum between the two electrodes. The electrons making their way to the anode are thus outnumbered by the electrons emitted from the cathode.

It has been established that the anode current and potential are related by the Langmuir three halves law⁵¹

$$i = \frac{2\sqrt{2}}{9} \sqrt{\frac{e}{m}} \frac{V_a^{3/2}}{R\beta^2} \quad (7.1)$$

R is the radius of the anode and

$$\beta = \gamma - \frac{2}{5}\gamma^2 + \frac{11}{120}\gamma^3 + \dots \quad (7.2)$$

$$\gamma = \ln(R/a) \quad (7.3)$$

a is the cathode wire radius. The value of β can be taken as 1 if R is much greater than a , as shown in Fig 7.1.

The current i therefore, increases with the anode potential V_a in the space-charge limited mode. The potential distribution along the radius and the position of the minimum point depends upon the cathode temperature. The Fig 7.2 shows $V(r)$ (at $T=950$ K, $a=0.1$ cm, $V=5.0$ volt) computed as a function of radial distance between the cathode and anode⁵².

If the diode is filled with a gas or metal vapor at low pressure and if ions are produced in the diode, they will be trapped in the negative space-charge potential well for a long time. Thus, the negative potential is reduced and the electrons are able to reach the anode. The escape continues until the potential minimum is again established. The prolonged electron current

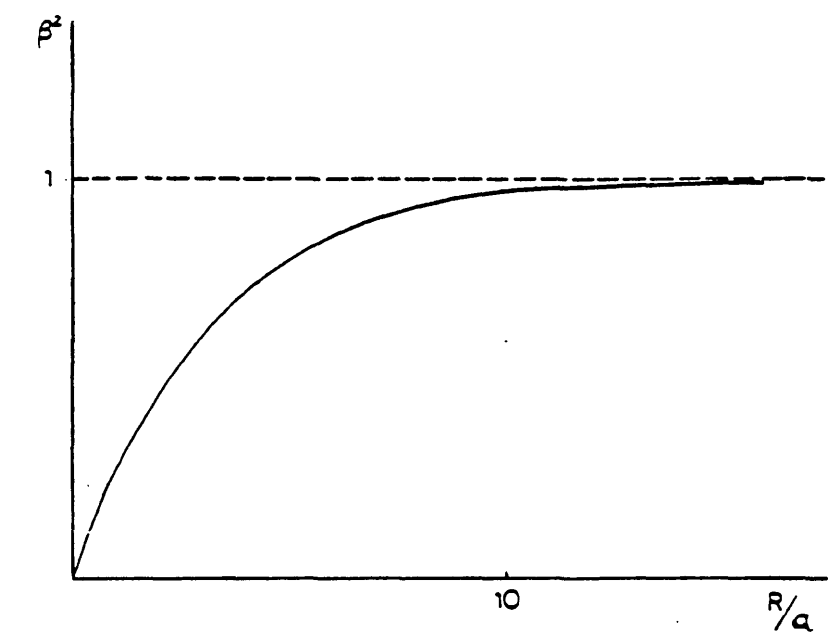


Figure 7.1: A plot of β^2 as a function of R/a

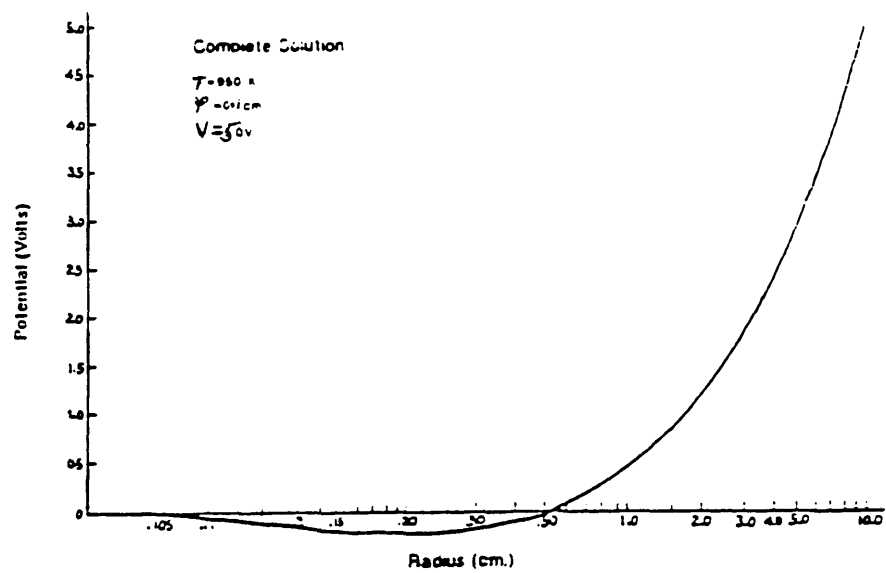


Figure 7.2: Dependence of V on radial distance between the cathode and anode

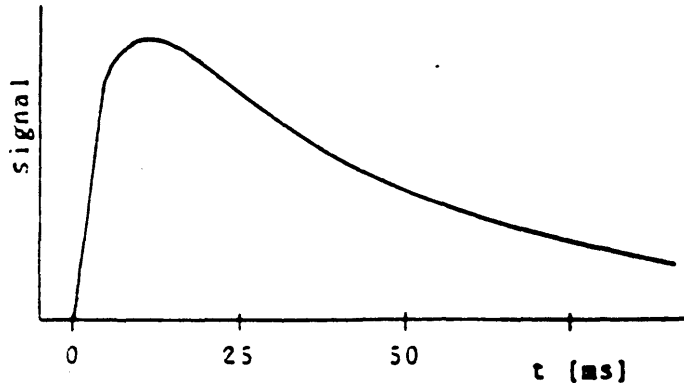


Figure 7.3: Diode current signal as a function of time

offers a substantial gain of the ion signal. The rise time of the signal is dependent on the diffusion time of the ion trapped in the space-charge region. A typical diode signal after photoionisation of atoms is shown in Fig 7.3 . The signal decays because ions get lost. Ions can either deposit on the cathode surface and get neutralized or can recombine with electrons. The electron-ion recombination cross-section is generally very small and hence this mode of ion loss is usually neglected. The signal amplification factor is determined by the ratio $\Delta I_c/Q$, where ΔI_c is the increase of the diode current and Q is the amount of positive charge produced per second. Thus, it is very important to have high emission current from the cathode surface forming a pronounced space-charge region to achieve large gain. An amplification factor as high as 10^6 is reported⁵³. The thermionic diode or *hot-wire* (as it is often called) detector has the edge over other conventional ion detectors

due to its high signal gain. This high signal gain, as just discussed, is due to long trapping and neutralization of ions in space-charge, while ordinary ion detectors collect each single ion produced and thus have very small gain. Also, ordinary ion detectors require high voltage to drive ions towards the electrodes (ions are much heavier than the electrons). This high voltage may introduce line broadening and induce transitions. In a thermionic diode a small bias voltage is enough to push electrons towards the anode.

7.4.1 Choice of Cathode

As we have described earlier, the high gain of the thermionic diode detector is dependent on the high space-charge, which in turn is due to high electron emission from the cathode surface. Hence, the selection of the proper cathode is very important. The cathode should be made from conducting material of low work function which can withstand high temperature. When working with alkali or alkaline-earths (as is the case in this work), the work function is further lowered by the adsorbed alkali or alkaline-earth layer on the cathode surface. In the previous experiments with the thermionic diode, thoriated tungsten wires were used as cathode⁵¹. In the present work, however, the cathode was made from a molybdenum wire, because molybdenum like tungsten, has a low work function which is lowered further when working with alkali or alkaline-earths.

Another important restriction is made on the diameter of the cathode wire. Most of the ions are neutralized by hitting the cathode surface. To achieve high gain, the probability of an ion striking against cathode has to

be minimized. Thus, cathode wires of small diameter are recommended⁵³. We have used a molybdenum wire of 0.125 mm throughout the experiment. Going further down is not possible because the wire could not be stretched without breaking.

7.4.2 Directly Heated Cathode

Some of the previous investigations^{51,54,55} were made without directly heating the cathode. The space charge was produced by indirect heating of the cathode wire. Only a small bias voltage was applied to push the electrons. This technique has a few drawbacks: the temperature of the oven is maintained according to the requirement of vapor pressure of the element under investigation, and not to maximize the space charge—thus resulting in somewhat low gain. Also, the system can be used to study only those elements which require an oven, i.e. low pressure elements like gases can not be studied by this configuration. In an externally heated diode (as we discuss in the next section), the center of the tube is at the lowest temperature and the vapors tend to condense onto the cathode wire.

In the present work, the cathode is heated independently of the oven, thus enhancing the signal gain and overcoming the problems of limited space-charge and selection of the elements to be studied. The cathode wire is now at relatively higher temperature, reducing the huge deposition of vapors on it, and hence, increasing the chances of interaction.

7.5 Thermionic Diode as an Oven

If high vapor pressure elements like alkaline-earths are to be studied, they need to be heated up to evaporate the material, so that the light-matter interaction probability can be increased. This requires careful selection of the diode tube material. The constraints are imposed by the need that the tube must withstand high temperatures (typically up to 1000 °C for the alkaline-earths), should be an electrical conductor with a high work function (one must avoid stray electric field due to the electrons emitted from the tube) and be of good vacuum quality. We therefore used a stainless steel tube. Heating is done externally by a coaxial heating element as discussed in the next section.

7.6 The Gain

The neutralization of the space charge by the ions produced is the key to the operation of the thermionic detector. The potential minimum developed due to the space charge is filled as an ion is trapped, so electrons start moving towards the anode. The prolonged trap time of the ion (being much heavier than electrons, it needs more time to reach the cathode) allows a great number of electrons to escape. The ion-electron recombination cross-section is much smaller and is generally ignored at low pressures (less than a few torr). Therefore, the very high gain of the detector arises from the long life time of the trapped ion. The gain of the diode detector depends on many factors, including geometry, cathode and anode material, temperature,

operating conditions and so on. A gain of 10^6 has been reported⁵⁶. A quantitative calculation gives us the relation⁵⁷

$$G \propto (i_c/i)^{T_c/T} \quad (7.4)$$

where G is the detector gain and T_c is the cathode temperature. This relation indicates that as the emission current increases so does the space-charge, ions are trapped for a longer time, and hence gain increases. The cathode emission current is given by

$$i_c = AT_c^2 e^{-U/KT_c} \quad (7.5)$$

A and U are constants dependent upon the cathode material.

The optimum working conditions are achieved by adjusting different operation parameters.

7.7 Design and Construction

In a previous study of the atomic spectra (Ref.51), the thermionic diode detector had eight cylindrically symmetric cathode wires, which were held at the same potential with respect to the anode. This sort of arrangement is necessary for high Rydberg spectroscopy, to avoid Stark effect. The electric field components due to eight cathodes cancel each other at the center, thus providing a field free region to pass the laser beam. This arrangement avoids

any line broadening due to the Stark effect. However, in the study of the autoionising resonances the Stark broadening is not so important as the levels are already very broad ($\sim 10^5$ times more broad than the Rydberg levels). Thus, in the present study, a simple thermionic diode detector with a single wire has been used. The anode is a stainless steel tube of 3.5 cm inner dia and 40 cm long. Both ends of the tube are machined to fit standard vacuum components. The ends are water cooled externally by welding three turns of copper tubing (5 mm i.d.) on each side. The middle 30 cm of the anode tube are wound with thermocoax heating wires plus insulation materials. A bridge rectifier followed by a large capacitor ($1000 \mu\text{F}$) filters the ac power supply to a nearly dc current reducing the ac noise. Bifilar winding of the thermocoax wire is used to minimize the magnetic field at the pipe axis. The cathode is made from a molybdenum wire of 0.125 mm dia and is 50 cm long, mounted in the tube slightly off axis with the help of thin copper rods embedded deep into the two PTFE supports. The copper rods, in turn, through the vacuum tight blanks, are connected with BNC connectors for heating the cathode independent of the tube. Figure 7.4 represents the geometry of the diode.

7.8 Diode Circuit

When the diode is working in the space charge limited mode, any ion trapped in it helps electrons to escape towards the anode, as discussed earlier. This current signal is converted into a voltage pulse by a $50 \text{ K}\Omega$ resistor (matching the impedance of the diode detector). A typical diode pulse observed⁵³ is

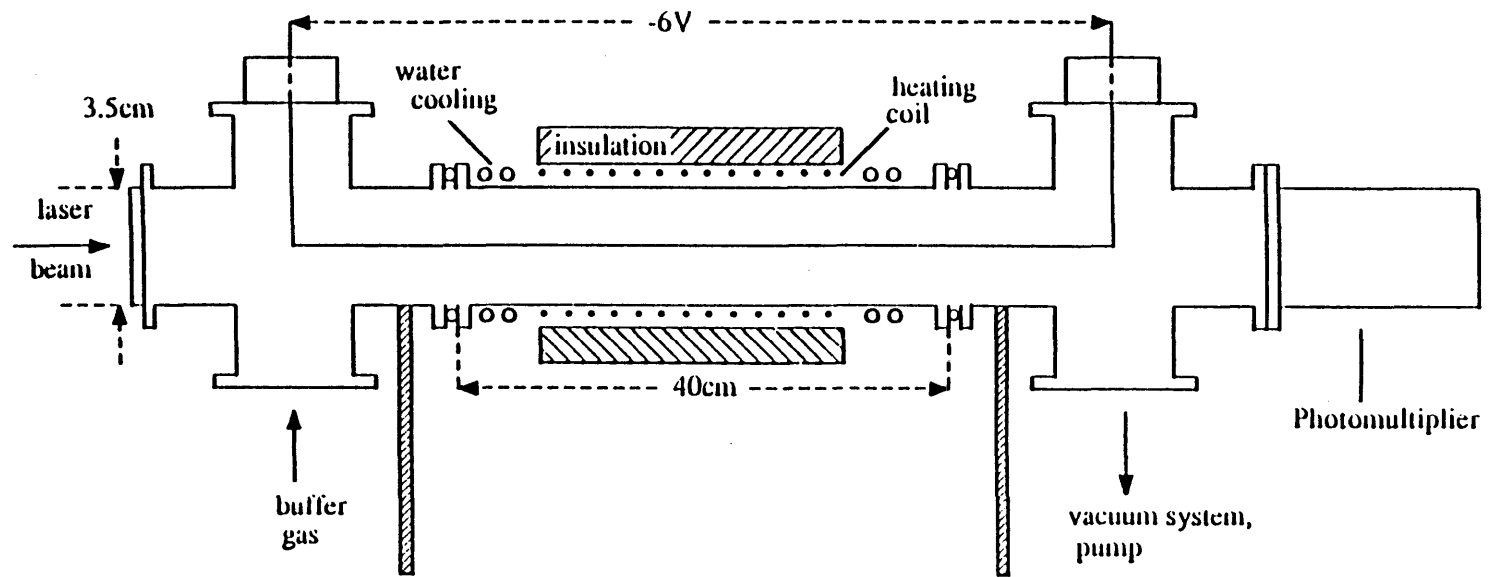


Figure 7.4: The diode tube assembly

shown in Fig 7.3 . The rise time of the signal depends on the diffusion time of the ions to the space charge region. The slow decrease of the signal in 40 ms range gives a measure of the long trapping time. The signal decreases because ions get lost if they have gained enough thermal energy by collisions to leave the space charge well or because they are neutralized if they strike the cathode surface. The diode signal through a BNC cable is input to the lock-in-amplifier, which processes the signal as discussed in the next section.

The cathode is heated independently of the tube by a variable dc power supply which can supply up to 6 volts with 3.5 amp. maximum current. The complete layout is as shown in Fig 7.5.

7.9 Optimization and Operation

For the efficient use of the thermionic diode, one has to optimise certain parameters. When the diode tube is heated externally to evaporate the material, vapors formed tend to accumulate at the cold ends and there is danger of windows being coated. To avoid this and to confine vapors in the hot zone of the tube, some inert gas (Argon in the present experiment) is added into the system. In the study of the highly excited Rydberg levels, inert gas atoms help to ionise excited levels by collisions. The optimisation of the inert gas pressure is very important in these sorts of studies, because the interaction between the absorbing atoms and the inert gas atoms can result in line broadening. Similarly, the temperature optimisation is required to satisfy on one hand, the need for enough vapors for interaction, and on

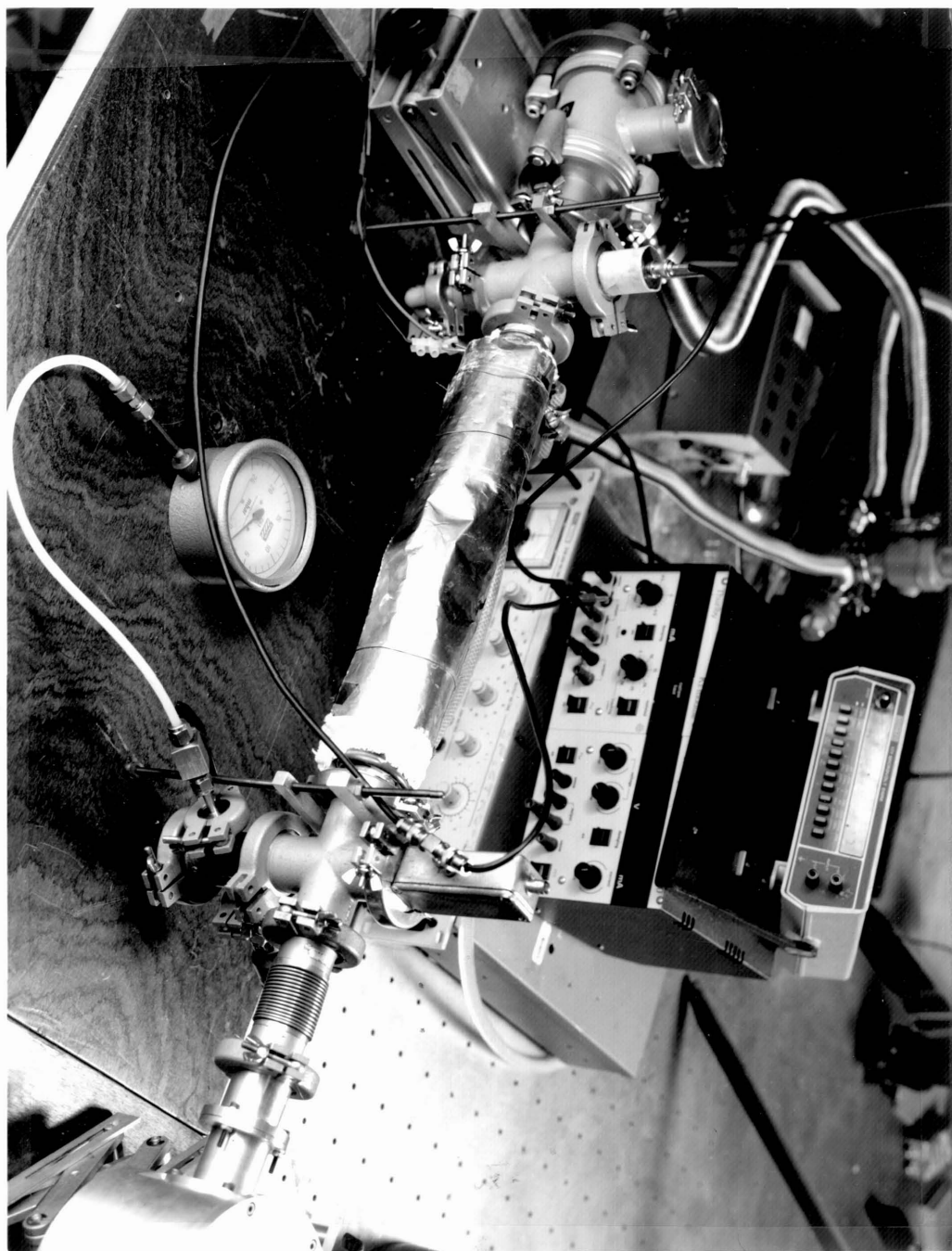


Figure 7.5: Complete layout of the thermionic diode detector system

the other hand, to avoid opacity effects.

7.9.1 Operational Procedure

This section describes in detail the procedure normally followed in the preparation of the experiments which is the same for all the elements studied. The specific needs of each case, however, are discussed in the experiment itself. The operational procedure described in the present section is confined to the matters relating to the thermionic diode itself.

The thermionic diode is coupled to the vacuum system—consisting of a rotary backed diffusion pump, which can develop a vacuum of the order of 10^{-6} Torr. Initially the tube is sealed at both ends by two quartz windows without loading any sample in it. The diode is put under vacuum and within half an hour a high vacuum of the order of 10^{-6} Torr is established in the system. Then the diode is heated up to the maximum experimental temperature (about 750°C). The cathode is also heated independent of the tube. The vacuum then deteriorates, due to the degassing of both the tube and the cathode at high temperature. The system is left under these conditions (i.e. heating and vacuum) for a certain length of time during which all the impurities are removed, and again, a vacuum of the order of 10^{-6} is achieved. The system is then cooled down by letting in some argon gas. Fresh calcium (and similarly Ba and Sr) is cut into small pieces and put on to a stainless steel mesh, mesh is then loaded into the middle of the tube. The capillary action of the mesh also helped bringing the condensed vapors (because the ends of the diode tube are water cooled to protect windows from

heat, hot vapors tend to escape towards the ends) back into the middle of the tube. One end of the diode is attached to the monochromator by a stainless steel bellows, and a photo multiplier tube (PMT) is mounted on the other end. Because the experiment has to be conducted in a vacuum environment, both the monochromator and the PMT are also under vacuum. The diode ends are sealed by a Li F lens on the entrance side (monochromator end) and by a Li F window on the PMT end.

The system is , again, put under vacuum and heated to moderate temperature (50 °C). Due to the degassing of calcium, the vacuum deteriorates. The process of heating and cooling is repeated for some times at low temperatures. At high temperatures the system is isolated from the vacuum pump and small amount of the argon gas (1 mbar) is introduced, which helps confine vapors in the hot zone.

7.10 Noise and Sensitivity

The typical noise sources in the thermionic diode detector are shot and flicker noises⁵⁷. Because the cathode emission current is composed of a large number of discrete charges, statistical fluctuations in the rate of emission lead to the shot noise in the current. For a space charge limited diode, the shot noise is given by

$$\Delta I_a^2 = C I_a \Gamma^2 \quad (7.6)$$

where ΔI_a^2 is the mean-square deviation of the anode current, C is a constant and $\Gamma_a^2(\leq 1)$ is the space charge reduction factor, and depends on the function $U = e V_a / KT$, and decreases from nearly unity at $U=1$ to just over 0.1 at $U=10$, and levelling off for large U ⁶⁶.

The second source of noise is flicker noise. It is considered to be due to the fluctuations in the electron emission properties of the cathode. Its obvious effect—though difficult to explain—is the slow modulation of the signal which is effectively a gain drift. This noise, in the present study is taken care of by repeating each scan to check gain drift, also the cathode is frequently replaced by a new one.

Since, the thermionic diode measures the ion signal (with high gain), an increased photon flux will increase the signal but not the noise level (if the saturation is not reached), whereas a large photon flux does not usually give a better signal to noise ratio in the classical measurements (photographic or photo-electronic), because the background level increases proportionally.

7.11 Linearity

The linearity of the thermionic detector has previously been studied by many groups^{51,53}, and it has to be checked if the diode signals are very strong. A higher density of atoms, a strong transition, or a larger laser intensity may produce so many ions that the space charge is depleted and thus the amplification reduced significantly.

In this experiment, the linearity is checked by using various laser intensities and by comparing the thermionic signal with the corresponding VUV intensity. The opacity effects due to the high vapor density at high temperature (as described in chapter 2) are monitored by simultaneously recording the PMT output signal.

Chapter 8

Data Acquisition System

8.1 Introduction

The thermionic diode current signal was converted into a voltage pulse across a load resistor ($50\text{ K}\Omega$) which matched the impedance of the diode detector. The diode signal was input to the lock-in amplifier and the digital output of the lock-in (converted into a digital signal by an in-built analogue to digital convertor) was input to the IBM PC XT machine. The laser light transmission was monitored by placing a Photo Multiplier Tube (PMT) at the rear of the diode detector. The PMT output pulse was then fed into a pulse integrator and box car averager unit, which filtered the signal from noise and then after analogue to digital conversion (by the same ADC inbuilt to the lock-in) it was also input to the same IBM PC by the same lock-in computer interface (SRS 232). The block diagram of the system is shown in the Figure 8.1.

8.2 Lock-in Technique

A Lock-in amplifier is most commonly used to measure very small a.c. signals buried in the noise. It can make accurate measurements of small signals even when the signals are obscured by noise which may be a thousand times larger. Essentially a lock-in has the function of a high Q band pass filter and a high gain amplifier. In addition, the amplification acts only on a constant phase relative to the reference and therefore any noise with random phase is eliminated even at the reference frequency. Fig 8.2 shows the basic circuit of the lock-in amplifier.

The Lock-in used in these experiments is a dual phase lock-in amplifier (Model SR530) made by Stanford Research Systems. The lock-in was triggered by the synchronous output pulse of the laser power supply. The repetition rate was ~ 16 Hz, corresponding to the minimum interval possible between pulses from the detector. To avoid distortion of the trigger pulse by the electronic noise, the signal was carried by optical fiber. The trigger pulse was 15 V and 15 μ s duration—suitable to trigger the lock-in.

The Lock-in output was a near dc voltage corresponding to the amplitude of the 16 Hz pulses. By choosing a 100 ms low-pass filter, a smooth signal output was obtained. An in-built analogue to digital converter (ADC) converted the signal which was then stored in an IBM PC through a lock-in computer interface (SRS 232).

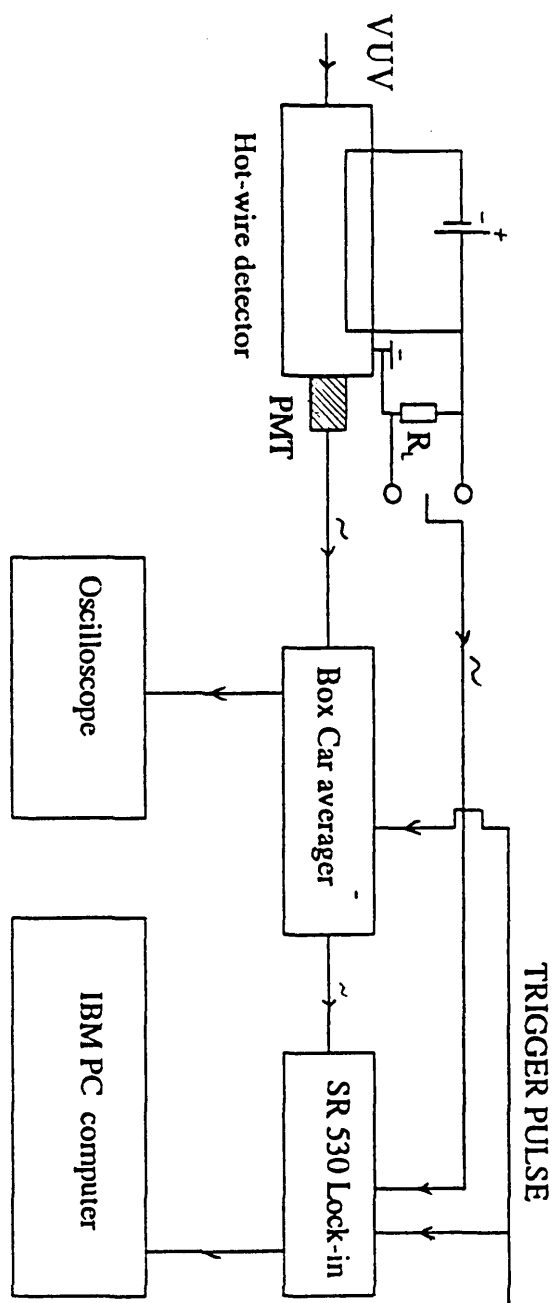


Figure 8.1: Data acquisition system used in the present experiments

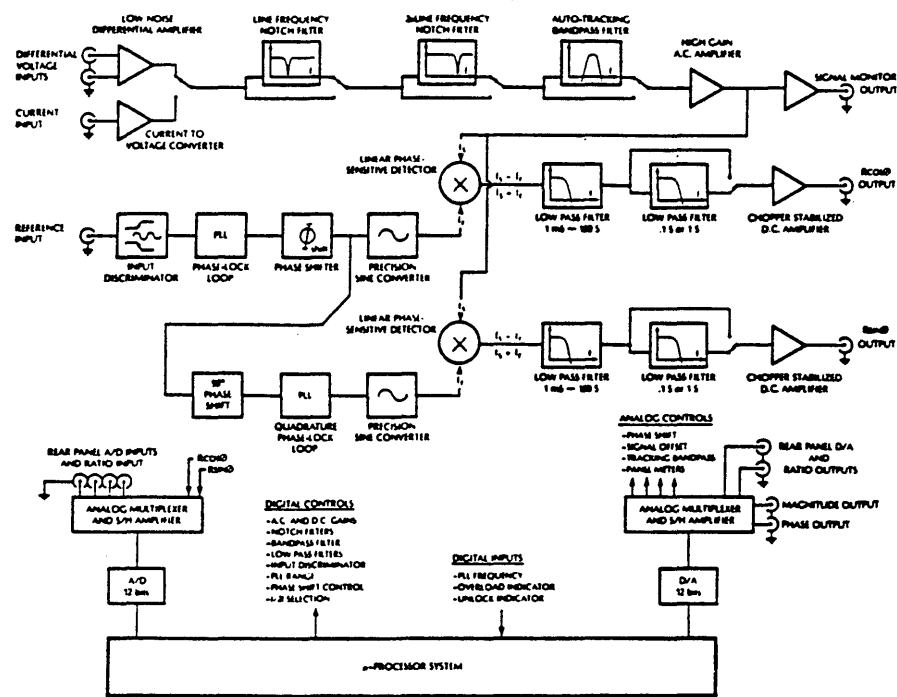


Figure 8.2: Lock-in amplifier circuit diagram

8.3 Laser Beam Monitoring

Laser light signal transmission through the diode was monitored by attaching a photomultiplier tube (PMT) to the rear of the diode. The monitoring served three purposes: first, to detect shot to shot fluctuations of the VUV intensity, second, to look for opacity effects, and third, to record the VUV signal for the data normalization.

8.3.1 Working Principle of PMT

Detectors used with lasers can be divided into two general categories: *thermal detectors* , which produce a response when heated by the absorption of radiation, and *quantum detectors* , which produce an electrical signal di-

rectly through the production of charge carriers (electrons or electron-hole pairs) by absorption of the light photons. With both thermal and quantum detectors, the response at a particular wavelength is proportional to the number of received photons. Since quantum detectors depend on the excitation of atoms to well defined energy levels, the energy of the exciting photons must be greater than the gap energy ($h\nu > \Delta E$) for operation of the detector. Thermal detectors on the other hand, respond to the total absorbed energy and do not exhibit a threshold wavelength for operation. Thermal detectors thus cover a wider range of wavelengths, but they are neither as fast nor as sensitive as quantum detectors.

Photomultiplier falls in the category of quantum detectors. They are especially appropriate when both high sensitivity and good response over a wide frequency bandwidth is required. The operation of the Photomultiplier is based on the photoelectric effect. Light incident on a metallic surface, called photocathode, can eject electrons from the surface. The lower the work function of photocathode, the longer the wavelength of the radiation the photomultiplier can detect. Although a single photocathode can act as a detector, at low radiation levels the current produced is extremely small to be conveniently processed and must consequently be amplified. This amplification is achieved by the photomultiplier tube itself. Electrons emitted from photocathode are accelerated by an applied voltage to a secondary electrode called *dynode*. The dynode emits several electrons for each electron that strikes it, thereby providing current amplification (Fig 8.3). These secondary electrons are then accelerated towards another dynode, and the process repeated. Each dynode is held at a positive potential with respect

Make:	EMI
Type:	G-26E314LF
Photocathode:	CsI
Window:	MgF
No. of Dynodes:	14 (Linearly Focussed)
Q.E.	12% at 130 nm
	1% at 180 nm
	8% at 160 nm
Spectral Range:	110-220 nm
Max Anode voltage	3500 V
Gain at 2500 V	10 ⁶
Gain at 2900 V	10 ⁷
Dark Emission (at 10 ⁶ Gain)	<0.01-0.1 nAmp

Table 8.1: General characteristics of the PMT employed to detect VUV radiation

to the dynode preceding it by means of a large voltage applied across a chain of resistors. A final anode collects all the electrons emitted from the last dynode. The current amplification achieved in typical PMT is on the order of 10^6 . Incident powers as low as 10^{-19} Watts can be detected using photomultipliers whose photocathodes have been cooled to reduce thermal noise.

In the present work, a solar blind photomultiplier tube detected the VUV radiation. The photomultipliers employed were an EMI G-26E314LF with a CsI photocathode. The general characteristics of the PMT are listed in the table 8.1.

The PMT output was integrated by a box-car integrator and averager (Stanford Research Corp. Model SR 250). A few layers of fine mesh were

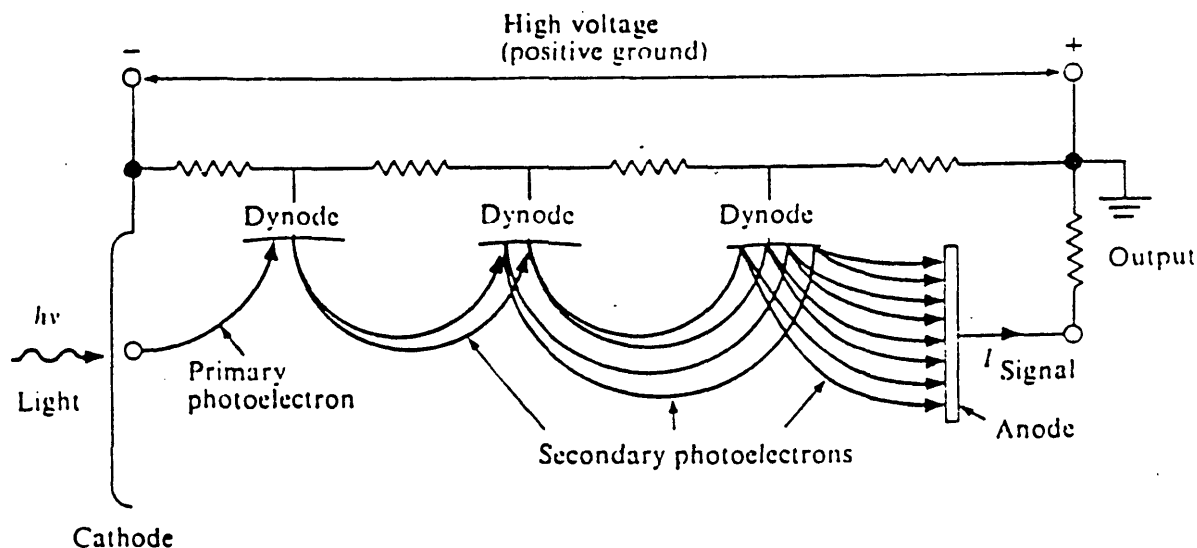


Figure 8.3: Circuit diagram of the PMT

placed before the photocathode to avoid saturation due to the intense VUV radiation beam.

8.4 Box-car Technique

The gated integrator is a versatile, high speed module which can recover fast analogue signals from a noisy background. Since the PMT output signal was a sharp 15 ns pulse, we decided to integrate it by a box car integrator. A box car consists of a gate generator, a fast gated integrator and an exponential averaging circuit. The gate generator was triggered synchronously with the lock-in by the same trigger pulse. The delay was adjusted to 100 ns, the continuously adjustable gate was opened for a 30 ns duration. A computerized oscilloscope (Lecroy Model 4900) was used to monitor both

the gate and the PMT output. The fast gate integrator integrated the input signal during the gate. The gate output was then normalized by the gate width, and the output voltage signal was thus proportional to the average of the input signal. This output was amplified by a factor of 2 and sampled by a low droop sample and hold amplifier (in-built to the SRS250). The output thus provided shot to shot measurements of the VUV radiation. The analogue signal was converted into a digital one by the same ADC (in-built to the lock-in), and simultaneously stored into the same IBM PC by the lock-in computer interface (SRS232).

Both the hot-wire signal (through lock-in) and the monitor signal are simultaneously recorded during each scan. Files are stored in the computer and then digital data is filtered and normalized as discussed in chapter 12.

Chapter 9

Tunable VUV Generation

9.1 Introduction

The generation of coherent, tunable, narrow bandwidth vacuum ultraviolet (vuv) radiation by frequency mixing in gases and vapors is now a well known technique. Since the earlier work of Ward and New^{37,38} and Young *et al*³⁹ there have been many efforts to develop new mixing schemes with both increased conversion efficiency and greater tuning range. Four-wave mixing refers to nonlinear processes with four interacting electromagnetic waves. At the Blackett laboratory laser consortium, a narrow band, tunable VUV radiation source has been developed⁸² by sum-difference frequency mixing ($\omega_{VUV} = 2\omega_R - \omega_T$) in krypton gas. Before going into the details of the experimental setup for four-wave mixing, there is a need to review nonlinear optics. This chapter includes a comprehensive background of the

early achievements in this field. A separate section describes the theory of four-wave mixing with the special emphasis on the sum-difference mixing scheme, currently employed in the present work. Experimental details are described at length, starting from the description of the lasers being involved in the generation of VUV radiation.

9.2 Early Background

Harmonic generation in gases was first reported by New and Ward^{37,38}, and by Rado⁶⁷. In these early works, the conversion efficiencies were very low. However, after that, extensive research has taken place and several comprehensive reviews are now available^{68,69}. Harris and coworkers⁷⁰ showed that phase-matching in gases can be achieved by a suitable mixture in which one component has been selected according to its nonlinear susceptibility, while the other component has to provide the appropriate overall refractive index for phase-matching of the gas mixture, and thus overall conversion efficiency can be enhanced by several orders of magnitude. Latter, Bloom *et al*⁷¹, Hodgson *et al*⁷², and Leung *et al*⁷³ demonstrated that the efficiency can further be raised by exploiting a two-photon resonance enhancement of the nonlinear susceptibility.

Peak power of about 400 Watts at the wavelength of the Lyman Alpha line has been reported by Langer *et al*⁷⁴, from nonresonant harmonic generation in phase-matched Krypton Argon mixtures, using high power dye lasers. Hilbig and Wallenstein^{75,76} have achieved powers as high as 0.5—3

KW, by two-photon resonant sum and difference frequency mixing in mercury, covering selective spectral regions between 109 and 196 nm. Hilber *et al* ⁸¹ used krypton gas as the nonlinear medium and by two-photon resonance enhancement were able to generate VUV up to 127 nm.

Similarly, work is also carried out by CW (continuous wave) lasers. The first CW setup was reported by Freemann *et al* ⁷⁷, who achieved a two-photon resonant enhancement of the nonlinear susceptibility by applying large magnetic fields to a strontium-xenon mixture. They tuned the nonlinear medium into resonance with the incident CW laser beams by means of a superconducting solenoid. CW lasers up until now have achieved small conversion efficiencies (in the range of 10^{-12} — 10^{-11}) and thus pulsed lasers are the favoured choice now-a-days.

9.3 Four wave frequency mixing (sum-difference) theory

Generally, the domain of nonlinear optics is understood to encompass those phenomena for which the electric and magnetic field intensities of higher powers than the first play a dominant role. The usual classical treatment of the propagation of light—superposition, reflection, refraction and so on—assume a linear relationship between the electromagnetic light field and the responding atomic system constituting the medium. However, an extremely intense beam of coherent light can generate appreciable nonlinear optical effects. The electromagnetic field of a light wave propagating through a

medium exerts forces on the loosely bound valence electrons. Ordinarily these forces are quite small, and in a linear isotropic medium the resulting polarization P^L is parallel with and directly proportional to the applied field.

$$P^L = N\chi^{(1)}E \quad (9.1)$$

where N is the number density of atoms and the proportionality constant $\chi^{(1)}$ is the complex linear susceptibility.

$$\chi^{(1)} = \frac{1}{\hbar} \sum_a \frac{|\mu_{ag}|^2}{(\Omega_{ag} - \omega)} \quad (9.2)$$

where μ_{ag} is the dipole matrix element for transition between state $|g\rangle$ and state $|a\rangle$, and $\Omega_{ag} = \omega_{ag} - i\Gamma_{ag}$ is the corresponding complex transition frequency containing the damping constant Γ .

Quite obviously in the extreme case of a very high field, one can expect that P will become saturated; in other words, it cannot simply increase linearly and indefinitely with E . Thus one can anticipate a gradual increase of the ever-present, but usually insignificant, nonlinearity as E increases. Thus higher-order nonlinear terms in the electric field have to be included. They may be incorporated by an additional nonlinear correction which can be given as a series expansion

$$P^{NL} = \sum_2^{\infty} P^{(n)} \quad (9.3)$$

The n th order terms $P^{(n)}$ in Eq 9.3 are given as⁶⁸

$$P_{(\alpha_s)}^{(n)}(r, \omega_s) \propto \sum_{\alpha_1 \cdots \alpha_n} \chi_{\alpha_s \alpha_1 \cdots \alpha_n}^{(n)}(-\omega_s; \omega_1 \cdots \omega_n) E_{\alpha_1}(r, \omega_1) \cdots E_{\alpha_n}(r, \omega_n) \quad (9.4)$$

The indices α_n are Cartesian subscripts (x,y or z). P and E are vector quantities and so in general $\chi^{(n)}$'s are tensors. The nonlinear optical tensors are key quantities of nonlinear optics characterising the nonlinear response of the medium to the simultaneous interaction with different incident waves. These tensors can be determined by quantum mechanical time-dependent perturbation treatment of the nonlinear medium, where one is interested in the expectation value of the field induced polarization.

$$\langle P(t) \rangle = N_t \sum_{mn} \rho(t) \mu_{mn} \quad (9.5)$$

where $\mu = er$. N_t is the total number of interacting particles, μ is the dipole moment operator. ρ 's are the density matrix elements. P is the macroscopic observable related to the effect of E field on a medium.

The most important nonlinear susceptibilities for consideration at present are the $\chi^{(3)}$ terms characterizing a four-wave interaction with the medium, which is the lowest-order nonlinearity of the gaseous media. Similarly to nonlinear crystals with a center of symmetry such as calcites, the even-order terms $\chi^{(2)}$, $\chi^{(4)} \dots$ generally vanish for the isotropic gaseous media, because the nonlinear polarization must be unaffected by reflection of the coordinate system at the origin.

9.3.1 Third Order Processes

In the light of above discussion, the only nonlinear polarization to be considered is

$$P^{(3)} = N\chi(3)(-\omega_4; \omega_1\omega_2\omega_3)E_1E_2E_3 \quad (9.6)$$

as all other nonlinear polarizations are assumed to be negligible, Eq 9.6 represents the polarization induced by three fields of strengths E_1, E_2, E_3 and frequencies $\omega_1, \omega_2, \omega_3$ respectively. This polarization is related to the field at frequency ω_4 by differential equation (derived from the Maxwell's equations)

$$\frac{dE}{dz} = i \frac{2\pi\omega_4}{cn_4} P^{(3)} \exp(-ikz) - \frac{\kappa_4}{2} E_4 \quad (9.7)$$

The second term on the R.H.S. is due to absorption at the generated frequency and κ is the absorption coefficient. Substitution of Eq 9.6 into Eq 9.7 shows how E_4 is related to the E_1, E_2, E_3 . The fields are being coupled together by $\chi^{(3)}$ (i.e. the atom) to produce a fourth field. In general $\omega_4 = \omega_1 \pm \omega_2 \pm \omega_3$. For collinear incident beams within the plane-wave approximation, we get from Eq 9.7

$$\frac{dE_4}{dz} = i \frac{3\pi\omega_4}{cn_4} N \chi^{(3)} E_{10} E_{20} E_{30} \exp\left[\left(-\frac{\kappa_1 + \kappa_2 + \kappa_3}{2} - i\Delta k\right)z\right] - \frac{\kappa_4}{2} E_4 \quad (9.8)$$

where $\Delta k = K_4 - (K_1 + K_2 + K_3)$ (wave-vector mismatch for frequency tripling)

and $\Delta k = K_4 - (K_1 + K_2 - K_3)$ (wave-vector mismatch for sum-difference mixing). If we define the optical depth τ_j as

$$\tau_j = \kappa_j L = \sigma_j(\omega_j) N L \quad (9.9)$$

where L is the length of the nonlinear medium and $\sigma_j(\omega_j)$ is the one-photon absorption cross-section at the frequency ω_j , Then the total optical depth for all incident waves is

$$\tau_i = \tau_1 + \tau_2 + \tau_3 \quad (9.10)$$

then Eq 9.8 after integration gives

$$E_4(L) = i \frac{3\pi\omega_4}{cn_4} N \chi^{(3)} E_{10} E_{20} E_{30} \exp(-\frac{\tau_4}{2}) [\frac{\tau_4 - \tau_i}{2} - i\Delta k L]^{-1} \times [\exp(\frac{\tau_4 - \tau_i}{2} - i\Delta k L) - 1] \quad (9.11)$$

Now by replacing the electric field amplitude E by the intensity I ($I = n_j c |E_j|^2 / 8\pi$) one gets

$$\frac{I_4}{n_4} = [\frac{24\pi^2\omega_4}{c^2 n_4} N L \chi^{(3)} (-\omega_4 : \omega_1 \omega_2 \omega_3)]^2 \frac{I_{10} I_{20} I_{30}}{n_1 n_2 n_3} F(\Delta k L, \tau_i, \tau_4) \quad (9.12)$$

where F is the phase-matching factor given as

$$F(\Delta k L, \tau_i, \tau_4) = \frac{\exp(-\tau_i) + \exp(-\tau_4) - 2\exp[-(\tau_i + \tau_4)/2] \cos(\Delta k L)}{[(\tau_4 - \tau_i)/2]^2 + (\Delta k L)^2} \quad (9.13)$$

This result was first reported by Bey and co-workers^{41,42}.

According to Eq 9.13, the phase-matching factor F depends on three variables which one tries to optimise in order for F to approach maximum value of unity. In the small absorption limit, F has the form

$$F(\Delta k L, \tau_i = 0, \tau_4 = 0) = [\frac{\sin(\Delta k L/2)}{(\Delta k L/2)}]^2 \quad (9.14)$$

Thus, in the small absorption limit, F shows strongly oscillatory behavior as a function of distance in the cell. This is due to constructive and destructive interference. For an optically thick medium with $\tau_4 \gg 1$, or $\tau_i \gg 1$, the minima of the distribution fill up and one obtains a Lorentzian profile for the phase-matching factor

$$F(\Delta k L, \tau_i \gg 1, \tau_4 \ll 1) = F(\Delta k L, \tau_i \ll 1, \tau_4 \gg 1) = \frac{1}{[(\tau_4 - \tau_i)/2]^2 + (\Delta k L)^2} \quad (9.15)$$

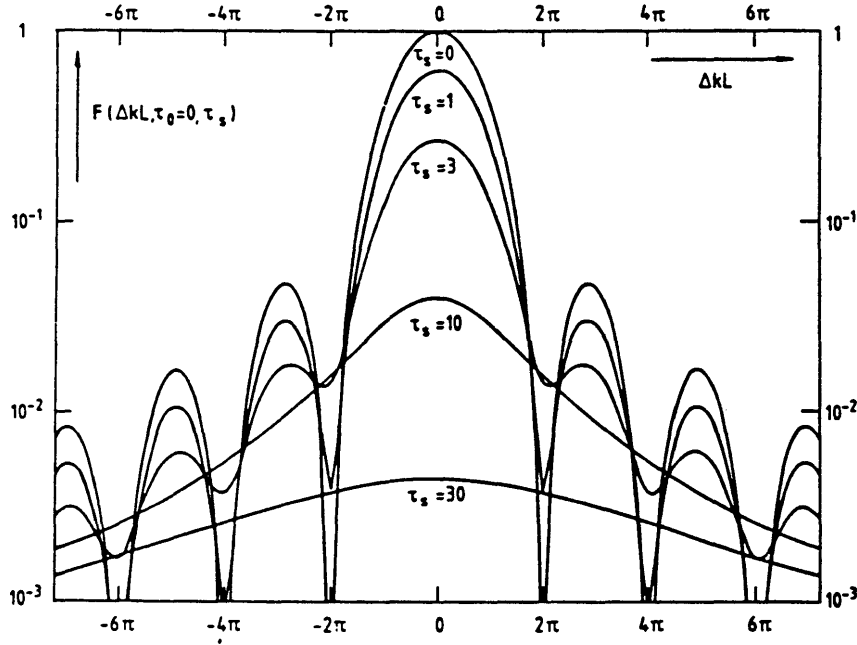


Figure 9.1: Phase-matching factor as a function of optical depth

For practical applications, it is generally not very difficult to keep the incident waves away from resonance with any electric-dipole allowed transition of the nonlinear medium, such that $\tau_1 \ll 1$, $\tau_2 \ll 1$, $\tau_3 \ll 1$ and hence $\tau_i \ll 1$. In Fig 9.1 the phase-matching factor is plotted for $\tau_i = 0$ and for different values of τ_4 as a parameter.

9.3.2 Gaussian beams

In order to raise the conversion efficiency of a nonlinear medium, one frequently focuses the incident laser beams to increase the intensity. However, focusing is only advantageous as long as higher-order nonlinearities do not reduce the conversion efficiency. For focused beams the plane-wave approximation is no longer valid and the incident beam has to be described by a Gaussian intensity distribution. Assuming a TEM_{00} -mode, which among all possible modes provides the highest intensity for a given input power, one has

$$E_j = E_j(r, z) \frac{b}{b + i2z} \exp\left(\frac{-k_j r^2}{b + i2z}\right) \exp(ik_j z) \quad (9.16)$$

with

$$b = \frac{2\pi W_0^2}{\lambda} \quad (9.17)$$

where b is the confocal parameter and W_0 is the beam waist $W_0 = f\theta$, f is the focal length of lens and θ is the beam divergence. In the plane wave approximation $b \rightarrow \infty$. $b/2$ is the distance from the center of the beam waist over which the beam area doubles. It also corresponds to the region of the focus over which the focussed beam changes its phase by π radians. In order to understand the effects of focusing on the phase-matching curves, absorption effects are neglected for the moment. Since we are mainly interested in the situation where the phase-matching condition is already closely satisfied, one can, to a good approximation consider $\Delta k \ll k_j$. Assuming that all the beams have same confocal parameters, one can find the expression for the

driving polarization at ω_4 . For sum-difference mixing $\omega_4 = \omega_1 + \omega_2 - \omega_3$

$$P_4(r) = \frac{3}{2} N \chi^{(3)}(-\omega_4; \omega_1, \omega_2, -\omega_3) E_{10} E_{20} E_{30} B(z) \times e^{(ik'z)(1+i\xi)^{-2}(1-i\xi)^{-1}} \exp\left[\frac{(-k'' + i\xi k')(x^2 + y^2)}{b(1 + \xi^2)}\right], \quad (9.18)$$

where $k' = k_1 + k_2 - k_3$ and $k'' = k_1 + k_2 + k_3$. x , y , and z are the Cartesian coordinates. $\xi = \frac{2(z-f)}{b}$ is a reduced coordinate in the z -direction where the focus is at $z = f$.

$$B(z) = 0 \text{ for } z < 0 \text{ and } B(z) = 1 \text{ for } z > 1.$$

In the expression for the electric field $E_i \sim \exp(ik_i z)$, $i = 1, 2$. and $E_3 \sim \exp(-ik_3 z)$.

To derive an expression for $E_4(r)$ from this via equation 9.18, it is necessary to perform a uniform Fourier decomposition of $P_4(r)$ into plane-wave components. The E_4 field for each component can then be found and the total electric field $E_4(r)$ can be obtained by summing over all these components. Thus, for sum-difference mixing we have

$$E_4(r) = i \frac{3N\pi k_0^2}{2k_4} b \chi(-\omega_4; \omega_1, \omega_2, -\omega_3) E_{10} E_{20} E_{30} \exp(ik'z) \times \int_{-T}^{\xi} d\xi' \exp\left(\frac{[ib/z]\Delta k(\xi - \xi')}{(1 + i\xi')(k'' - ik'\xi')H}\right) \exp\left(\frac{-(x^2 + y^2)}{bH}\right) \quad (9.19)$$

where

$$H = H(\xi, \xi') = \frac{1+\xi'^2}{k''-ik'\xi'} - i \frac{\xi'-\xi}{K'} \quad \xi = \frac{2(L-f)}{b}, \quad T = \frac{2f}{b}, \quad (\text{corresponding to the entrance and exit windows of the mixing cell}).$$

The equation 9.19 describes the amplitude of the generated field at the output window, i.e. at $z = L$.

Unless $k' = k''$, $E_4(r)$ is not a lowest order Gaussian beam, but rather a multimode output results. The total generated intensity derived from the amplitude is

$$I_4 = \int_0^\infty 2\pi r |E_4(r)|^2 dr \quad (9.20)$$

Thus

$$I_4 = C \frac{k_0^4 k_1 k_2 k_3}{k_4^2 k'} N^2 \chi^2 I_1 I_2 I_3 \times F(b\Delta k, b/L, f/L, k''/k') \quad (9.21)$$

where

$b\Delta k$ = Confocal parameter $\times$ wave vector mismatch

b/L = Confocal parameter per length of the cell.

f/L = Lens focal length per length of the cell.

F is the phase-matching factor, originating in the integration over the z -coordinate in the evaluation of the E_4 components in equation 9.19. Now in the tight focussing condition, $b/L \ll 1$, for the sum-difference mixing case

$$F(b\Delta K, 0, 0.5, 1) = \pi^2 \exp[-b |\Delta k|] \text{ for } 0 \geq \Delta k > 0 \quad (9.22)$$

In the sum-difference process there is an automatic phase-matching, which is maximized if $b\Delta k = 0$.

The power of the VUV radiation is given by the relationship

$$P_{VUV} \propto P_R^2 P_T N^2 \chi^2 F, \quad (9.23)$$

where P_R and P_T are the powers of the resonant and tunable radiation, respectively, N is the number density of the nonlinear atoms, and χ is the third order nonlinear susceptibility. F , the dimensionless phase-matching function depends on the wave-vector mismatch, $\Delta k [= k_{VUV} - (2k_R - k_T)]$, the confocal parameters of the incident beams, b_R and b_T , and the focussing conditions.

If the phase mismatch per atom C is defined by $C = \Delta k/N$, then the generated power is given by $P_{VUV} \propto N^2 \exp(-b_R C N)$, a function that peaks when $N = 2/b_R C$. By changing the gas pressure to achieve optimal N , the VUV output can be maximized for any given b .⁷⁶

9.4 Experimental Setup For the VUV Generation

9.4.1 Nonlinear Medium Used

At the Blackett laboratory laser consortium, narrow band tunable VUV is generated by exploiting the two-photon resonance enhancement of nonlinear susceptibility in krypton gas, using sum-difference frequency mixing. The scheme employed by Hilber et al⁸¹ had a short wavelength limit of 127 nm. In the present source the $4p - 5p[1/2, 0]$ two-photon resonance at 212.55 nm

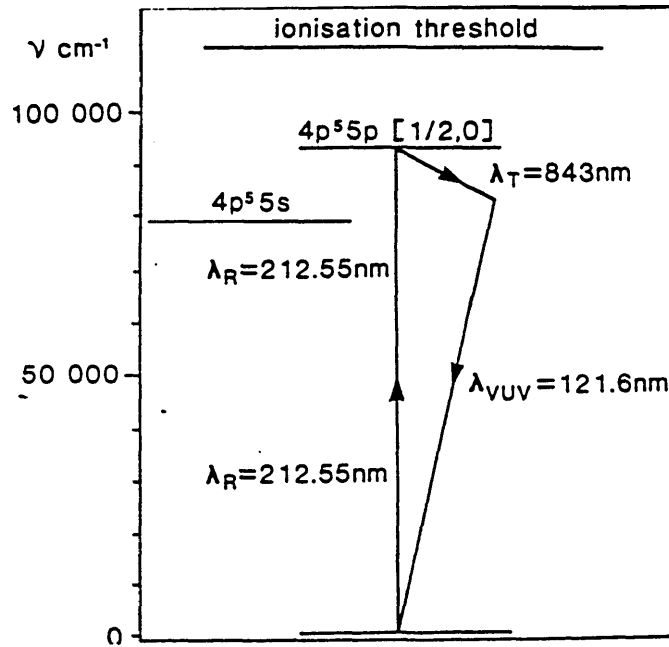


Figure 9.2: Partial energy level scheme for Kr, showing resonance enhanced sum-difference mixing to generate VUV radiation.

is used (as suggested by Hillber et al in Ref 81), thus extending the short wavelength limit to 121 nm (Fig 9.2). This means that the spectroscopically important H Lyman- α line (121.6 nm) is accessible in this scheme. While one laser is tuned to the two-photon resonance in Krypton ($\omega_R = 212.55 \text{ nm}$), the other can be scanned over a continuous wavelength range from 220 to 870 nm, the short-wavelength end of the range being extended by frequency doubling. This was sufficient for generating VUV wavelengths of 121–190 nm.

9.4.2 Laser system

The laser system used in these experiments consists of two identical Lambda-physik dye lasers (FL 3002) synchronously pumped by a Lambda-physik excimer laser (EMG 201 MSC). The dye lasers are tunable from 360 to 870 nm with pulse energies of 6 - 30 mJ. The band-width was 5 GHz, which can be reduced to 1.5 GHz with an intracavity etalon. The XeCl excimer pump laser can be operated to a maximum repetition rate of 80 Hz. This section presents a brief description of each laser involved in the experiment.

Excimer Laser

Excimer lasers are the most commonly used fixed wavelength, pulsed lasers for pumping a wide range of dyes, which can lase in a continuous range of wavelengths from IR to the UV. The short wavelength end of the range can be extended by frequency doubling of the dye laser output. Table 9.1 shows a range of excimer outputs that can be achieved with different halide—inert gas combinations.

The excimer laser used in our experiments is a XeCl laser with an output of 308 nm. The Lambda-physik EMG 201 MSC excimer laser can be operated up to a maximum repetition rate of 80 Hz. The output is an unpolarized, multimode laser pulse of 20 ns duration, with a typical pulse energy of 600—800 mJ (depending on the quality of gases in the laser, maximum is attainable when fresh gases are filled). Average pulse power is 30 MW.

The intensity after the first 5000 shots drops to 70%. Synchronous output from the power supply unit can trigger the data acquisition system.

Tunable Dye Lasers

Tunable dye lasers are in use for a multitude of applications in most research laboratories worldwide. These systems range from 10 Hz pulsed dye lasers to the ultranarrow line-width CW dye lasers. Dye lasers can be tunable or fixed depending upon the ability to change the cavity length either by moving the grating or by rotating the end mirror.

Many different designs for pulsed laser cavities are commercially available today. Almost all of these are based on the principles set out by Hansch⁷⁸ in 1972. Broadly speaking, commercially available systems fall into two categories—those utilizing a Littrow grating configuration and those utilizing a grazing incidence grating configuration.

Littrow grating configuration

The Littrow (or retro-reflective) grating configuration in its basic form is illustrated in Fig 9.3. It consists of a transversely pumped dye cell, an output coupler and a grating with associated beam expanding optics, where prisms have now replaced the telescope as the beam expanding component. The prism is also responsible for the polarization of the output. The grating acts as both the laser cavity rear reflector and the tuning element. One

Gas mixtures for EMG 201 - 203 MSC								
Active Medium	F ₂	ArF	KrCl	KrF	XeCl	N ₂	XeF	
Wavelength	157	193	222	248	308	337	351	nm
Helium (99.995 %)	2650	1410	1720	2300*	----	960	2570	mbar
Neon (99.99 %)	----	----	----	----	2760 ⁺	----	----	mbar
Argon (99.995 %)	----	270	----	----	----	----	----	mbar
Krypton (99.99 %)	----	----	200	120	----	----	----	mbar
Xenon (99.99 %)	----	----	----	----	60	----	10	mbar
5 % Fluorine (99.9 %) diluted in He	50	120	----	80	----	----	120	mbar
5 % HCl (99.995 %) diluted in He	----	----	80	----	80	----	----	mbar
Nitrogen (99.99)	----	----	----	----	----	40	----	mbar
Total pressure	2700	1800	2000	2500	2900	1000	2700	mbar
Number of fillings before replacement of halogen filters	50	25	75	35	75	----	25	

* Instead of Ne, He may be used. This will reduce the output power by approx. 40 %

* The use of Ne instead of He will increase the laser output.

Table 9.1: Excimer laser output wavelengths attainable with different gas combinations

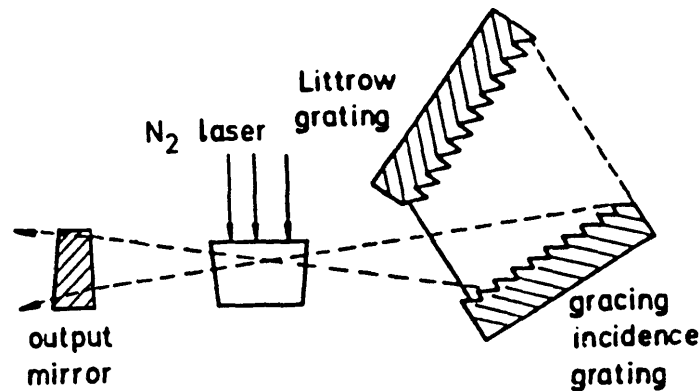


Figure 9.3: Littrow grating configuration

of the advantages of this type of design is the high efficiency of the tuning element and the ease of alignment. The line-width of the dye laser output is not as narrow as that which is achievable with grazing incidence design. The line-width can be reduced by insertion of a synchronously scanned etalon into the cavity.

Apart from the line-width, another important aspect of performance is the Amplified Spontaneous Emission (ASE) background in the output. One way of reducing this ASE background is to take the reflection from the beam expander prism face and reflect it from the grating once more before it leaves the oscillator, usually to an amplifier stage. This design was patented by Lambda physik GmbH and is known as "Lambda-pure^(R) filter." It reduces the ASE background to less than 10^{-3} of the final output.

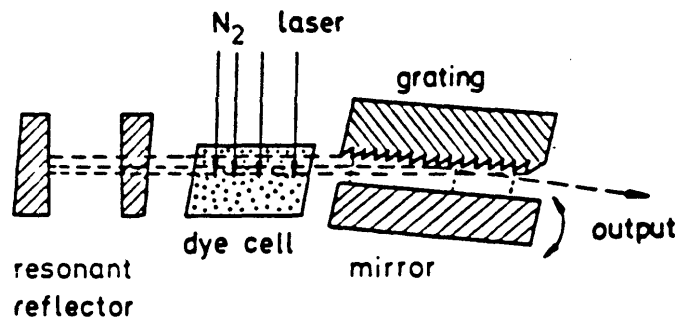


Figure 9.4: Grazing incidence design

The grazing incidence design

The grazing angle design was independently developed at approximately the same time by Littman⁷⁹ and Shoshan⁸⁰. The configuration is illustrated in Fig 9.4. The line-width that can be achieved depends on the number of grating lines that are illuminated. In the Littrow configuration the number of lines illuminated can be increased by expanding the beam in one dimension to fill the grating. In the grazing incidence configuration, the grating is rotated to an angle close to 90° (between 89° and 89.5°) such that the unexpanded beam fills the grating. A plane mirror is then added to reflect a particular wavelength back to the grating. To tune the laser, the mirror is rotated about an axis through the center of the grating, whilst the grating itself remains stationary.

The principal advantage of the grazing incidence design is that the narrow line-width output is achieved without the need for an intracavity etalon. It simplifies a smooth tuning over a broad range. Despite these advantages, grazing incidence can suffer from several problems. Whilst these problems are not insurmountable, they do need careful attention in any grazing incidence design:

1. The overall efficiency of the tuning element is quite low (a few percent). This is not a problem in the oscillator/amplifier configurations, where the overall efficiency is not strongly dependent on the oscillator efficiency.
2. The long and short term frequency stability is liable to be low. This is overcome by careful design of the critical components.

The dye lasers used in the experiments (Lambda-physik FL 3002) have Littrow configuration—Lambda-pure^(R) design. The system description is further divided into the following categories : a general layout of the system and the pump-beam path, description of the oscillator and its beam path, and finally the main amplifier.

1. General layout and pump-beam path.

Fig 9.5 presents a general layout of the dye laser system. The pump beam from the excimer laser enters the dye laser through a shutter, controlled by an interlock switch. The beam then passes a beam-shaping lens for EMG pumping. In addition, the lens mount carries the swing-in attenuator. The pump-beam then goes through the oscillator beam splitter, where a small fraction of the pump-beam is split-off and reflected towards the oscillator/preamplifier cuvette. The split off beam for the oscillator has

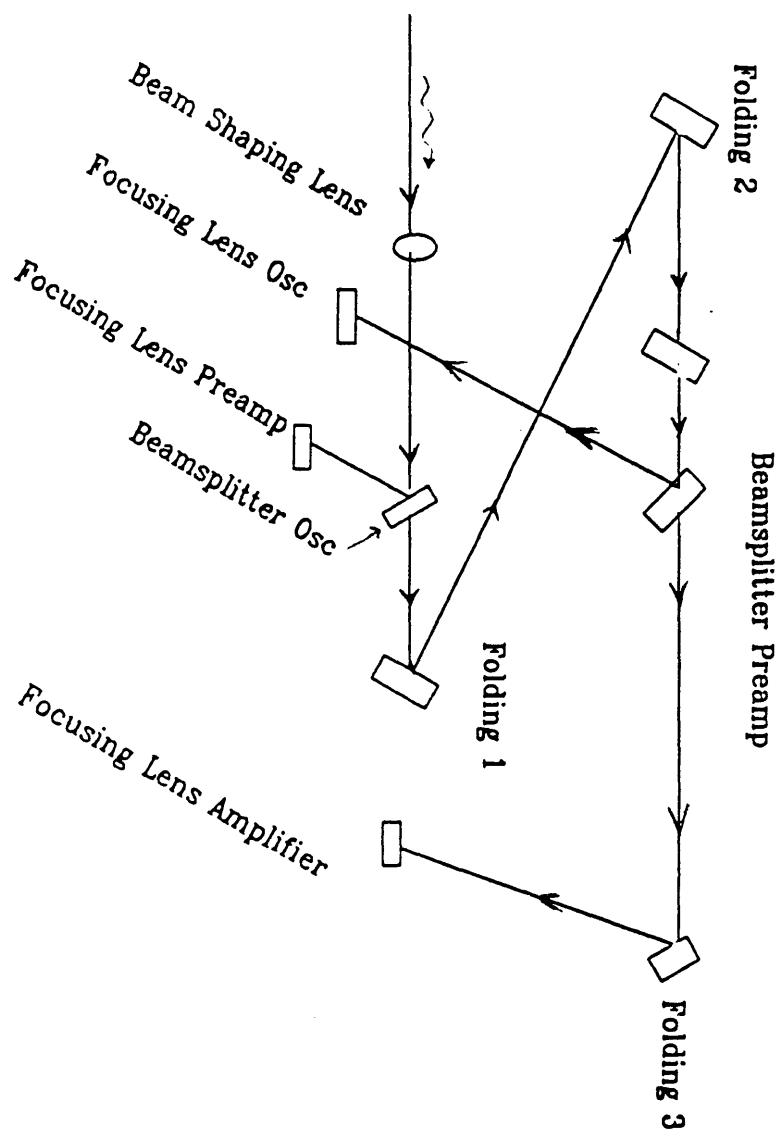


Figure 9.5: General layout of the dye laser FL 3002

predominantly vertical polarization. The remaining beam continues on its path and hits the folding mirror 1, and is folded back and falls on the folding mirror 2, slightly higher than 1. From mirror 2 beam one again runs parallel to the table but slightly higher. When the beam crosses the pre-amplifier beam splitter, 10% of the pump beam is split off and reflected towards the oscillator/pre-amplifier cuvette. The delay between the pump-beam for the oscillator and the pump-beam for the pre and main amplifier is 4 ns. This delay ensures that tuned photons are available to the amplifiers before they are pumped. This time delay plays an important role in reducing the ASE. Lastly, the pump-beam hits the folding mirror 3 and is completely deflected by 90° towards the main amplifier.

The oscillator and pre-amplifier beams are focussed into the dye-flow cuvette by cylindrical lenses with focus line closely behind the pump window. The focus of the pump-beam in the main amplifier is behind the cuvette, because focusing the pump-beam at the pump window results in the immediate damaging of the cuvette.

2. The oscillator unit.

As discussed previously, the laser (FL 3002) has a Littrow configuration. The grating has 600 lines/mm, 2.7 micron blaze. It can be tilted between Littrow angles of $(42.5^\circ - 72.5^\circ)$, and can be used in the third to eighth order (in our experiments, it was in fourth and fifth order). The laser tuning (wavelength linear tuning) is achieved by tuning the grating angle by a motor controlled sine drive. The lead screw of the sine drive is driven by a stepper motor and a gear box using non-slip belts. Laser tuning is limited by the dye

used. A typical bandwidth is 5 GHz, which can be reduced to 1.5 GHz by inserting a synchronously scannable intracavity etalon (also available with the laser system). When this dye laser is pumped by a XeCl excimer laser ($\lambda_{pump} = 308nm$), it can scan through a wavelength range of 332—970 nm by changing dyes. Wavelength accuracy is up to 1 Å (i.e. the accuracy of the scale reading), and wavelength reproducibility is $\pm 6.3 \text{ mÅ}$. The prism-beam expander consists of a set of five prisms on a platform. The magnification is 66 $\times$. The prism-beam expander acts as a 20:1 polarizer in favour of vertical polarization. The tuning block (which encloses the grating, prism-beam expander, and the intracavity etalon) can be sealed to achieve pressure tuning. The beam path is sealed by a Brewster's window. The monitor reflex is an important criterion for oscillator alignment and performance, since it is a reduced image of the expanded beam on the grating surface and appears only if the oscillator is working. It disappears if the grating is partially covered, and the covered area appears as a dark zone in the monitor reflex. The end mirror mount carries a mirror with three dielectric coatings, which can be shifted into position for a certain wavelength range. The system arrangement is shown in Fig 9.6.

3. The beam path.

The oscillator beam-path runs between the cavity end mirror, through the dye cell, and into the prism beam-expander. Inside the prism beam-expander the beam is expanded vertically. The expanded beam then leaves the expander as a light ribbon falling onto the grating perpendicular to the grooves. For a beam-path wavelength matching the Littrow condition

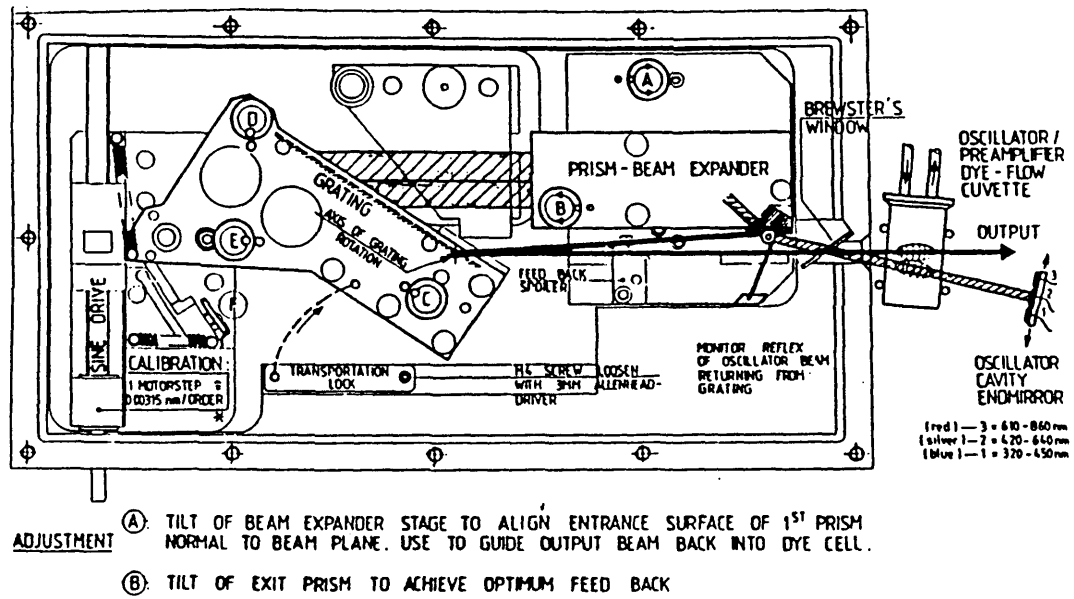


Figure 9.6: Dye laser setup

$\lambda_0 = 2(\sin \alpha)/(K \times N)$, light is reflected back, following the incoming path through the beam-expander and the pump region onto the end mirror. In the above equation, K is the grating constant of 600 lines/mm, and N is the grating order used.

The beam-expander is needed to reduce the band-width of the oscillator radiation, which is a function of the divergence $d\beta$ of the oscillator and the angle—determined by the Littrow condition at which the grating is used: $d\lambda = d\alpha \times \lambda_0/2$. The beam-expander reduces the acceptance angle $d\alpha$ by its magnification M ; $d\alpha = d\beta/M$. Only the magnification in the plane of diffraction is needed. Thus photons maintain a continuous travel back and forth through the pump region.

The oscillator output is derived from the reflection of the oscillator beam at the entrance prism. 25% of the oscillator beam is split off and routed to

the grating, hitting it at the point of rotation, where it is reflected at 4° back into the oscillator/preamplifier dye cell cuvette. The grating thus acts as a wavelength selector.

4. Intermediate telescope.

In order to align the oscillator/preamplifier output parallel to the table top, a telescope is set up before the main amplifier. The oscillator/preamplifier output first passes through an ocular lens ($f = -50mm$) and then an objective lens ($f = 150mm$), this combination is in effect, a Galilean telescope, which expands the output three times, filling the cross-section of the main amplifier. The controls of the ocular and objective lenses are manipulated to steer the beam horizontally and vertically.

5. Main amplifier.

The main amplifier is almost double the volume of the oscillator/preamplifier dye-flow cuvette. It has a separate dye circulating pump. The dye concentration is typically 1 : 3, i.e. 1/3 liter oscillator dye solution and 2/3 liter pure solvent.

6. Second harmonic generation

The two-photon resonance wavelength ($\lambda_R = 212.55nm$) in Krypton which is used in the generation of VUV can be achieved by frequency doubling the dye laser output. Also, in most of the scan range in the VUV, the second laser output needs to be in the UV, obtained by frequency doubling of the fundamental laser light from the dye laser. The Lambda-physik FL

3002 dye laser is equipped with a computer controlled system for the second harmonic generation (SHG). This system (FL 532 B) comprises a motorized crystal tilter, a motor driver P.C. board, an attenuation filter ($T = 0.025$) and an UG 5 filter. Each crystal is mounted in a sealed case. These crystals are mounted directly to the crystal-tilter axle. The attenuation filter is used to protect the crystal during installation procedure. The SHG crystal is mounted after the main amplifier. The fundamental beam has to be polarized. The beam of the FL 3002 has a preferred vertical polarization. The second harmonic generated has a preferred horizontal polarization. The second harmonic is separated from the fundamental by using a filter which transmits in the UV only. In the case of fixed laser (i.e., laser A tuned at 212.55 nm, the two photon resonance in Kr), the UV is separated from the visible by using a prism as a dispersive element.

9.5 Experimental setup for VUV generation

The experimental setup for the VUV generation is as shown in figure 9.7. A dye solution of Stilbene 3 in methanol was used in laser A, giving output energies ~ 10 mJ per pulse at 425 nm. A barium β borate (BBO) crystal was used to generate the second harmonic at 212.55 nm. The two-photon resonance enhancement in Kr was confirmed by measuring the two-photon resonantly enhanced signal in an ionisation chamber (highly excited atoms were ionised by the applied field across the chamber electrodes). The output after frequency doubling was as much as ~ 1 mJ. Laser B in the Figure 9.7 was tunable between 360—870 nm. The short wavelength end can be ex-

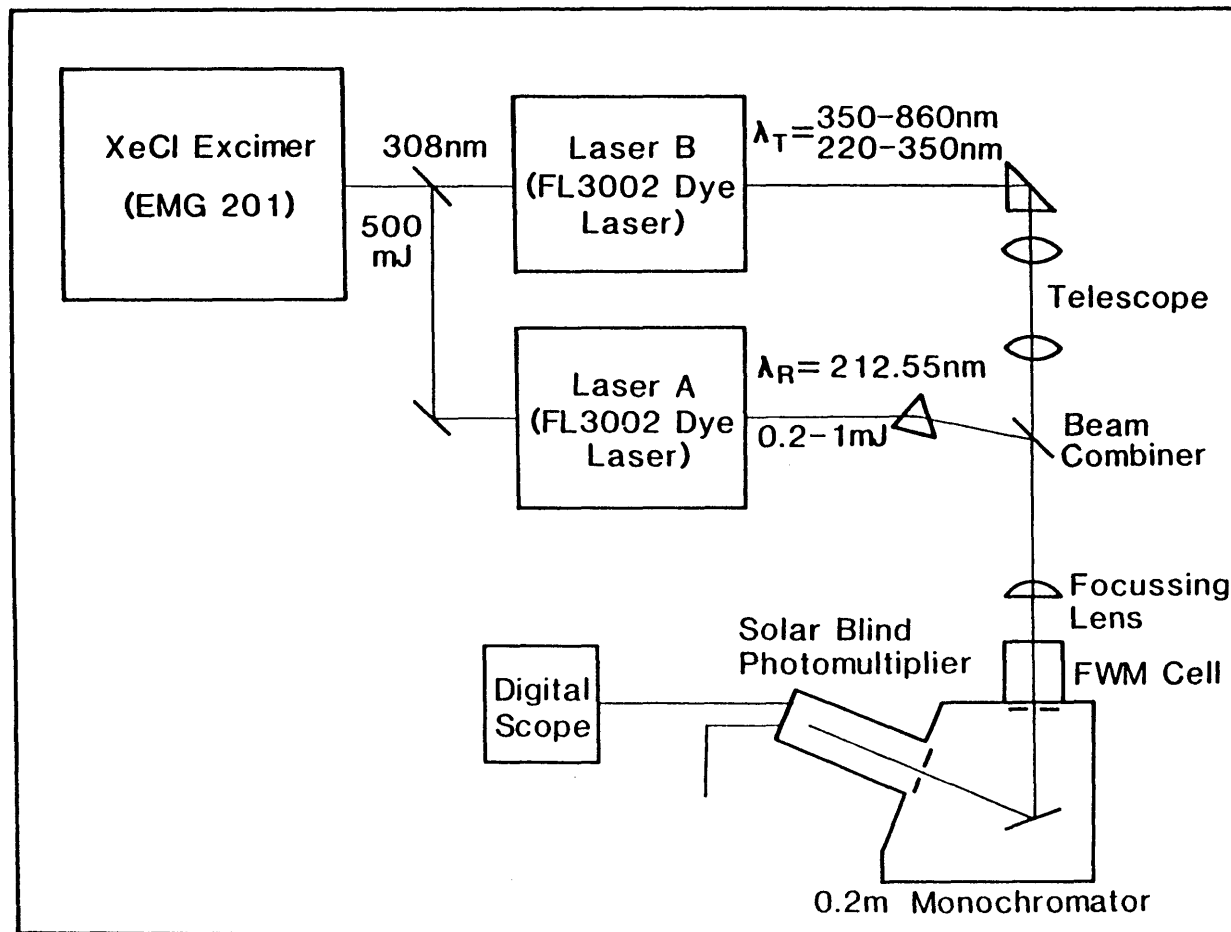


Figure 9.7: The VUV generation setup.

tended by using second harmonics. Both the dye lasers were synchronously pumped by the same XeCl excimer laser operated at a repetition rate of ~ 16 Hz. This was to match the slow decay of the thermionic diode signal pulse, so that each single pulse can be detected separately. A 50:50 beam splitter placed at 45° to the excimer output pulse, divided it into two equal parts. The transmitted half pumped laser B, while the reflected half after a further 90° reflection was input to laser A. When laser B was used with a second harmonic generation crystal, a filter was employed in the beam line which transmits only in the UV. In the case of laser A, the second harmonic frequency was separated from the fundamental one by placing the dispersive element, a prism, in the beam path. A telescope was set up in the tunable beam to compensate for the differing laser beam divergences and the chromatic aberrations in the lens focussing the two beams into the mixing cell. The telescope comprised of lenses of 50 and 200 mm focal lengths. The two beams were combined by a dichroic mirror, which transmitted all the wavelengths greater than 212 nm. A 225 mm focal length was used to focus the two beams into the mixing cell.

The mixing cell was a 100 mm long stainless steel cylinder with a quartz input and LiF exit window. Optimum VUV intensities were obtained if the beams were focussed a few centimeters in front of the exit window. This reduced the chances of reabsorption of the generated VUV in the medium. However, if the beams were focussed too close to the exit window, then the window could easily be damaged. Spatial alignment of the two incoming beams was checked at different points between the beam combiner and the focussing lens. The mixing cell was filled with laboratory grade krypton gas

Demonstrated Characteristics of VUV Radiation Source

Tuning Range	121.0 - 200.0 nm
Bandwidth	< 5 GHz
Pulse Brightness	10^{10} - 10^{12} Photons / pulse
Pulse Power	10 W - 1 KW
Max. Rep. Rate	80 Hz
Beam Divergence	0.1 mrad

Table 9.2: General characteristics of the VUV radiation generated by sum-difference frequency mixing in Kr

and the generated VUV was filtered with a 0.2 meter grating monochromator (Acton Research Corp. Model VM-502), the grating (1200 lines/mm) effectively rejected both λ_R and λ_T wavelengths to a background level of 1%. A solar blind photomultiplier tube (EMI Model G-26E314LF) detected the now monochromatic VUV radiation.

The dependence of the VUV intensity on Kr pressure was investigated. The optimum pressure value is different for different VUV wavelengths generated. A complete study of pressure dependence and focussing parameters (confocal parameters) is reported in Ref.63. Table 9.2 gives general characteristics of the VUV generated.

Chapter 10

Synchrotron Experiment

10.1 Introduction

The Spectroscopy group at the Imperial college has a long working collaboration with the research group at the university of Bonn, Germany, and much of the experiments are jointly conducted at the synchrotron radiation source at the HASYLAB. However, with the construction of a storage ring at the Daresbury (U.K.), it was planned to conduct synchrotron experiments at this home facility provided it offers better service (in terms of the resolution and the photon flux). The first such experiment (by the spectroscopy group at the I.C.) planned was the reinvestigation of the doubly excited autoionising series in calcium. This spectrum was previously studied by the same group⁶² using the storage ring facility at the HASYLAB. The HASYLAB experiment provided much improved results as compared to the

previous investigations and showed the excellence of the configuration of the *hot-wire* detector with a synchrotron (first study of its kind), however, due to low resolution ($\pm 0.75 \text{ \AA}$), triplets were not fully resolved from their singlet states and correct measurement of the widths of autoionising lines, and hence the q values, was not possible. With the 5 meter long normal incidence grating monochromator, and the storage ring facility (with wiggler), at the Daresbury Synchrotron Laboratory we expected to achieve better resolution

A brief experimental review, as discussed before, is that this doubly excited series (3dnp) lies above the first ionisation threshold in the vacuum ultraviolet region. This series was first discovered by Kaiser (1960), followed by Garton (1966) and many others, and most recently studied by Griesmann *et al* (1988), using the storage ring at the HASYLAB. This chapter presents a general introduction about the synchrotron radiation source (SRS) and storage ring, it is followed by a brief description of the 5 meter long normal incidence grating monochromator at the Daresbury Synchrotron Laboratory. Experimental setup is described in detail and the results are discussed.

10.2 Synchrotron Radiation Source (SRS)

A synchrotron is a primary standard source of light. A primary standard source, by definition, is a source for which the radiated power is known theoretically as a function of the wavelength. When electrons (positrons) travel with a velocity close to that of light arc around the bending magnets in their

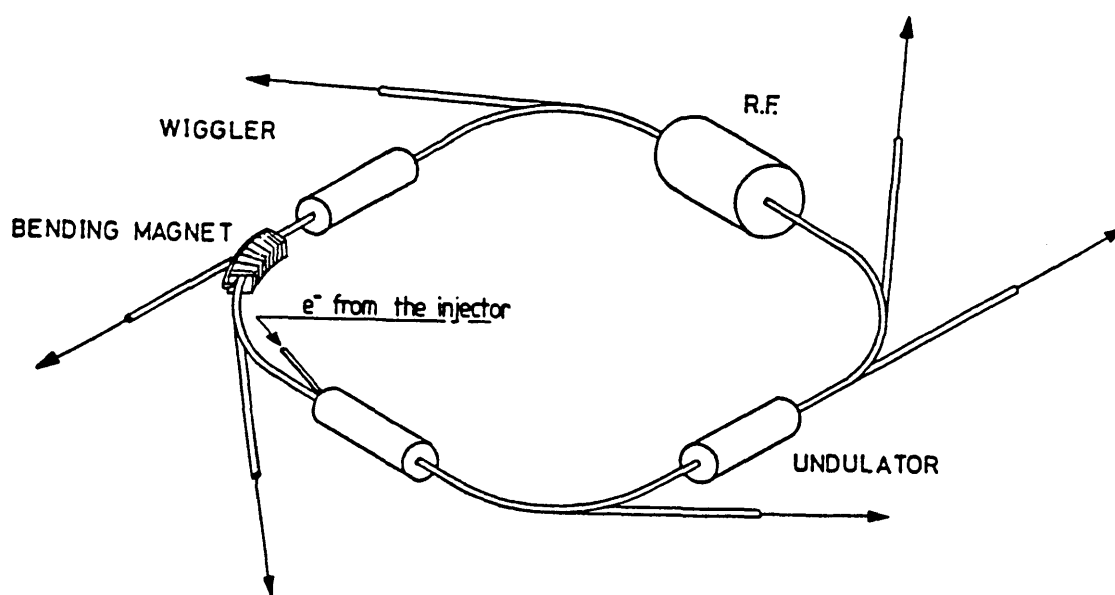


Figure 10.1: Main components of a synchrotron radiation source assembly

circular orbits, they emit electromagnetic radiation called synchrotron radiation (S.R.). In practice S.R. is produced by high energy electrons (positrons) circulating in a horizontal toroidal high vacuum chamber and maintained on a closed orbit by dipole and quadropole magnets (Fig 10.1). The "torus" is composed of arcs of a circle, placed in the magnetic field, and joined by straight sections. The radiation is concentrated into a narrow cone in the direction of the instantaneous motion of the electrons. The opening angle of this cone is $1/\gamma = m_e c^2/E_e$ (see below for detail). The greater the energy, the smaller is the angle of the cone. The radiation is therefore virtually confined to the orbital plane, and it is plane polarized with the electric vector in this plane. The radiation from a bending magnet maintains this narrow angular divergence in the vertical direction but spreads horizontally over several degrees as the electron curves around in the magnetic field (Fig 10.2). The power radiated at any wavelength can be calculated from the radius

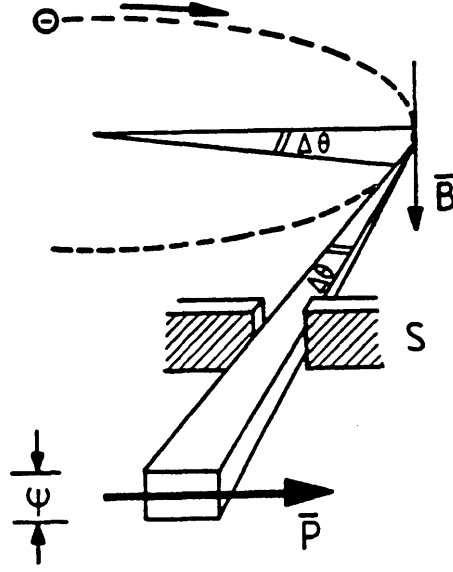


Figure 10.2: Emission of the synchrotron radiation from moving electrons round bending magnet

of the orbit and the energy of the electrons, hence this source is in the same category as the black-body as a true absolute intensity standard. The important parameter is the 'characteristic wavelength, λ_c ', which divides the spectrum into two parts of equal radiated power, and is given by

$$\lambda_c = \frac{4\pi}{3} \frac{R}{\gamma^3} \quad (10.1)$$

$$\lambda_c = 0.56 \frac{R}{E_e^3} = \frac{1.864}{E_e^2 B}, \quad (10.2)$$

where wavelength is measured in nm, R is the radius of the orbit in meters and E_e is the electron energy in GeV. B is the magnetic field in Tesla, γ is the ratio of the energy E_e to the rest mass energy of the electron.

$$\gamma = \frac{E_e}{m_e c^2} = 1957 E_e (GeV) \quad (10.3)$$

Nowadays this kind of radiation source can be divided into three categories. According to this rough categorization, the first generation consists of circular accelerators originally intended for other purposes: they provided synchrotron radiation to parasitic experiments or, in some cases, they have become partially dedicated to such uses. The second generation comprises facilities specifically designed to support synchrotron radiation experiments, with the radiation produced primarily as electrons or positrons curved in the field of the machine's bending magnets. By contrast, the third-generation machines are designed to optimize the radiation that is produced as the electrons or positrons traverse devices known as Wigglers or Undulators. The most advanced source of synchrotron radiation is the storage ring. The basic elements of a storage ring are very similar to those of a synchrotron. However, a storage ring operates at much higher vacuum (10^{-12} Torr) than a synchrotron (10^{-8} Torr) so that electrons can stay in the orbit for few hours, whereas in a synchrotron, the process of injection and acceleration of a new group of electrons is repeated, usually at 50-60 Hz. Thus, in a synchrotron, the electron energy and consequently the radiation spectrum, are not constant. The high vacuum maintained in the storage ring enables the electrons to travel for several hours along a closed orbit, provided that the loss of energy due to emission of radiation is compensated. This is done by creating an electromagnetic field (at one or several places along the orbit) that accelerates the electrons, thereby restoring the exact amount of energy lost to radiation. The required field values are generally high so that

cavity-like structures operated at high frequencies are needed to generate them. These are called RF cavities (see Fig 10.1). Therefore, the electrons travel in the ring in bunches, and thus radiation reaches the detector in short flashes separated by longer periods of time depending on the parameters of the storage ring. Furthermore, in addition to the pulsed structure of the synchrotron radiation present in both storage ring and synchrotron, owing to the orbiting of the electron groups, there is also a modulation at mains frequency (50-60 Hz).

10.2.1 Undulators and Wigglers

Undulators and wigglers are devices inserted into straight sections between the bending magnets (see Fig 10.1). They consist of linear arrays of magnetic dipoles with alternating polarities that produce fields perpendicular to the plane of the beam. These devices may be a few meters long and may incorporate up to a hundred or so poles (fewer for the wiggler). As a charged particle traverses the magnetic region, in which the field vectors point first upward and then downward, it curves first one way, then the other, in the orbit plane. Moving along in this manner, the electron or positron constantly emits photons.

Undulators and wigglers have the same construction but produce different types of radiation. The difference is determined by a certain parameter, K , which is a measure of bending angle of the electron per pole in units of $1/\gamma$. The value of K depends on the magnetic field strength and the period of alternation of the magnetic poles. When K is larger than 1, the electron

path swings outside the radiation cone, the radiation adds incoherently and the device is called a wiggler. The radiation from a wiggler has roughly the same spectral shape as that from a bending magnet, but it is brighter by a factor roughly equal to the number of magnet poles. (Brightness is a measure of the number of photons per second per solid angle per source area, and is usually specified in terms of some percentage of the bandwidth $d\lambda/\lambda$, the wavelength at which the spectrum peaks can be tuned by changing the strength of the magnetic field).

When K is of the order of or less than 1, the electron does not move outside the radiation cone, so that the radiation cones from successive bends overlap and interfere coherently with one another. In this case the device is called an Undulator. The undulator spectrum is characterized by sharp peaks at some fundamental spectral wavelength, with successively less intense peaks at higher harmonics. The undulator thus produces a laser-like beam of intense radiation at specific wavelengths, and these wavelengths are tunable by changes in the size of vertical gaps in the magnets. The undulators on the new machines should produce brightness of 10^{18} or 10^{19} photons/(sec mm² mrad² 0.1% bandwidth).

10.2.2 General Characteristics Of SRS

- 1- High intensity
- 2- Broad spectral range
- 3- High polarization
- 4- Pulsed time structure

5- Natural collimation

A Storage ring, in addition, offers the following:

- 6- High vacuum environment
- 7- Small source spot size
- 8- Good stability

10.2.3 5 Meter Normal Incidence Monochromator at the Daresbury Laboratory SRS

Beamline and pre-monochromator optics

The beam port accepts a 28 milliradian (horizontal) by 5 milliradian (vertical) fan of radiation from the 2 GeV storage ring. From this, a 5 mrad by 5 mrad portion is intercepted by pre-focussing optical elements of the 5 meter normal incidence monochromator. The electron beam size at the tangent point is $H = 2.82$ mm and $V = 0.26$ mm FWHM. Fig 10.3 shows the optical layout of the beamline and monochromator. The center of the first mirror is 10.5 meter from the tangent point and the glancing angle is 5° . This plane mirror has been made from silicon carbide and is 590 mm long by 60 mm high. The surface was polished by Optical Surfaces Ltd and has

been platinum coated. Silicon carbide was chosen for the first mirror to help dissipate the heat load caused by the synchrotron radiation. A second mirror, at 11.6 meters from the tangent point, is an ellipsoid manufactured by Ferranti-Astron Ltd. The mirror parameters are: major axis 7733 mm, minor axis 584 mm, eccentricity 0.997, length 666mm and width 74 mm. The ellipsoid is located in a position such that the beam size is demagnified by 3 : 1 both horizontally and vertically. The mirror has been made from fused silica and the surface coated with platinum. A 5° glancing angle is used, and therefore, this mirror deflects the beam vertically and focuses onto the monochromator entrance slit. Both pre-monochromator mirrors have adjustment mechanisms which allow translational and rotational motions to be controlled outside the vacuum chamber. In particular, the ellipsoid has an external yaw adjustment which can be used to ensure a sharply focused image on the entrance slit.

Normal incidence monochromator

A 5 meter, vertically dispersing, normal incidence monochromator was built by McPherson Ltd, USA. The design follows the optical layout used in a 3 meter monochromator fitted to the DORIS storage ring in Hamburg³. The monochromator was specified to provide a resolving power in the region of 50,000 at 100 nm and to have constant deviation. The configuration chosen specified 5 meter radius of curvature, with two gratings interchangeable under vacuum to cover the wavelength range of 40-300 nm. For a ruling density of 1200 lines/mm this corresponds to a theoretical resolution of 0.0017 nm

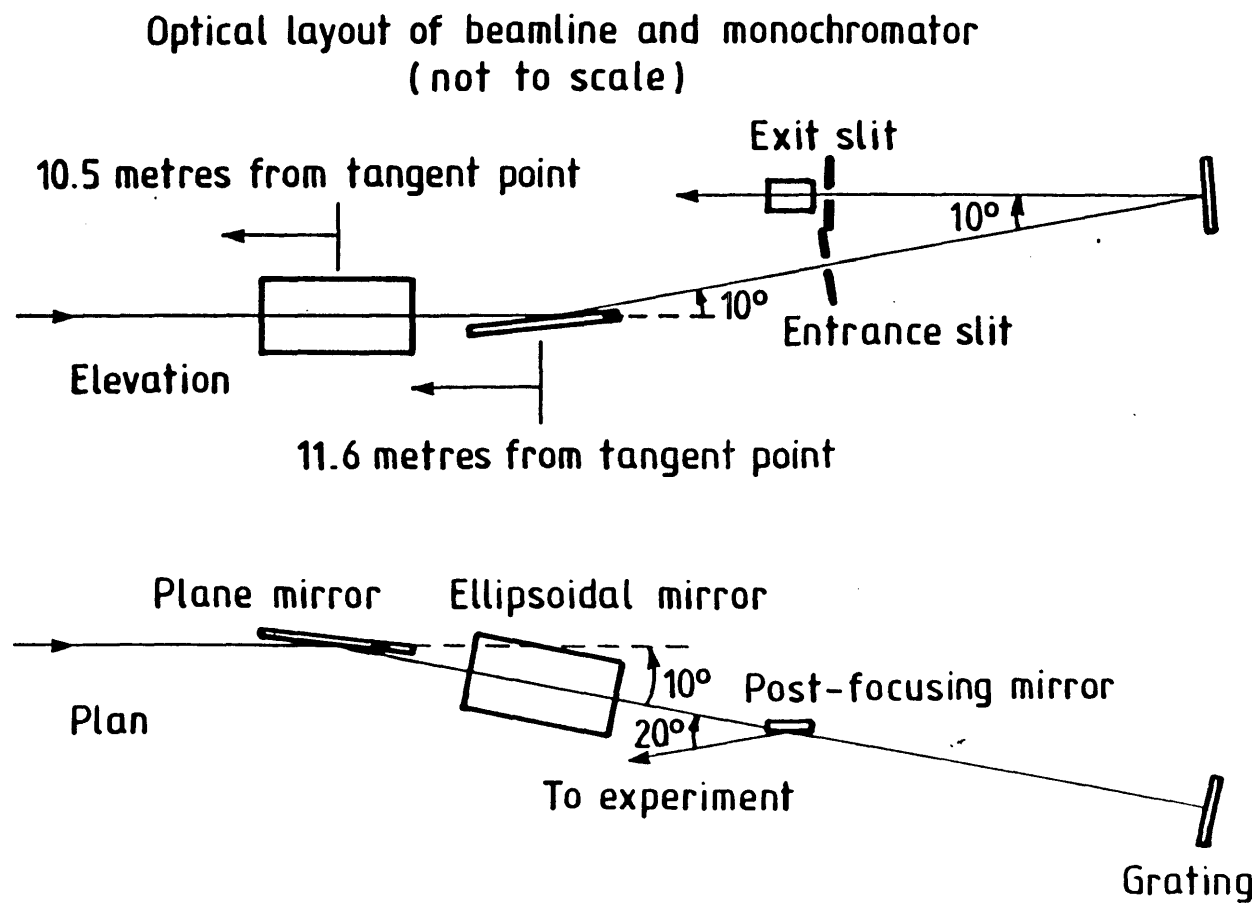


Figure 10.3: Beam line setup at the Daresbury Synchrotron Lab.

for 10 μm slit widths. Taking into account the 3 : 1 demagnification produced by the pre-monochromator optics, this leads to a source size limited resolution of 0.015 nm. At a wavelength of 100 nm, the photon intensity produced by the storage ring is 1.6×10^{13} photons/sec.mrad 0.1 A circulating current 0.1% bandwidth. This results in a theoretical flux limit, at 100 nm, of 1.2×10^{12} photons/sec.100 mA at full source size bandwidth (0.015 nm). The grating drive mechanism uses a cam system designed by McPherson. This mechanism rotates the grating whilst simultaneously translating it along the line bisecting the 10° angle between the entrance and exit slits, in such a way as to maintain focus at all wavelengths. The grating arm is driven along the cam via a system of antibacklash gears and micro-stepper motor. This motor may be driven manually or under computer control.

The mechanical stability of the monochromator is intended to permit operation, albeit with reduced photon flux, down to a resolution of approximately 0.001 nm. The monochromator vessel is pumped by a 400 liters/second ion pump and routinely achieves a base pressure of 5×10^{-9} mbar. The photon flux output curves of the two gratings, as measured by an aluminium photodiode, are as shown in Fig 10.4. The diode efficiency has been determined by using the data given by Saloman *et al* ⁹⁹. Both gratings have 1200 lines/mm and a ruled area of 150 mm by 70 mm. The rulings are parallel to the 70 mm dimension. Grating A is a 5 meter concave blazed grating manufactured by Hyperfine Incorporated. The base is fused silica and rulings are cut in the gold coated surface. Grating B is of laminar design and manufactured by Jobin Yvon. The base is spectrosil and the surface has been coated with iridium.

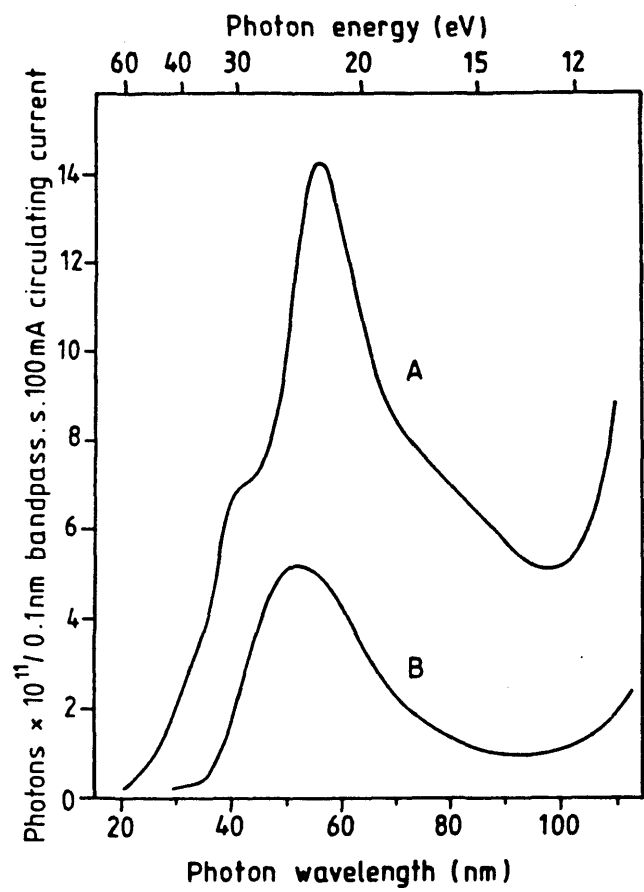


Figure 10.4: Photon flux output curves for the gratings used in the Daresbury Synchrotron

The overall efficiency of the optical system can be determined from the measured output photon flux and the calculated input intensity. Marks *et al*¹⁰⁰ gave a value for the vertically integrated flux, at 55 nm, of 2.1×10^{13} photons/sec.mrad 0.1 A circulating current, 0.1% bandwidth. Therefore, the input photon intensity can be calculated to be 1.5×10^{13} photons/sec.mrad.100 mA 0.1% bandwidth. The overall efficiency of the optical system at 55 nm is 7.4%.

Post Monochromator Optics

Attached to the exit port of the monochromator is a mirror chamber which contains a final stage of optics. Three mirrors are available, two are ellipsoids and are used when point image is required. The mirrors are 2:1 and 4:1 demagnifying. The third mirror is a paraboloid and can be used to form a parallel beam of radiation. The post monochromator mirror chamber also forms a stage of differential pumping between the experimental apparatus and the monochromator by positioning a capillary light guide in between.

10.3 Experiment

The experimental setup for the system is as shown in Fig 10.5. The vacuum line was sealed by placing a LiF window in front of detection system (before the chopper). In order to reconcile the need for phase-sensitive detection with the time structure of the synchrotron radiation source, we used

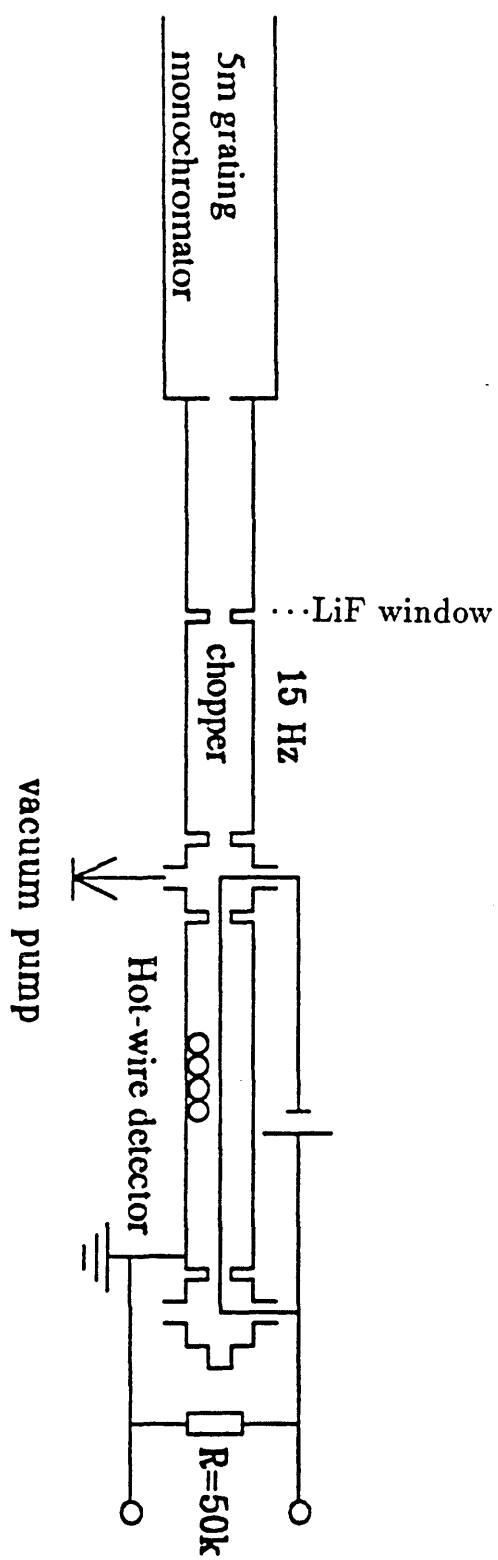


Figure 10.5: Setup for the synchrotron experiment

a low frequency chopper (about 15 Hz in our experiment). The chopper was placed in a vacuum chamber before the *hot wire* detector along with a dc servo motor. The chopper frequency was externally controlled by an electric voltage signal. The reference output of the chopper unit was used to lock the *hot-wire* signal. A 0.125 mm thick molybdenum wire was used as a cathode. Calcium chips were loaded in the detector. The oven was heated to a temperature of 750 °C by a dc power supply. The cathode was heated independently of the oven by applying a 5 volts dc (2.3 amp) across it. The signal was received across a 50 K Ω resistor. It was fed into a dual phase lock-in amplifier (EG & G Model 5206) triggered by the reference output of the chopper. The digital output from the lock-in (the lock-in has an in-built analogue to digital converter) was input to the computer at the Daresbury. Experimental resolution was 1.4 Å. Typical parameters of the synchrotron during our experiment were as follows.

Energy $\sim$ 2 GeV

Electron current $\sim$ 100 mA

Beam Life time $\sim$ 19 Hours

10.4 Results and Discussion

The spectrum recorded is as shown in Fig 10.6. Due to low photon flux, signal to noise ratio is not good. Increasing the flux by opening of the monochromator exit slit resulted in poor resolution. The spectrum shows

the 3d6p 1P_1 resonance line which has a vanishing particle width; on its shoulder is the 3d6p 3P_1 line, resolved somewhat better than in the previous investigation⁶², but yet not fully resolved to compare with the theoretical calculations^{32b}. This poor resolution is partially due to compromise for a still higher photon flux. All other transitions which are distinctly visible in previous work⁶² are buried in the noise except a little hump at the place of 3d7p resonance. One reason for such a poor performance of the radiation source (at least during our week long stay) may be that the facility was not operational for one complete month, and it was the first week after this closure, hence the apparatus was not fully optimised. Electron beam loss was a frequent event during the experiment. The first three days were spent on achieving a reasonable vacuum $\sim 10^{-9}$ Torr so that the beamline can be opened (The vacuum on the monochromator side was about 10^{-12} Torr).

The conclusion is that this experiment, unfortunately, did not provide improved results, but future plans for experiments on the Daresbury radiation source should not be decided by this single experiment.

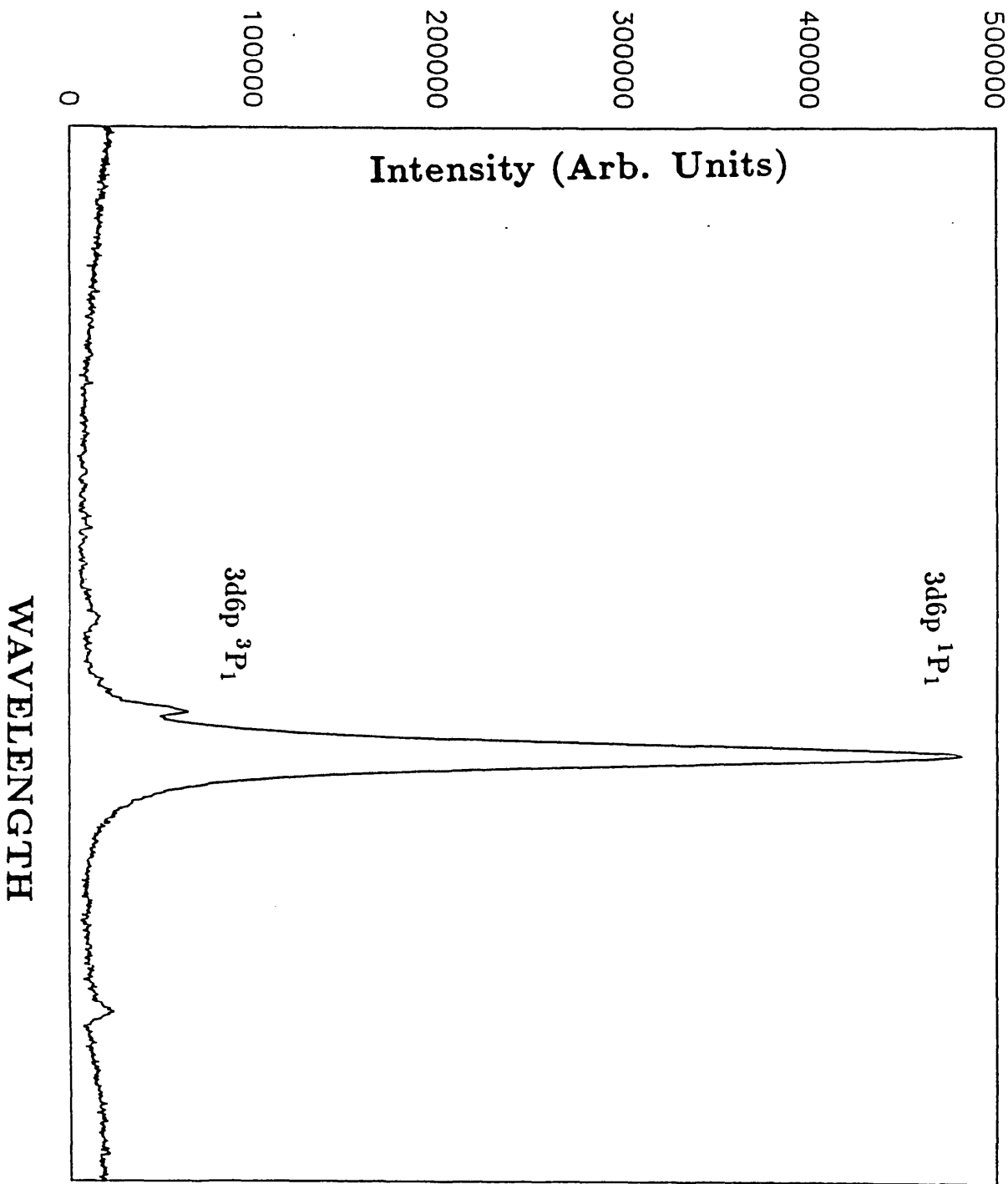


Figure 10.6: Calcium spectrum recorded by new thermionic diode detector at the Daresbury Synchrotron Laboratory

Chapter 11

Laser Based Experiments

11.1 Calcium Experiment

The doubly excited autoionising series (3dnp,3dnf) in calcium have been investigated. These series lie above the first ionisation threshold (6.11 eV) in the VUV. The spectra investigated in the present study lie in the vacuum ultraviolet from 178.0 to 158.0 nm. This range covers the complete series except the first two members (3d4p,3d5p). The 3d4p level lies below the first ionisation threshold and 3d5p—first member of the doubly excited series lying in the continuum—is too broad to be scanned by lasers and has been fully resolved in a previous synchrotron experiment⁶².

In order to generate VUV (see chapter 9) in the range 178.0 to 158.0 nm, according to the sum-difference formula ($\lambda_{VUV} = \frac{\lambda_T \lambda_R}{2\lambda_T - \lambda_R}$), the tuning laser was scanned from 526 to 648 nm. The frequency doubling of the fundamental

radiation provided photons in the wavelength range 263 - 324 nm. These photons were used in the mixing scheme to generate VUV in the required wavelength range. This wavelength range in the fundamental could not be scanned in a single dye; rather a number of dye solutions were used in laser B to run the experiment.

A dye solution of stilbene 3 in methanol was used in laser A, as discussed in chapter 6, giving output energies of ~ 10 mJ per pulse at 425 nm and ~ 1 mJ after frequency doubling at 212.55 nm. A Barium β borate (BBO) crystal was employed for the second harmonic generation. The XeCl excimer laser was operated at a repetition rate of about 16 Hz, corresponding to the minimum interval possible between pulses from the thermionic diode detector. Both the dye lasers were synchronously pumped by the same excimer laser (see chapter 9). While laser A was tuned to the two-photon resonance in Kr at 212.55 nm, laser B was scanned in steps between 0.007 Å to 0.05 Å depending upon the structure under investigation. Narrow structures needed to be resolved fully by taking smallest possible steps in the wavelength. The optimum scan steps in each case were achieved by repeating each scan at least twice. A repetition rate of 5 Hz was employed at each scan step, i.e. the laser fired five shots before the wavelength was changed by a recommended step. This was to average out the effect of shot to shot fluctuations at each wavelength. Similarly, the second harmonic generation crystal was programmed such that for each wavelength scan range it optimized itself at four equally separated positions; thus when synchronously scanned with the grating there was not much output variation. The laser pulse energies were measured by a Gen-Tech photodiode. The generated VUV was filtered

through a grating monochromator (Acton Research Model 502), and was collimated through the Ca vapor by a LiF lens (150 mm focal length). Wide slit widths were employed to increase throughput. The transmitted light was detected at the rear end of the diode by a photomultiplier tube. This helped in assessing the optical depth during the experiment.

Fresh, clean calcium chips were loaded into the *hot-wire* tube. The detector was vacuum sealed at both ends by placing the LiF lens at the entrance and the LiF window at the rear. The initial cleaning procedure (as explained in chapter 7) was adopted. Both the ends of the detector were water cooled. The oven was heated up to 750 C°, which gave a calcium vapor pressure of about 0.1 Torr. The Doppler width of calcium at this temperature is about 12 GHz at 1765 Å. The temperature was monitored by inserting a thermocouple beneath the thermal shielding. The error in temperature estimation can be about 20 C°. Ar at a pressure of 1 Torr was used as a buffer. Under these conditions the Ca vapor was confined to the hot zone, which protected the windows from getting coated. A 0.125 mm thick molybdenum wire—used as a cathode—was heated independently of the detector tube by a current of 2.3 A. The signal from the thermionic diode was taken across a 50 KΩ load resistor (matching the impedance of the diode) and fed into a lock-in amplifier (Stanford Research Model SR530). The amplifier was locked to the repetition frequency of the laser. The lock-in and PMT outputs were fed into the computer (see chapter 8). Each scan was repeated at least twice under stable conditions. The resulting spectrum is as shown in Figs 11.1 and 11.2. All the spectra presented in this chapter are on an absolute scale in terms of the wavelength and cross-section. The

wavelengths are calibrated against the photographic work of Brown *et al* . The absolute cross-sections are given only for calcium, where the calibration is done with the help of a previous synchrotron experiment (Griesmann *et al* , 1988) which made use of the Hook method. The detail of data handling is described in the next chapter.

11.2 Strontium Experiment

The doubly excited series in Sr I was investigated. This spectrum was previously studied by Brown *et al* ⁸¹ by the photographic detection technique, but the spectrum produced was not fully resolved below the $5p\ ^2P_{1/2}$ series limit, and the photographic detection technique is also nonlinear. The interest attached to this spectrum is due to the apparent discrepancy between the experiment and the recent theoretical calculations based on the R-matrix technique (Aymar, 1988). The detail of the previous experimental and theoretical works is given in chapter 6. Due to the poor experimental resolution and the nonlinear nature of the photographic detection the accuracy of the theoretical results could not be examined. With the narrow band width VUV source and the thermionic diode detector this spectrum is well resolved in the present work. By using the VUV radiation source (see chapter 9) the spectrum is scanned from 143.0 to 144.7 nm—below the $5p\ ^2P_{1/2}$ limit.

A dye solution of DPS in Dioxane solvent was filled in laser B. A scan range 400.0 to 413.7 nm in the fundamental corresponds to the VUV range

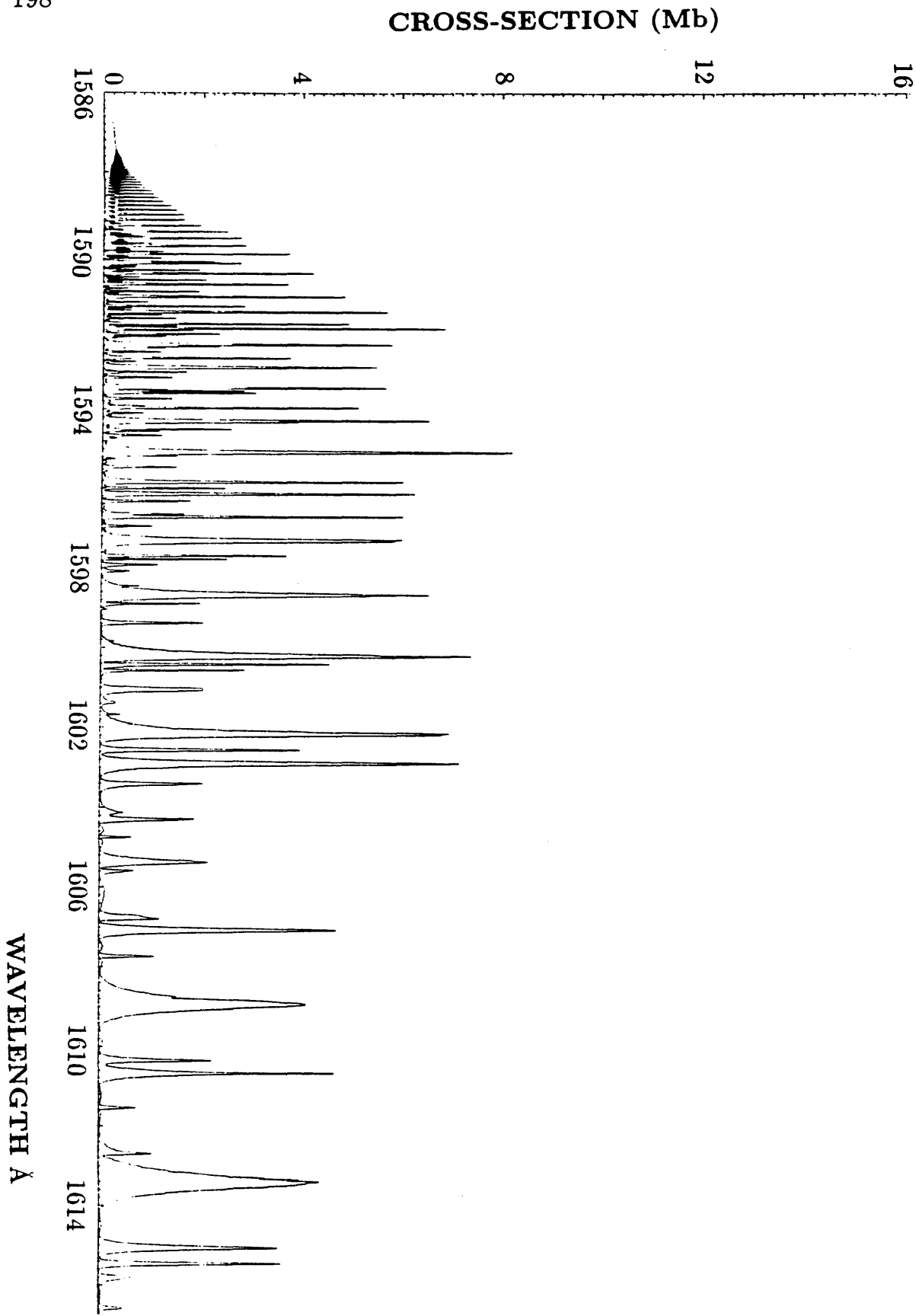


Figure 11.1: Absorption spectrum of the doubly excited autoionising series in Ca I

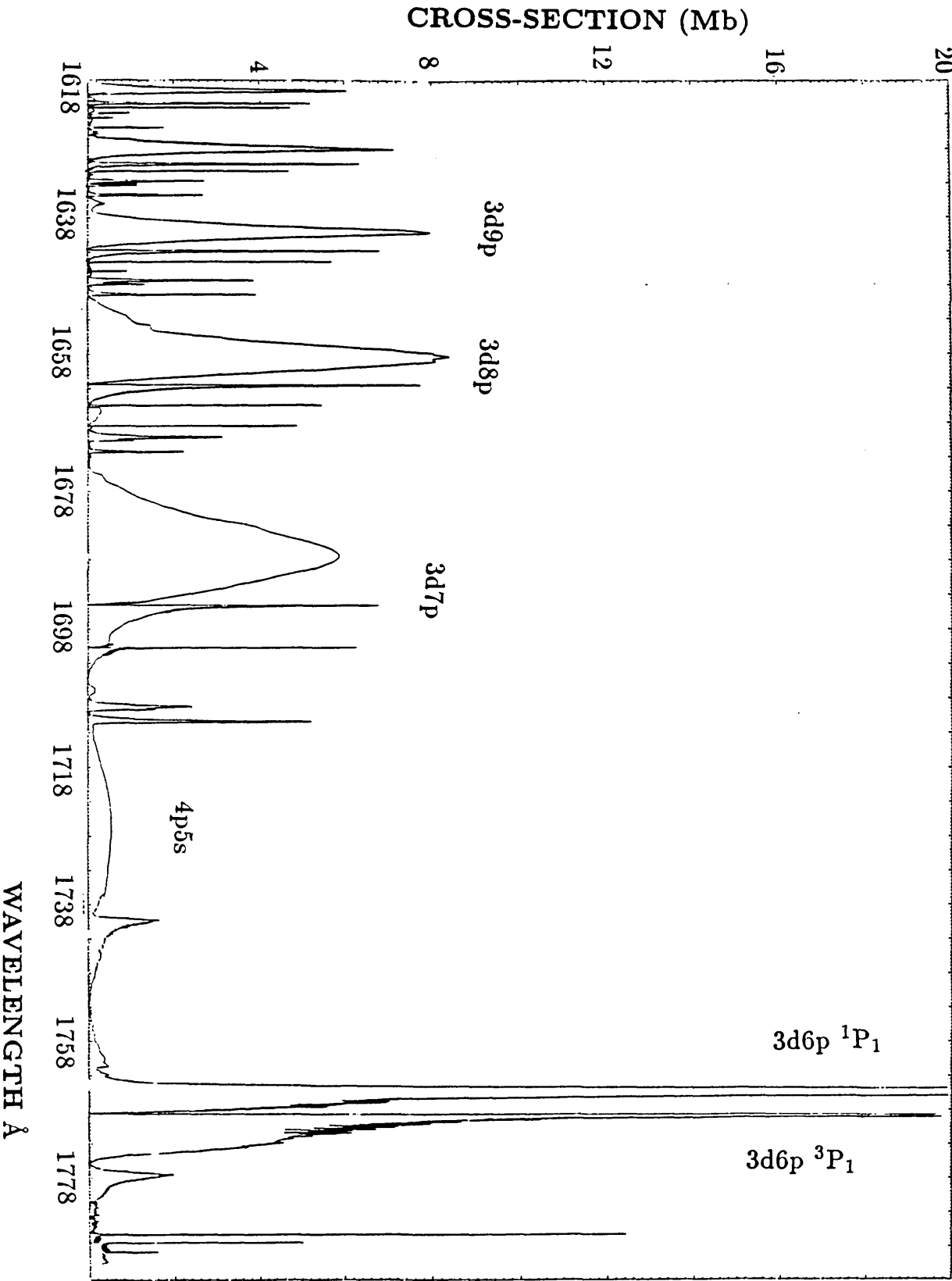


Figure 11.2: Absorption spectrum of the doubly excited series in Ca I

required. Thus we did not use any frequency doubling. The laser beam was very intense and to avoid any damage to the optics we used a filter in the tuning laser path, which cut the intensity by 50%. Laser A, as required, was fixed at the two-photon resonance frequency in Kr, and the lasing medium was Stilbene 3 solution in methanol. The rest of the optical system was the same as in the calcium experiment. The laser repetition rate was 16 Hz. A 100 mbar Kr pressure was found to be optimum to generate VUV in the required wavelength range of 143.0 - 144.7 nm.

The thermionic diode detector tube was thoroughly cleaned as it had been employed to study the calcium spectrum (no calcium lines were observed after this cleaning), and a new cathode wire was installed. Strontium metal was stored in a petroleum liquid to avoid oxidation. It was also thoroughly cleaned to remove oil contents from the surface and was cut into small pieces and loaded into the detector using a stainless steel mesh. Further cleaning procedure was the same as laid down in chapter 7. The oven was heated to a temperature of about 650 °C , which gives a Sr vapor pressure of about 0.5 Torr. At this temperature, Sr has a Doppler width of about 11 GHz at 143.5 nm. Ar at a pressure of 0.8 Torr was used as a buffer. The cathode wire was heated by a current of 2.2 Amp. The rest of the system was the same as used in the calcium experiment. Each of the scans was repeated at least twice, and fine adjustments to the temperature and laser scan steps were made. The results are as shown in Fig. 11.3.

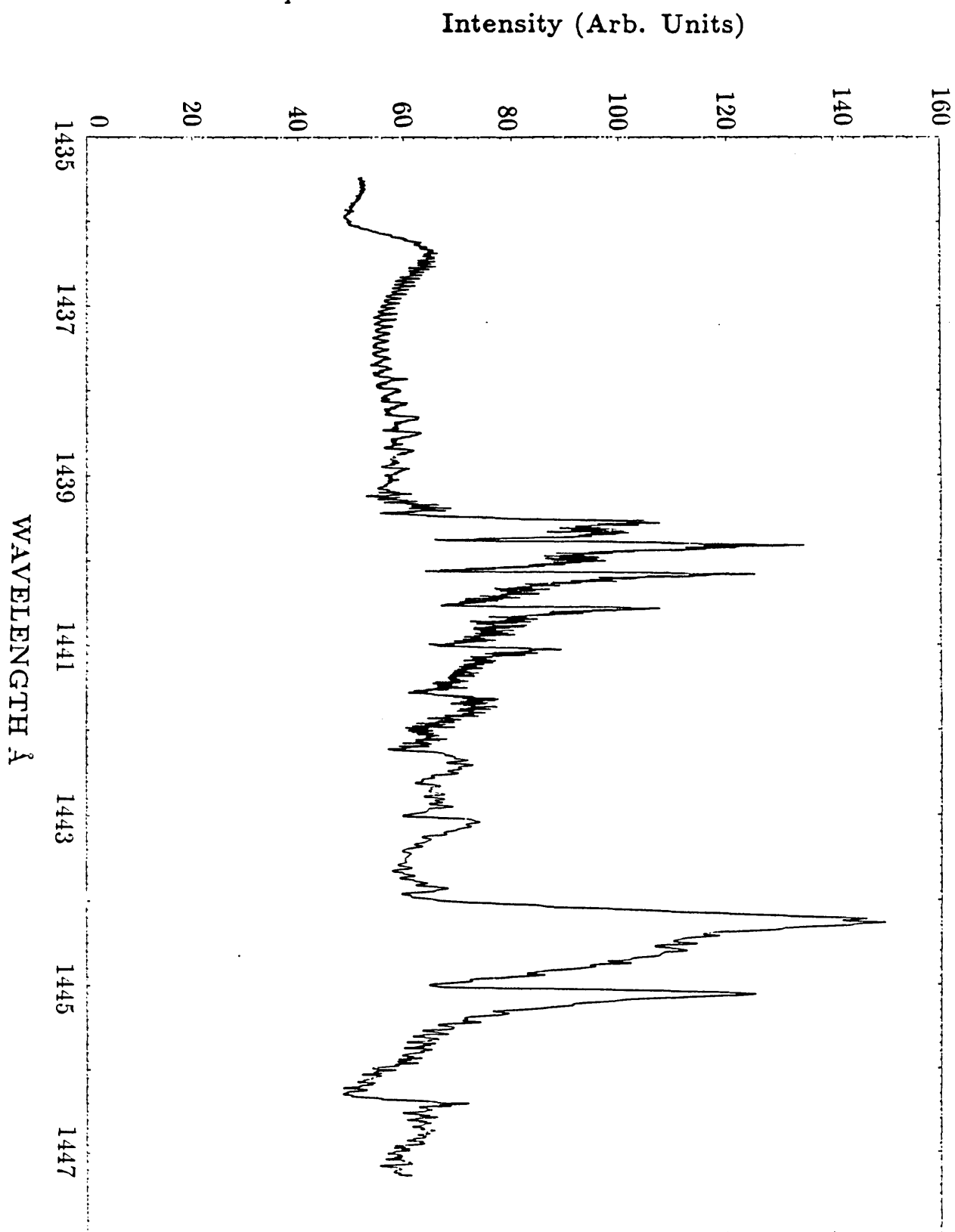


Figure 11.3: Absorption spectrum of the doubly excited autoionising series in Sr I, below the $5p_{1/2}$ limit

11.3 Barium Experiment

The doubly excited series in Ba I below the $6p_{1/2}$ series limit was investigated in the wavelength range of 161.64 to 160.52 nm, by using the same experimental setup as employed in the present study of calcium and strontium. This spectrum was previously investigated by Brown and Tilford⁹⁰ by photographic detection technique. This series, like the one investigated in Sr, lies above the second threshold. Chapter 6 presents a review of the earlier work on this spectrum. Briefly, it was the vanishing of the fluctuations in this spectrum (see Fig 6.1) which led to the theoretical analysis of the spectrum (Lane, 1987), but the effect was not justified for this complicated spectrum and doubt was raised about the genuineness of effect. These doubts were further strengthened when the authors (Brown *et al*) themselves pointed out that instrumental interference effect can occur amongst high members of Rydberg series when the spacings between adjacent lines gradually approach the resolution limit of a classical spectrograph. The present experiment reinvestigates the spectrum to examine the genuineness of the effect. The experimental setup is the same as that employed in the study of calcium and strontium spectra.

A dye solution of Rhodamine 101 in methanol provided photons in the wavelength range of 620.6 - 628.7 nm, which after frequency doubling produced photons of the wavelength needed to generate VUV by sum-difference frequency mixing scheme. A Barium β borate (BBO) crystal was used to generate the second harmonic. As in the previous two studies with this VUV system (Ca & Mg), the laser repetition frequency was 16 Hz. A Kr pressure

of about 260 mbar was sufficient to give an optimum VUV output.

The oven, loaded with fresh, clean pieces of barium and made ready for the experiment by adopting the cleaning procedure discussed so far, was heated up to a temperature of 800 C° . Ba has a vapor pressure of about 0.5 Torr at this temperature and Doppler width of about 8 GHz at 161 nm. An Ar buffer gas pressure of 1.0 Torr was applied. The cathode heating current was 2.2 A. The rest of the data acquisition system was the same as used in the cases of calcium and strontium. The resulting spectrum is as shown in Fig. 11.4.

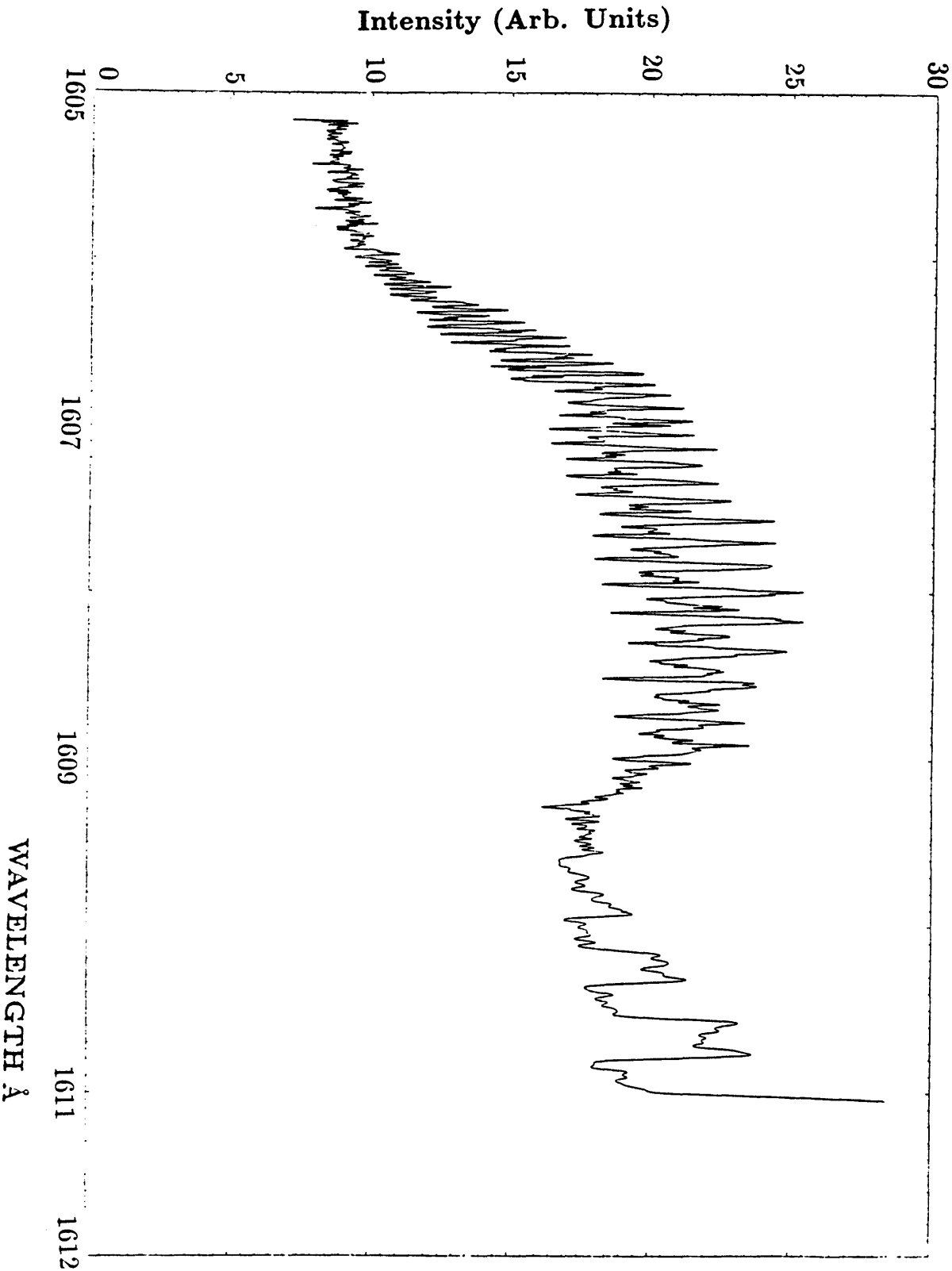


Figure 11.4: Ba I spectrum investigated by using the VUV light source

Chapter 12

Data Handling

This chapter describes at length the procedure adopted in handling the data. The output of the lock-in-amplifier (the ion signal converted into the digital signal by an in-built ADC) and the box car averager (the monitor signal) are fed into the IBM PC computer run under lock-in-amplifier software SRS 575. Data is saved in the computer as binary files. The binary to digital conversion is done by a computer code called B2A2. This code also creates a wavelength column from start and end values of the wavelength, by dividing the difference in equal intervals such that each data point now has a wavelength value. The wavelengths are calibrated at a later stage. Thus the ASC file has three columns corresponding to the wavelength, ion signal and monitor signal respectively.

The ion and the monitor signals have superimposed on them a random noise which needs to be filtered out in order to have clean data for analysis.

Wiener filters were developed at the CERN Laboratories and are based on the Fourier transform technique. They take the Fourier transform of a signal and separate the periodic signal from the random noise, and then take the inverse Fourier transform of the signal. Thus, the method is useful especially to cut the random noise, but it is not of much help in the case of periodic noise. In the present experiment there is mainly a random noise problem, so these filters are used on the data. The executable file 'LESEN.FOR' needs three column input file with ASC extension. It filters both the ion signal and the monitor signal (second and third column respectively) in separate attempts and the outputs are saved with the same name but with DAT and MON extensions. It also normalises the signal by dividing the DAT file by the MON, and stores it with the same name but with NOR extension.

The inspection of a normalised data file revealed that the base line (background noise level) is no longer uniform, rather it decayed at one side. This is not the case in the filtered or unfiltered original data files (see Fig 12.1). The reason for this nonuniformity is : during the laser scan, the VUV generated is also scanning but the monochromator is fixed at one position (normally at the middle of the scan range), and hence the VUV signal drops if its wavelength is far away from the monochromator position. On the other hand, the base level which is the background noise has nothing to do with the laser light signal; rather it is dependent on the detection chamber environment (temperature, bias voltage etc). This environment remains almost unchanged during a scan, as the system is given enough time to get stabilised. Thus, when the lock-in data is divided by the monitor signal, this otherwise constant noise is also divided. This is avoided by use of a com-

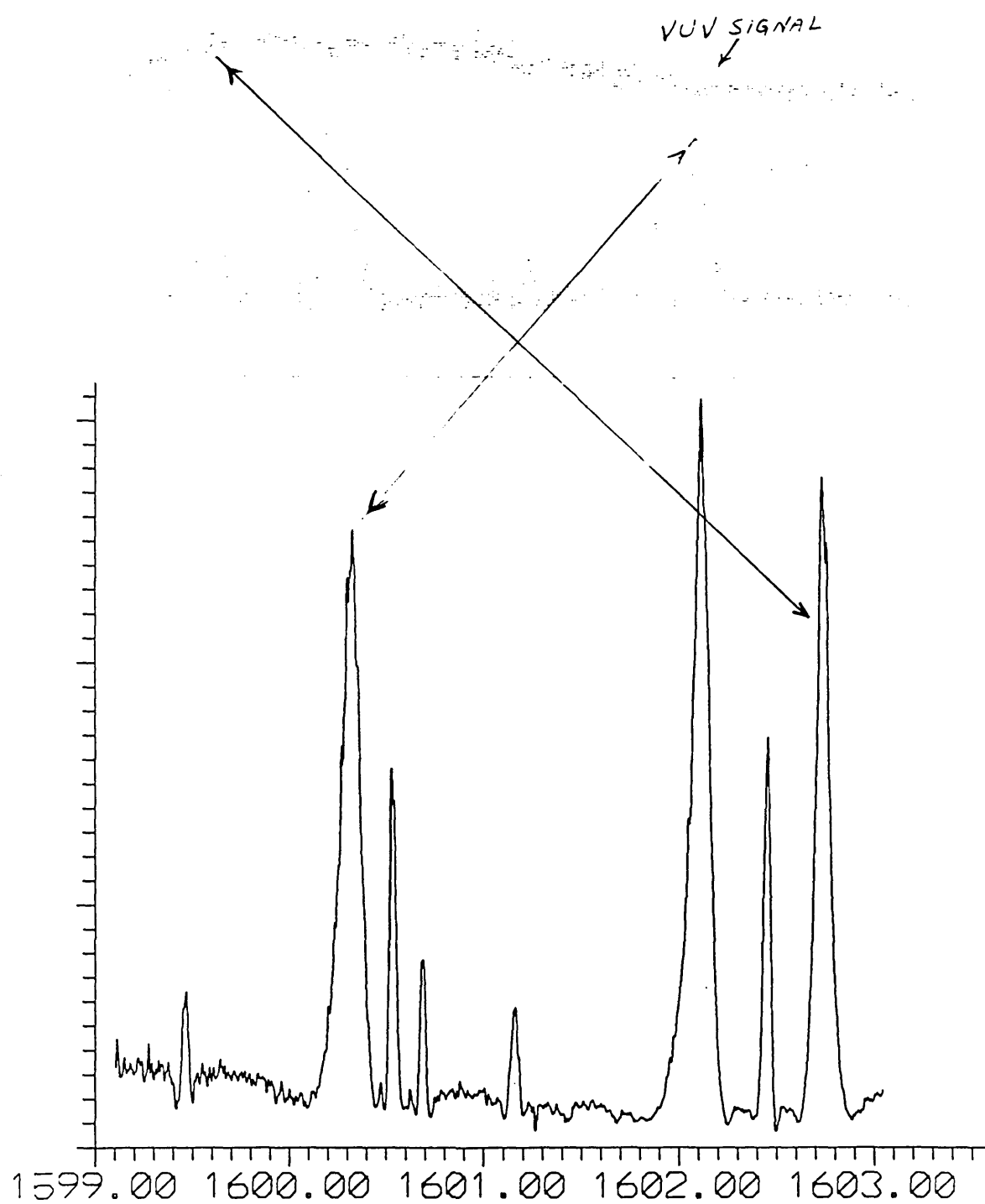


Figure 12.1: A normalised data file in which the background base line has shifted

puter code (MIN.FOR) which finds the minimum value in the data file and then subtracts this minimum from the whole data file (this procedure is mainly adopted in the case of calcium where the resonances lie above the first ionisation threshold). Thus now normalised data has a uniform base.

During the experiment, the data was stored in over a hundred separate files. This was mainly due to the restriction of the limited scan in one go and partially due to the very high resolution scans (very small steps in nm) in which case the computer file becomes full for a very small scan range. The restriction of a limited scan range is due to a number of reasons, the important ones of them are outlined here. Firstly, each dye has a small stable region (in nm) in which the output light intensity remains almost the same. If the scan range is more than the uniform region then the laser output will be of different intensities at different wavelengths in a single scan, and will generate an unstable VUV signal. Secondly, for most of the data, the visible output of the scanning laser was frequency doubled by a computer controlled crystal (depending upon the wavelength range the crystals were changed). Each crystal optimises itself at four equal intervals of the scan range. Hence, for a wide scan range the UV output also varies in shape. Thirdly, in the beam path of the scanning laser a telescope is used. As discussed previously, its function is to help focus two laser beams in the mixing cell. This is done by moving the telescope lens in and out for a fixed wavelength (normally the middle of the scan range) of the tuning laser. If during a scan the tuning laser wavelength is far away from this average position of the telescope lens, the tight focussing of the two laser beams will not be achieved and hence the VUV output will rapidly fall. Fourthly, the monochromator after the

mixing cell is optimized at the mid of the scanning range and the VUV signal decays for large scan range in a manner discussed earlier.

Knowing all these factors, the scans were limited in wavelength range and the complete spectra were recorded in over a hundred separate data files. Each data file has some overlapping wavelength portions with the previous file and each portion of the spectrum is scanned twice. These overlapping portions are necessary for digitally joining the data files together. In the high energy region of the spectrum (towards the ionisation threshold), the absorption lines are narrow and closely spaced. Thus, two consecutive files have one or two resonances common in the overlapping region and the joining is done at the absorption peak. However, joining has proved to be more difficult at the lower energy end, where the absorption resonances are much broader and well separated. Thus, each scan could record hardly one or two absorption resonances, and the overlapping region between the two files has nothing in common but the tail ends of these lines, and joining had to be done by matching the slopes of these ends.

In the calcium spectrum, there are some absorption resonances ($3d5p\ ^1P_1$, $3d7p\ ^1P_1$ and $4p5s$) too broad to be scanned by the laser; however, they are fully resolved in the previous synchrotron experiment⁵¹. Thus, these are not scanned but are borrowed from the synchrotron experiment and are incorporated in the present laser data. Digital joining of the laser and the synchrotron data together posed much difficulty because the synchrotron data is not of high resolution (a typical wavelength step in the synchrotron file is of $0.1\ \text{\AA}$ as compared to the $\sim 0.001\ \text{m\AA}$ in the laser data) and

hence, the overlapping region does not contain many data points (in the synchrotron file) to match the slopes.

12.1 Wavelength Calibration

The wavelength calibration could be done in two possible ways: either to set up a reference or to rely on the previous high resolution photographic work by Brown *et al* . Setting up a reference in the VUV was a very complicated job, because not only does it require a setup in the vacuum, but also some element with a reasonable number of absorption lines in the scan range. One could also accomplish the job by adding some impurity in the sample and hence avoid the need for a separate vacuum system, as some Mg impurity lines were observed in the calcium spectrum. Another possibility was to set up an Iodine absorption cell in the visible range of the scanning laser and record the signal simultaneously with the ion signal and then work out corresponding VUV wavelengths. This was good only when the resonance laser was quite stable, but unfortunately the fixed laser was found to have fluctuations, though small enough to be neglected otherwise. Keeping in view all this and the fact that the present experiments were not meant to establish new calibration, the high resolution photographic results of Brown *et al* (in calcium, barium and strontium) were taken as a standard for the wavelength calibration purpose.

The wavelength calibration has been achieved by taking the identification of the broad resonances as a reference. A standard computer code, the

Tchebyshev polynomial least square fit which fits a third order polynomial and needs at least three known references, was run, and the spectra of calcium, barium and strontium were calibrated this way. The fit has a standard deviation of less than 10^{-3} Å.

12.2 Cross-section calibration.

The cross-sections were calibrated only for the calcium spectrum. As the resonances were lying above only one continuum, it was easy to establish a true zero in the cross-section. Secondly the previous synchrotron experiment⁶² had provided a calibrated spectrum. The situation was quite complicated for the barium and strontium, as the doubly excited states appear above the second ionisation thresholds, and no previously calibrated spectra were available in the region of interest.

The cross-section calibration was achieved by taking the 3d7p 1P_1 , and 3d5p 1P_1 absorption resonances in the synchrotron data file as absolute reference. The 3d6p resonance scanned in the present experiment had to be joined on both sides with some synchrotron data, and due to very sharp rise of this vanishing line this joining was bound to errors. Thus, it was decided to convolve laser data for this line with the sinc^2 function for the monochromator, then compare the convolved data with the synchrotron data. Varying the sinc^2 function width and multiplying convolved data with a suitable number matched the two data. The final sinc^2 function width was 1.75 Å which is very close to the one reported⁶².

All the data was plotted by Benson plotter at the Imperial College Computer Center (ICCC). The plotting programme used routines Mcurve and Linaxs, available at the ICCC. The programme was written in Fortran 77.

Chapter 13

Results and Discussion

In this chapter the results of the experiments on calcium, barium and strontium are presented. Each element is dealt with separately and the features observed are explained on the basis of K-matrix theory. The spectra are compared with the theoretical calculations performed (As discussed in the chapter on review).

13.1 Calcium

Interchannel interactions are very ubiquitous in atomic spectra once the first ionisation threshold is crossed towards higher energies, giving rise to many subtle effects. In the absence of disturbance by an interloper level, the Fano parameters (Fano 1961, see also the review in chapter 3) of the Rydberg series are constant, or at least smooth and monotonic. When a non-Rydberg

level—an intruder level—is present, drastic variations may appear. Effects of the interchannel interaction are more obvious when the interloper level is very broad. Connerade *et al*¹⁰⁴ have categorized the observed effects according to salient points they illustrate.

- (1) Intensity minimum amongst the Rydberg levels. The f value of the Rydberg levels interacting with a broad level often exhibits a minimum.
- (2) Enhancement of the upper series members. In several instances where the series limit of Rydberg levels lies just above the resonance energy of the broad level, an enhancement of upper series members also distorts the course of intensity. Examples are observed in Zn I¹³, Tl I⁷, and Pb I¹⁰³.
- (3) The q-reversal effect. The change in symmetry of the Rydberg levels as the series passes through the broad feature is referred to as q-reversal (see chapter 3).
- (4) Vanishing width effect. A very narrow line occurs for a specific detuning from the energy of the intruder level (see chapter 3).

Among these, the q-reversal effect plays a central role in assessing coupling strength. An important conclusion from the study of Connerade *et al*¹⁰⁴ was that q-reversals are the hallmark of weak coupling, i.e. they tend to disappear as the interaction strength is increased. In order to answer the question that how many q reversals can be expected when a Rydberg manifold is perturbed by a single intruder level, a theoretical study was made by Connerade and Lane¹⁰¹. General expressions were derived within K-matrix approach (see chapter 3) for the variation of q as a function of the detuning from the energy of the intruder, both in the elastic scattering and photoioni-

sation. It turned out that as many as six q reversals can occur in the general case in photoionisation but that, in elastic scattering, there are at most two. The q reversal can appear at a fixed detuning from the resonance energy of the perturber. It is always offset from the energy of the intruder level, moving closer to it as the mixing strength decreases. However, the q reversal can also appear at an interaction strength close to which there is a sudden switch between weak- and strong-mixing conditions.

The q -reversal effect is associated not only with the presence of a broad intruder level in an autoionising Rydberg series. It can also be due to a Cooper minimum in the background continuum (see chapter 5). In this case the q reversal will appear at an energy where the Cooper minimum lies, and all the profiles will reverse in symmetry at that point.

The doubly excited autoionising series in Ca I above the first ionisation threshold exhibits most of these effects, and has been a challenge for theorists to explain the spectrum in detail. There exists a distribution of experiments in this energy range as reviewed in chapter 5. It thus makes a good case to study the interacting resonances in the atomic spectra. Several questions need to be answered, such as what is the cause of the vanishing of the particle width of the $3d6p$ resonance? Is there any Cooper minimum below the $3d$ threshold (as predicted by the *ab initio* R-matrix calculations? How many q reversals are there? To answer these questions, a detailed experimental study of this spectrum was needed to help theorists get started. With the narrow bandwidth, tunable vacuum ultraviolet radiation source (see chapter 9), and thermionic diode detector (which is linear over many decades of the

laser intensity), the present work is the most detailed and highly resolved experimental study of this spectrum. The extent of the resolution achieved is demonstrated near the series limit, as shown in Fig. 13.1. Fig. 13.2 shows the fully resolved 3d4f levels at the low energy end of the spectrum. The spectrum has been scanned from 158 nm to 180 nm. This energy range is dominated by the doubly excited autoionising series converging on the 3d threshold. Altogether there are six such series (3dnp $^1,^3P_1$, 3dnp 3D_1 , 3dnf $^1,^3P_1$ and 3dnf 3D_1), and two intruder levels, 4p5s, and 4p4d (belonging to a doubly excited series converging on the 4p threshold). These series interact not only with the background continuum (due to the series converging on the 4s threshold), they also interact with each other, especially the narrow levels which lie close to a broad level, and are greatly influenced by the broad resonances. These interactions give rise to various interesting phenomena like q-reversal (see chapter 3) and the vanishing width phenomenon.

The most remarkable feature is the vanishing width of the 3d6p 1P_1 resonance, which lies next to the broad intruder level 4p5s. In the previous measurements this level along with many others was not fully resolved from its triplet and thus it was not possible to measure its linewidth and cross-section accurately. Also, there was no information available regarding the line profile (whether symmetric or asymmetric). In the present study the two levels are fully resolved, and both the width and the cross-section are measured with a reasonable accuracy. The 3d6p 3P_1 level exhibits a true zero in the cross-section. The full width at half maximum (FWHM) of the 3d6p resonance is measured to be 0.4 Å, and the absolute cross-section is

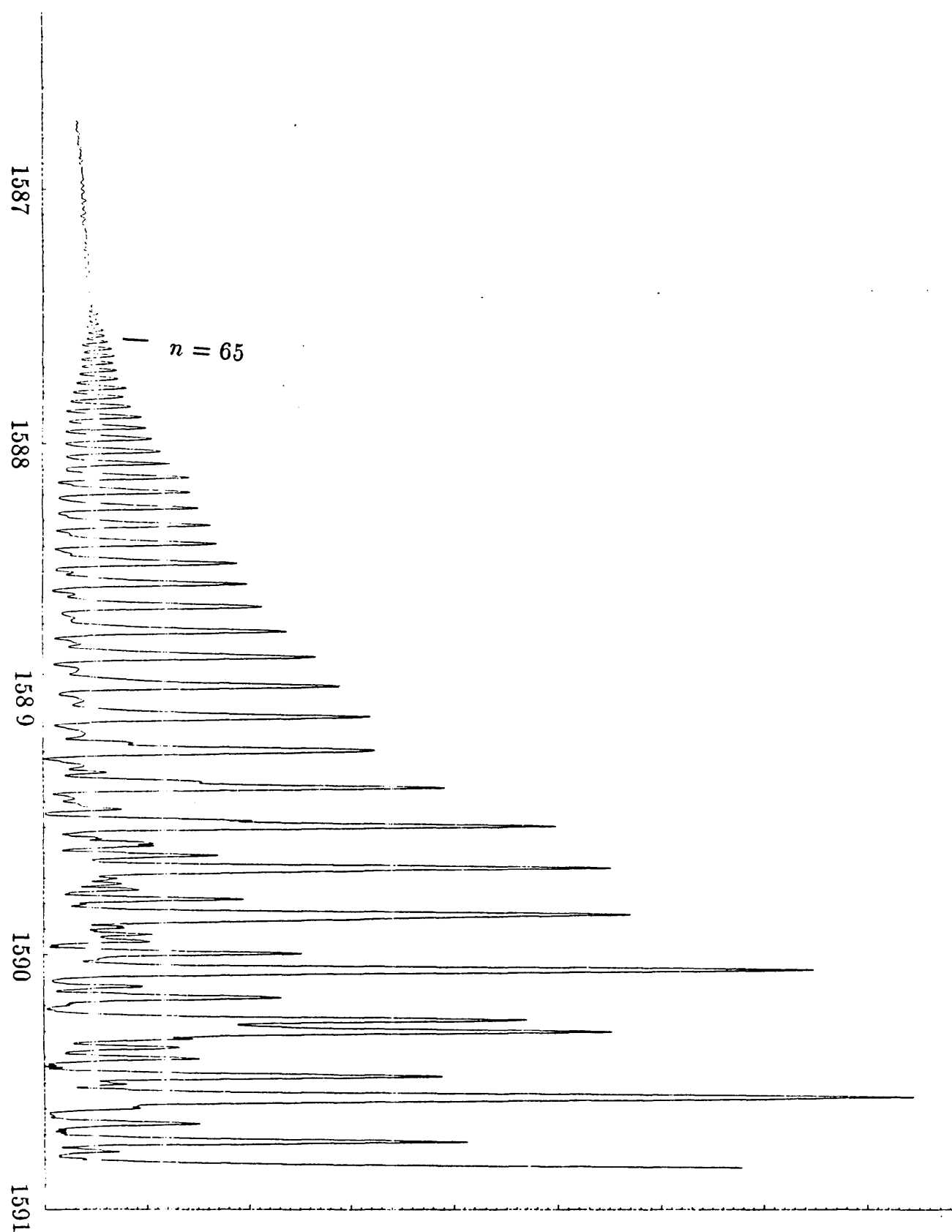


Figure 13.1: High resolution absorption spectrum of the 3dnp series in calcium near the series limit

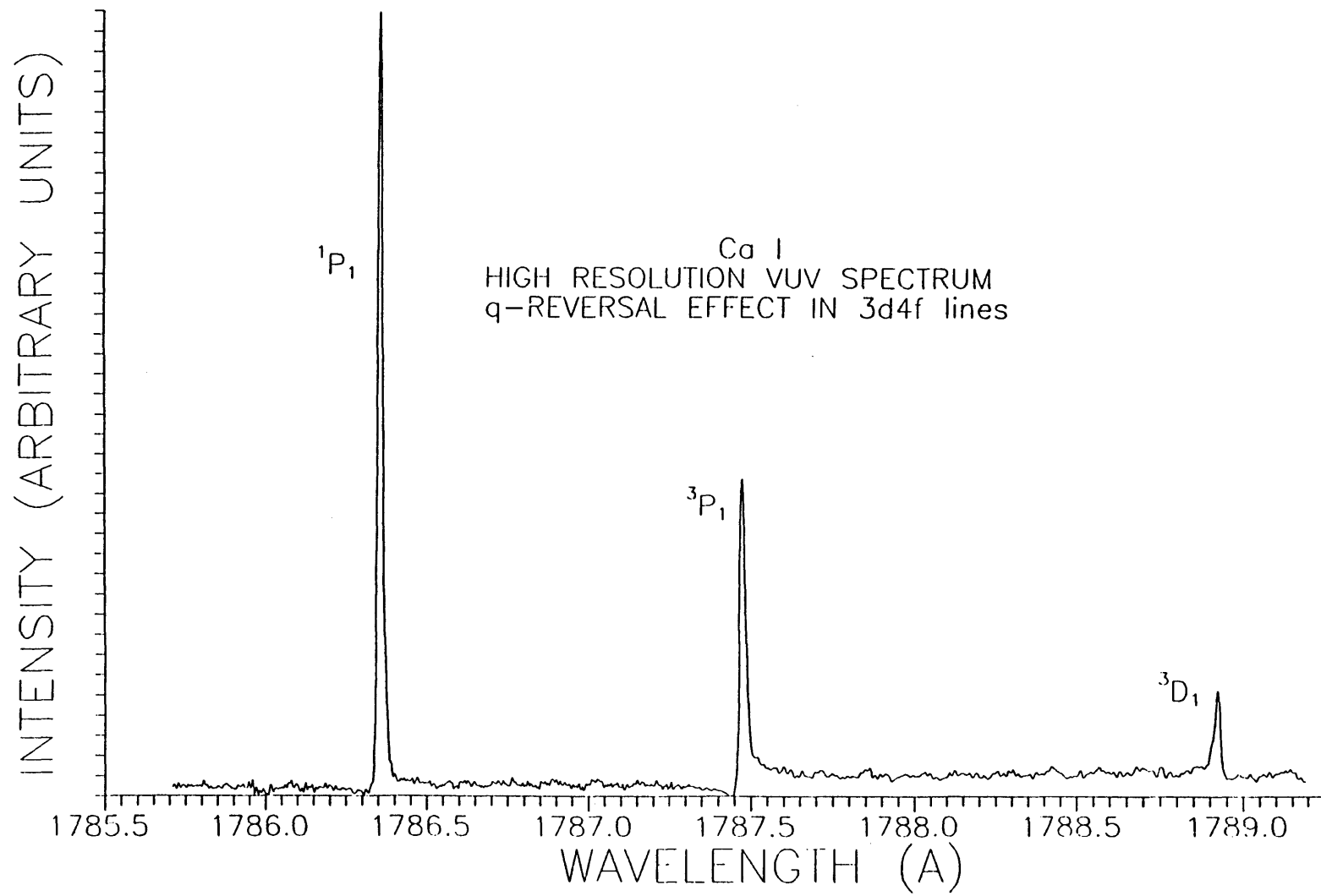


Figure 13.2: Absorption spectrum of the 3d4f levels near the low energy end

151.678±2.0 Mb (Fig. 13.3). Theoretical calculations by Greene¹ predict its FWHM around 1.2 Å, and the calculated cross-section is 83.249 Mb. Apart from this, narrow features due to the 3dnf series are also well resolved, which, according to Greene and Kim, play an important role in this complicated spectrum. Another important observation is that q is reversed each time a broad level is traversed. The narrow triplet states have typical Fano profiles (although the minima are not as deep as for isolated resonances) while the broad singlet levels are generally symmetric. The 3dnp 1P_1 series has been successfully scanned up to $n = 65$. Again, this is not surprising, since the 3d states of Ca^+ are metastable, and the widths of the autoionising series members fall off as $1/n^3$ (The high energy region near the series limit is not perturbed, so the series behaves in the normal fashion). Indeed, the observed half width of about 15 GHz for high members is reasonably close to the laser resolution of about 5 GHz. Previously this series was traced up to $n = 61$ by Brown *et al*¹⁹, thus we have extended this series by four new levels near the ionisation threshold. Similarly the 3dnf 1P_1 series is traced up to $n=44$, while Brown *et al* had observed this series up to $n = 39$. We have also observed the missing levels from $n = 27 - 34$, which were not observed by Brown *et al*.

¹The theoretical curves are the geometric mean of the length and velocity curves obtained from a jj-coupled eigenchannel calculation described by Greene and Aymar⁹³ and Greene¹¹⁶. The major difference of this approach from previous LS-coupled calculations in calcium^{32a,b} is that the LS-calculations ignored spin-orbit effects with the reaction zone, but included them in the final MQDT calculations through a frame transformation procedure. In contrast, the present jj-coupled approach includes the spin-orbit effects somewhat better.

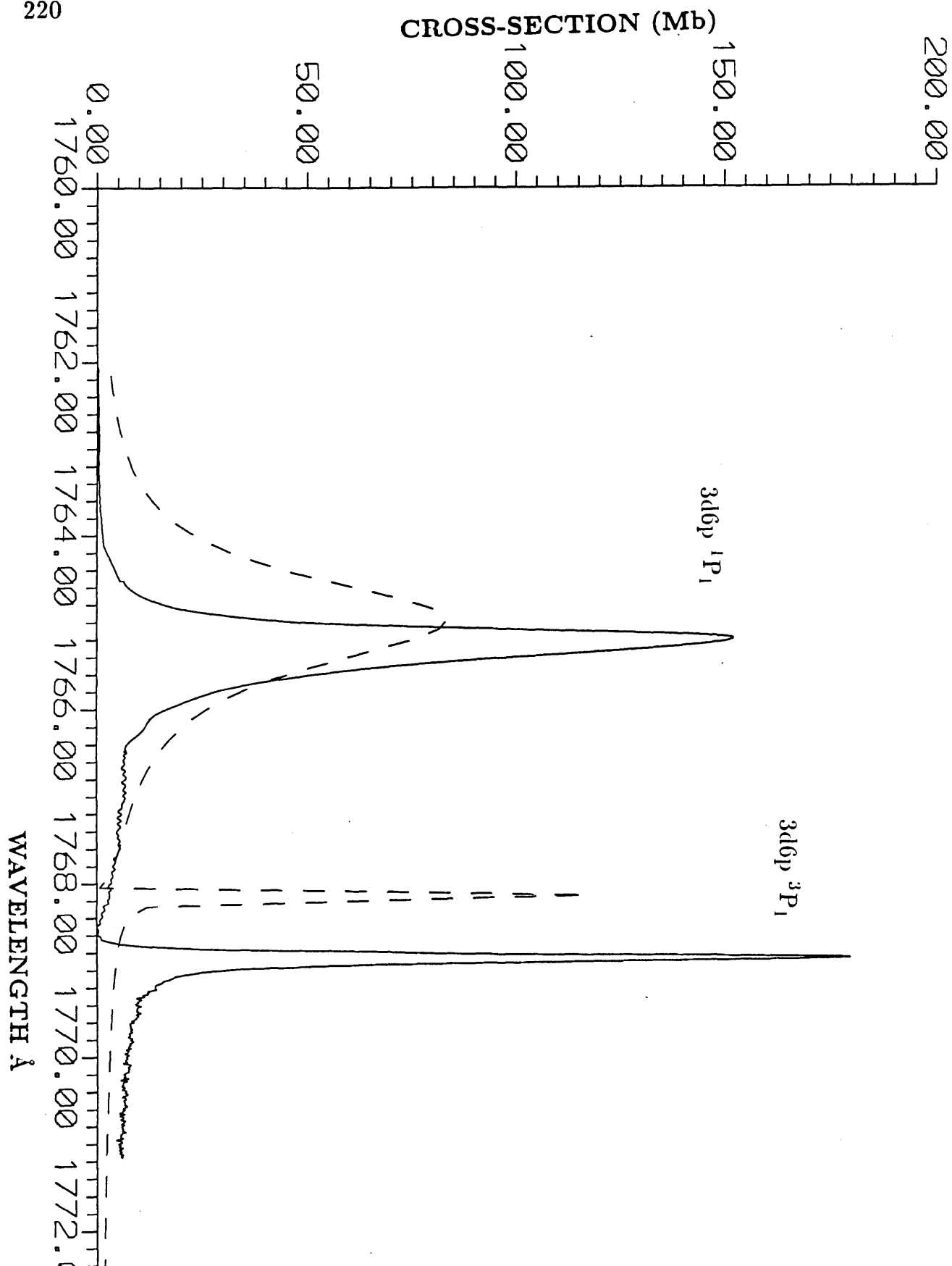


Figure 13.3: Absorption spectrum of the $3d6p\ ^1P_1$ level showing vanishing particle width effect. The dashed curve is the calculated spectrum by Greene

13.1.1 The 3dnp 1P_1 series

The $4s^2\ ^1S_0$ -3dnp $^1P_1^o$ series comprises very broad resonances. Apart from the 3d4p level, all of them lie above the first ionisation threshold. The 3d5p resonance is the first in this series that lies above the first ionisation threshold, however, it is not scanned in the present experiment for two reasons. Firstly it is very well resolved in the last synchrotron experiment⁶², and secondly it is too broad to be scanned with the laser (see laser limitations in chapter 12). Similarly the 3d7p resonance was too broad to be scanned with the laser, so we have borrowed it from the previous synchrotron data file⁶². The 3d6p resonance is strongly perturbed. The perturbation causes the particle widths to go to zero (not an exact zero but a much reduced value as compared to what it would have had in the absence of any perturbation). The main perturber, as is obvious from the semi-empirical R-matrix calculations by Kim and Greene, is the broad 4p5s intruder level. According to the K-matrix formalism (see chapter 3), a narrow line occurs for a specific detuning from the resonance energy of the intruder level, given by $\epsilon = -\mu^{-1}\Gamma_B^{1/2}$ for a Rydberg series of autoionising resonances interacting with a giant resonance. In general any very broad and intense resonance can be assumed to behave as a giant resonance, so the theory is equally applicable in the present situation. Indeed, it had been suggested in some of the R matrix calculations (Scott *et al* 1983, see also the review in chapter 5) that the vanishing width effect might be due, not to the perturbation, but to the occurrence of a Cooper minimum in the underlying continuum, as a result of which the autoionisation matrix element could exhibit phase cancellation. While the latter is undoubtedly an interesting alternative mechanism for

producing a vanishing particle width, it does not appear to be relevant for calcium. Indeed, the general agreement of Greene's calculations with the present experiment (Fig. 13.4 and 13.5)² confirms that the 4p5s perturber is the cause of this narrowing of the width of the 3d6p level. This is also confirmed by the parametric fit (based on the quantum defect theory) by Ueda⁸⁵. The theoretical cross-sections in these figures are somewhat higher than those observed experimentally. This may be due to the fact that the theory uses semi-empirical techniques. However, the joining of the digital data files (as discussed in chapter 12) is also bound to introduce certain errors, especially when some of the data files are joined at the background level, because there were no common peaks to join at the top. Similarly certain gaps are filled with the synchrotron data, because there were no levels in this energy range, so we decided to skip it. The synchrotron data was taken at a low resolution, and the number of data points is too small for the purpose of matching the slope.

The sequence of the series can be followed up to $n=14$. After that a strong mixing takes place (i.e. the sequential trend is difficult to follow, and the levels overlap). Levels are in general very broad and symmetric. Asymmetry is obvious in the 3d10p level. This trend is followed by the next

²The same spectrum in our paper (appendix A) was plotted with different plotting package available at the Imperial college computer center. The spectrum was, somehow, not plotted according to the scale, and unfortunately, was sent for publication where it was accepted as such. The fact is that none of the three figures in the paper is according to its data (the data is in fact on absolute scale both in terms of energy and cross-section), and as a result the 4 Åshift, mentioned in the paper, is not true. The theory has indeed, done a very good job. A detailed paper on the subject will follow soon, with correct figures.

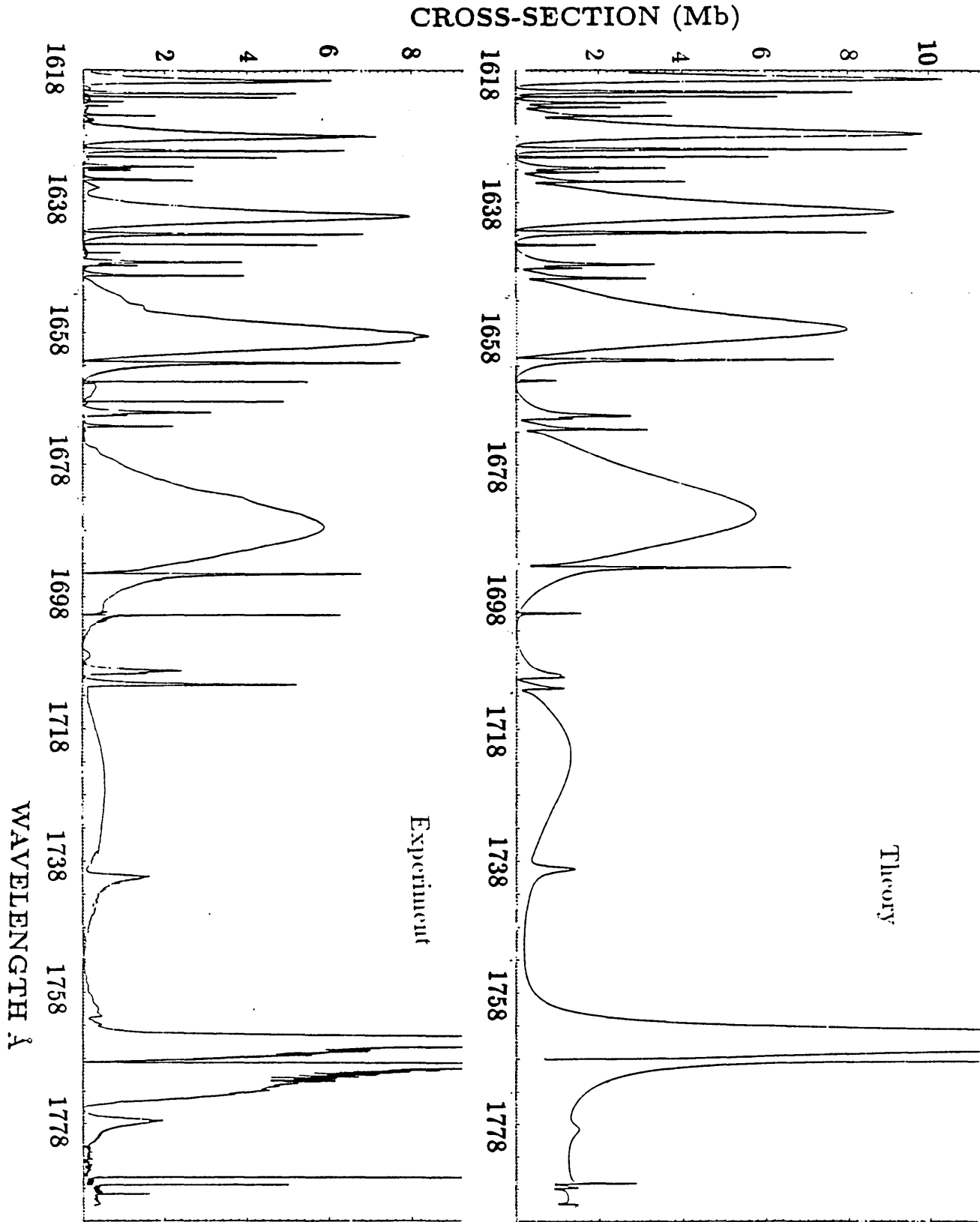


Figure 13.4: A comparison of the Greene's calculations with the present experiment

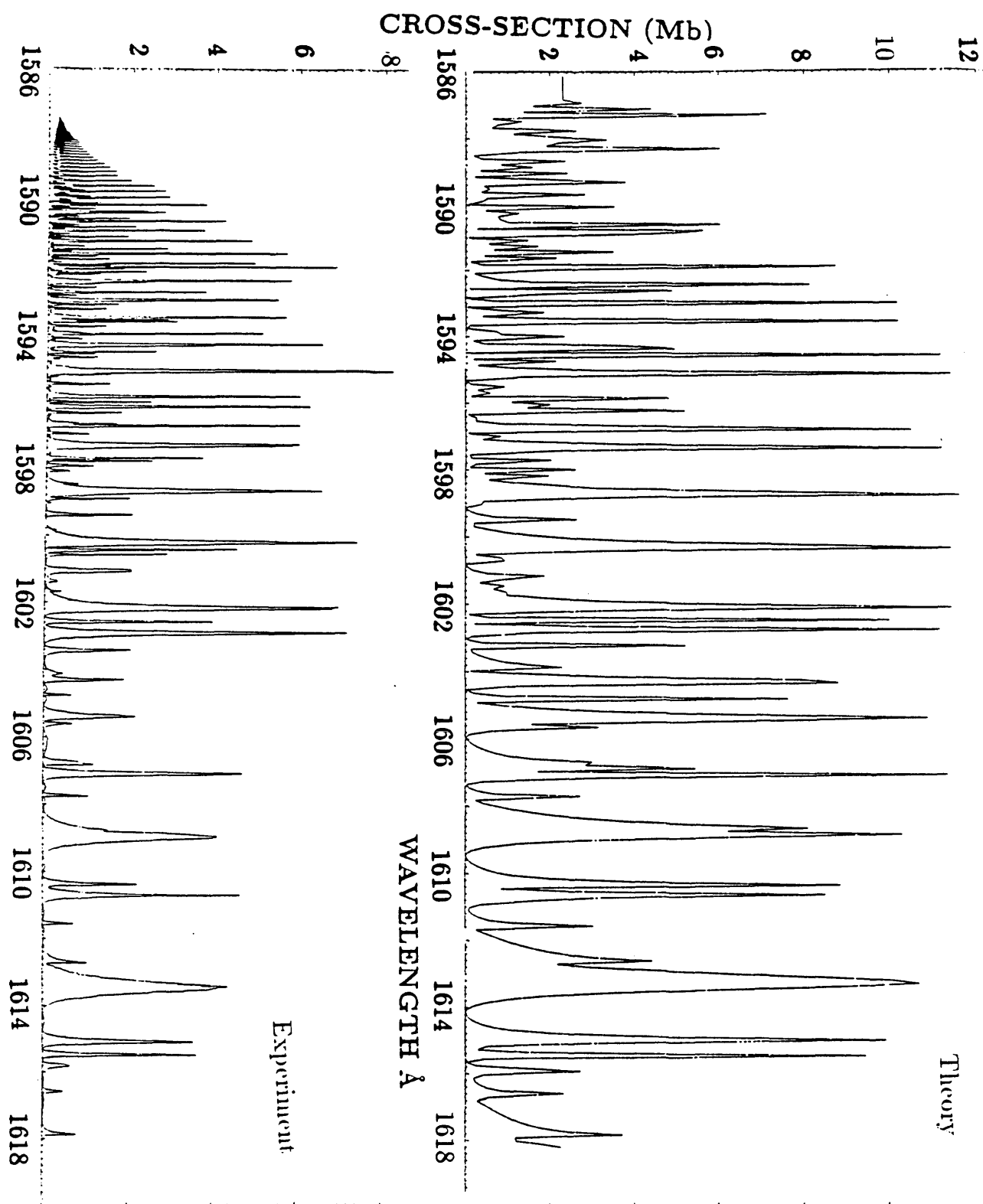


Figure 13.5: A comparison of the Greene's calculations with the experiment at high energy values

member of the series, however, the 3d14p level has its q reversed (see chapter 3) with respect to the 3d15p level. q reversals are also observed between n=16 and n=17 members of this series. In this region the series fluctuates in oscillator strength, and the transitions to the 3dnp 3D_1 levels are enhanced as compared to the allowed transitions. This region also contains another intruder level, the 4p4d level which belongs to a series that converges on the 4p (excited) state of the calcium ion. It appears as a shoulder to the high energy end of the 3d17p resonance, which has its q reversed with respect to the 3d16p level. Another q reversal is observed between the n=18 and n=19 members of the series, after which the levels become symmetric and the regular pattern emerges again from 3d25p to the series limit. The asymmetries observed are not very strong, and some of them need careful examination, though the theory (Greene and Kim) shows relatively strong asymmetry. As pointed out by Brown *et al* , in the presence of configuration interactions, all states are mixture of the members of the interacting basis sets, and no single pure-state identification is correct. For convenience, we label the observed series with L-S coupling term symbols. At low principal quantum numbers ($n < 15$), these L-S and orbital identifications are qualitatively in agreement with the expected behavior of such levels and with Hund's rules. In the region of maximum perturbation (1592 Å to 1630 Å) these regularities are much less evident. The asymmetric lines (in the 3dnp 1P_1 series) appear in this region of maximum perturbation. Altogether four q reversals are observed in this series. Although according to Connerade *et al* up to six q reversals can appear in a single Rydberg series perturbed by a broad interloper, due to the presence of other series in the region and the fact that they are strongly mixed, this theory is not applicable in this

situation .

Another observation is that the narrow levels (generally triplets) which appear at the either side of the broad singlet p resonances, have their q reversed with respect to each other (although they belong to different channels). In terms of the K-matrix treatment of the interacting resonances⁹⁴, this is due to the weak coupling between the triplet and the singlet levels, as q reversal is the hallmark of weak coupling.

Another consequence of perturbations is the anomaly in the course of intensities which occurs in a Rydberg series as a result of the perturbation. Fig 13.6 shows a plot of $n^{*3}f$ vs n , where n and n^* are the principal and effective quantum numbers, and f is the oscillator strength. This plot shows the extent of perturbation in this series. Fig 13.7 shows a theoretical fit of the Fano formula to the first four members of this series in the isolated line limit. There is a strong departure from the theory, especially in the wings, for very broad resonances. This is mainly due to the fact that the resonances are not isolated ones. It is interesting to fit the Dubau-Seaton formula⁹⁷ for the cross-section when the autoionising resonances overlap. Fig 13.8—13.15 present a portion of the spectrum in detail, also shown are some of the observed q reversals.

13.1.2 The $3dnp\ ^3P_1$ series

This series consists of narrow, sharp and generally asymmetric profiles, which are due to the $4s^2\ ^1S_0 \longrightarrow 3dnp\ ^3P_1^o$ transitions. Present observation

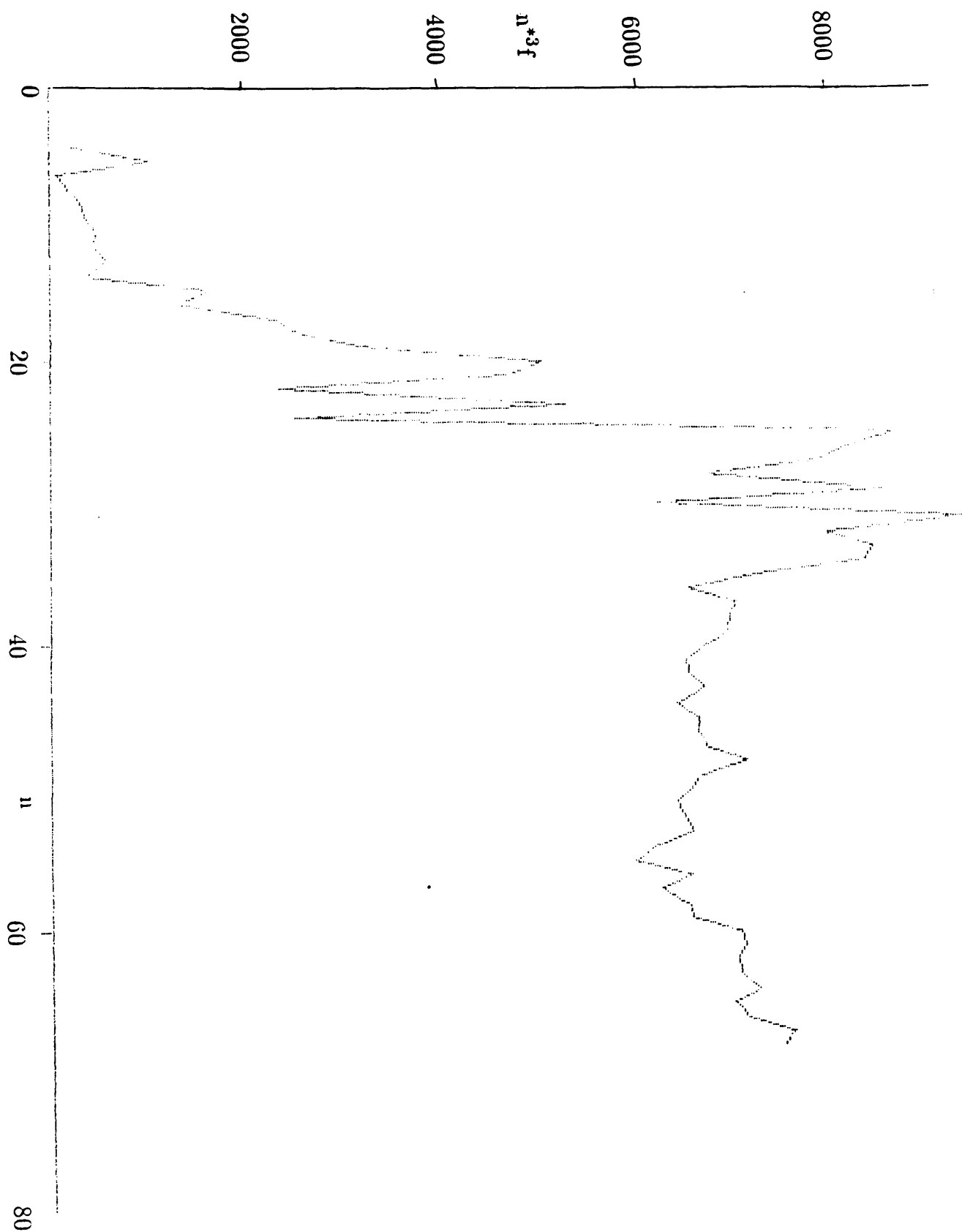


Figure 13.6: A plot of $n \cdot 3f$ Vs n for the $3dnp \ ^1P_1^o$ series in calcium

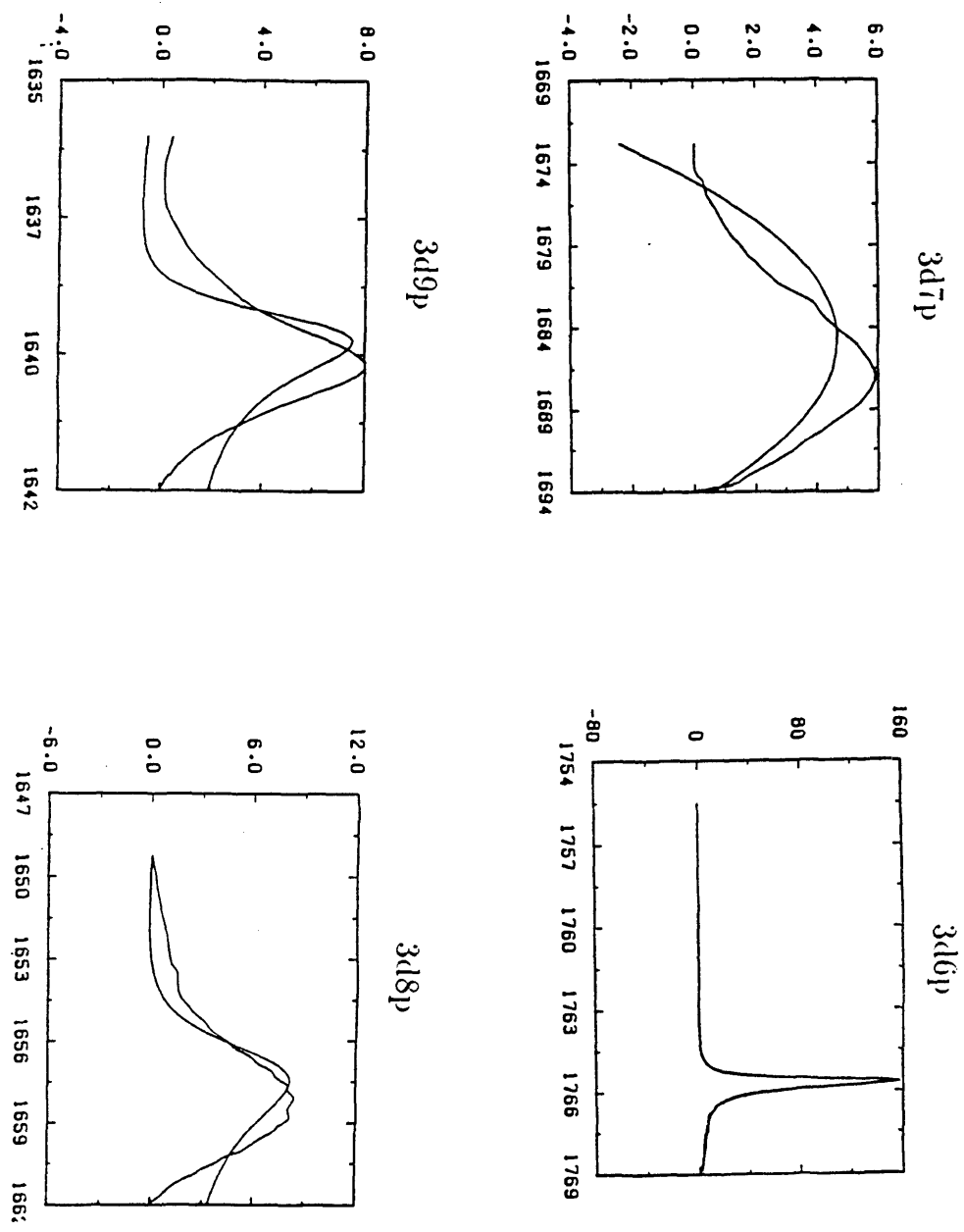


Figure 13.7: A theoretical fit of the Fano formula to the first four members ($n=6-9$) of the $3dnp \ ^1P_1^o$ series in calcium

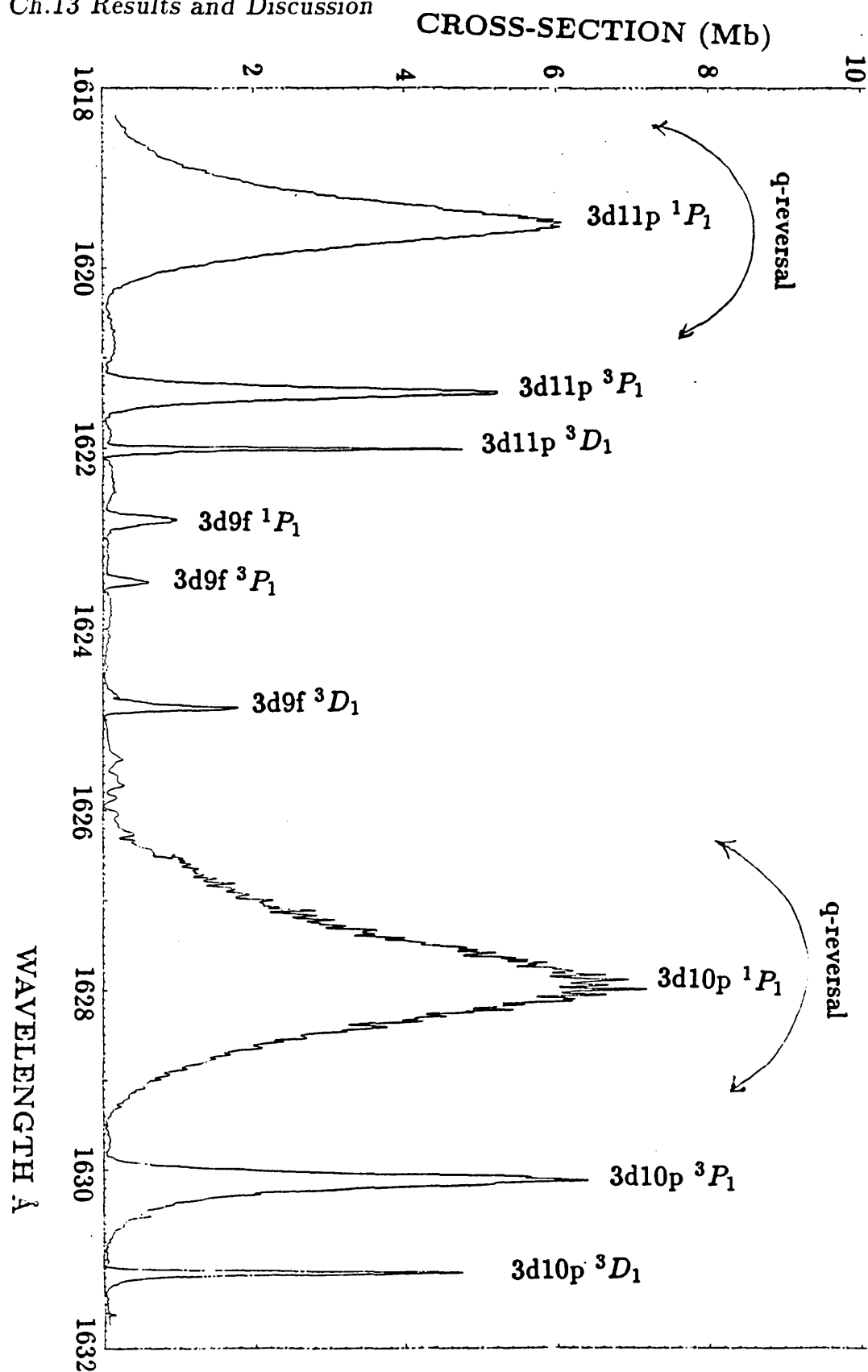


Figure 13.8: Absorption spectrum of the doubly excited series in Ca I below the 3d threshold

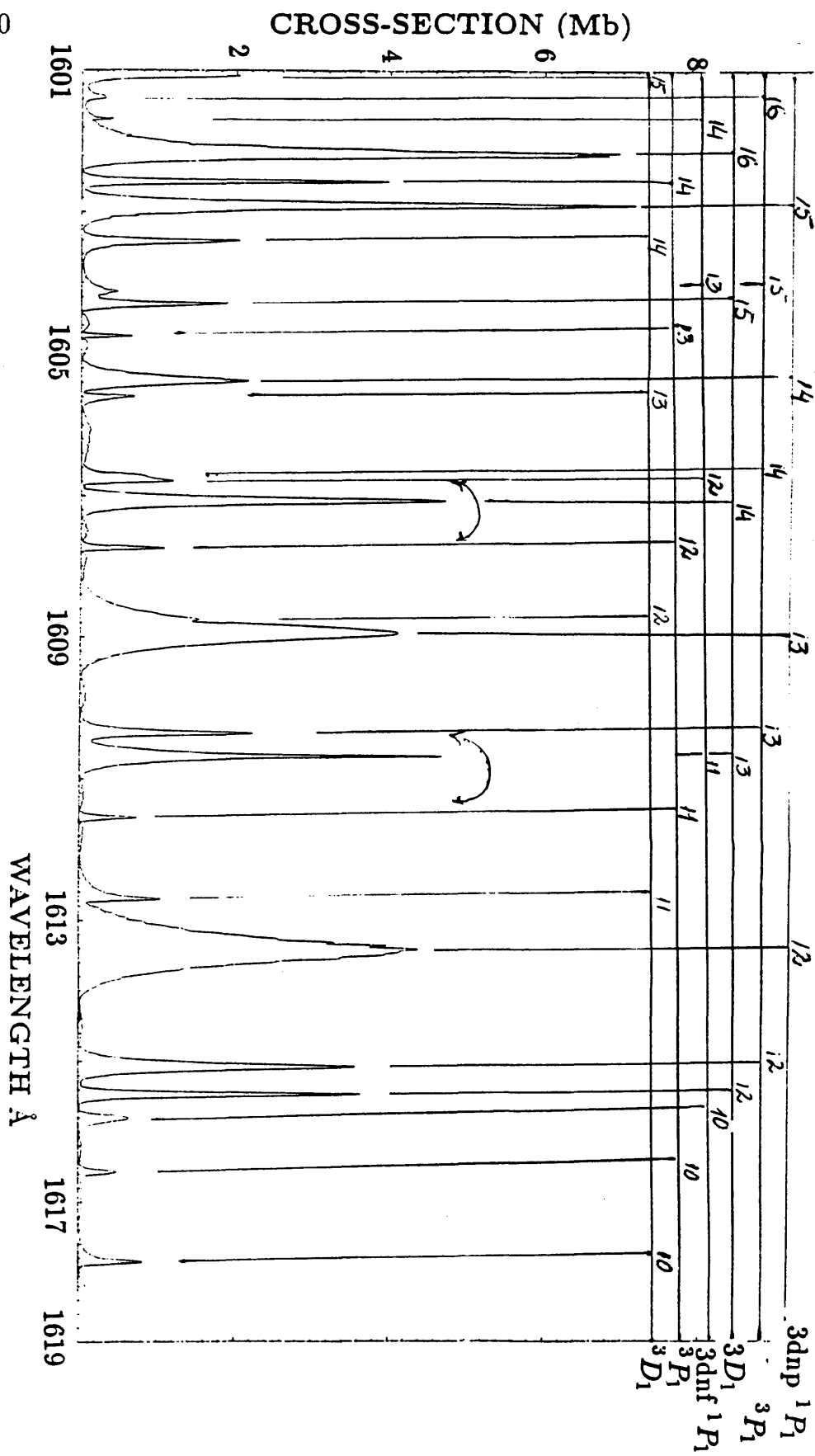


Figure 13.9: Absorption spectrum of the autoionising series in Ca I below the 3d threshold

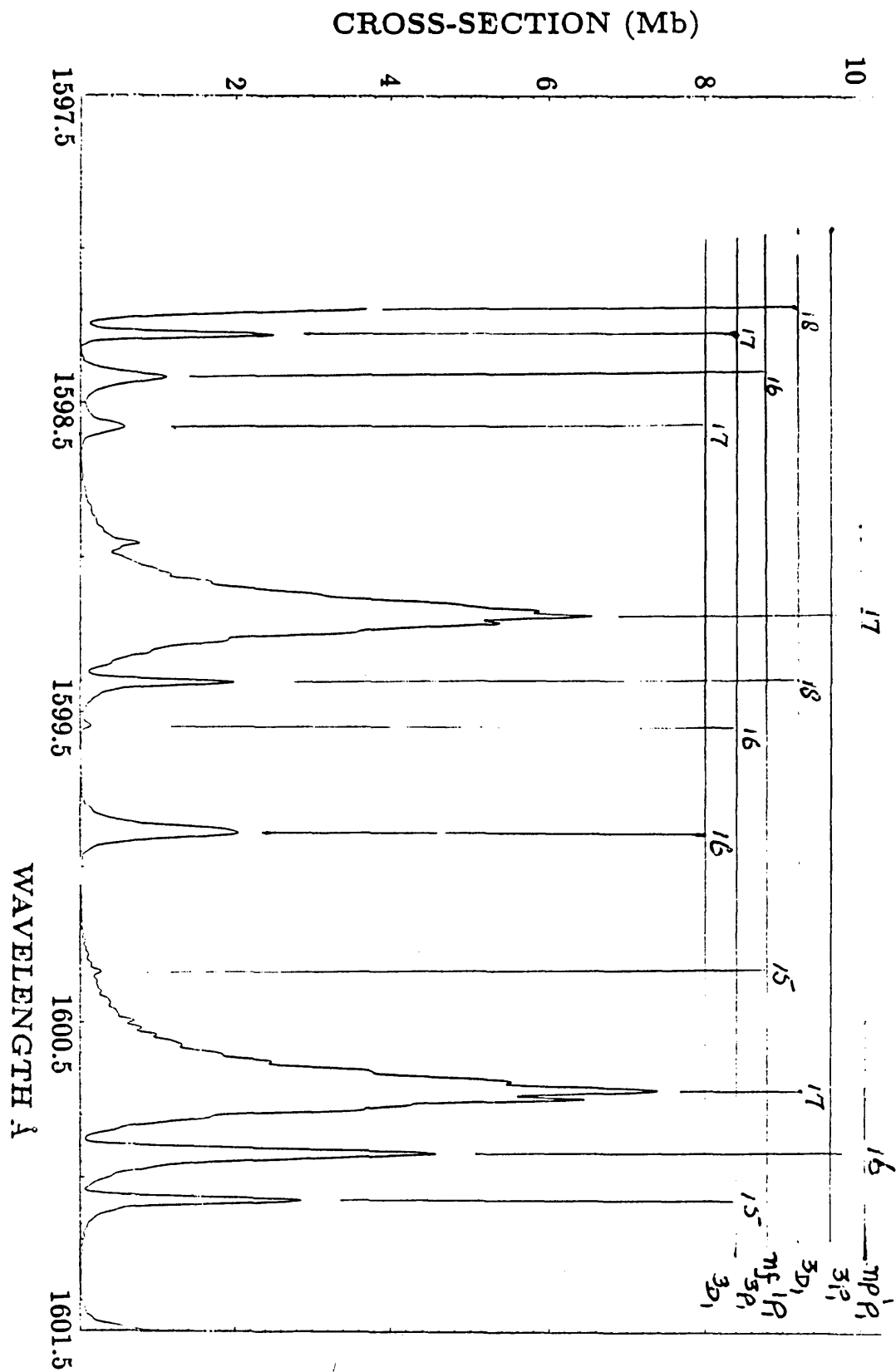


Figure 13.10: Absorption spectrum of the autoionising series in Ca I below the 3d threshold

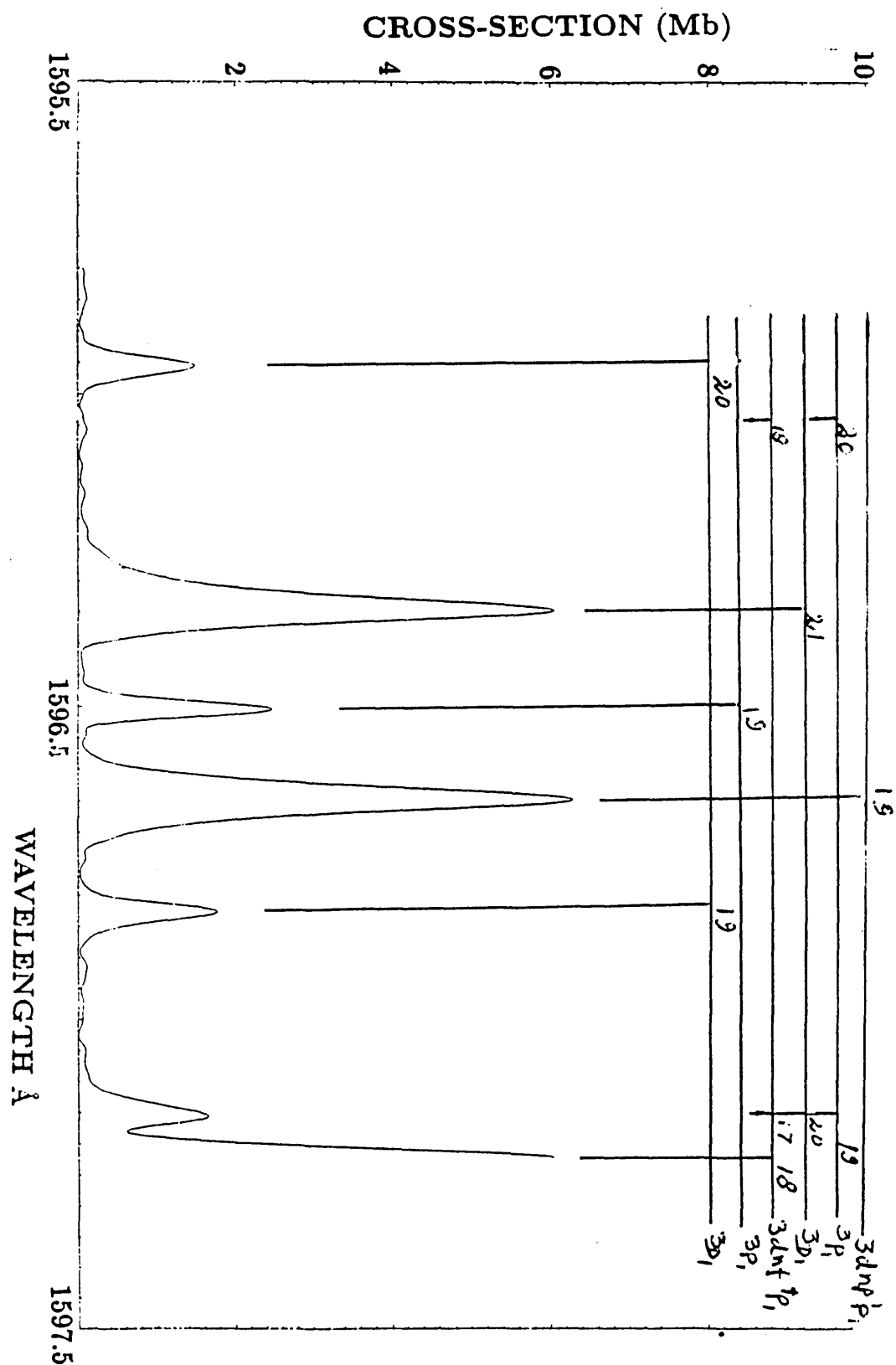


Figure 13.12: Absorption spectrum of the doubly excited series in Ca I below the 3d threshold

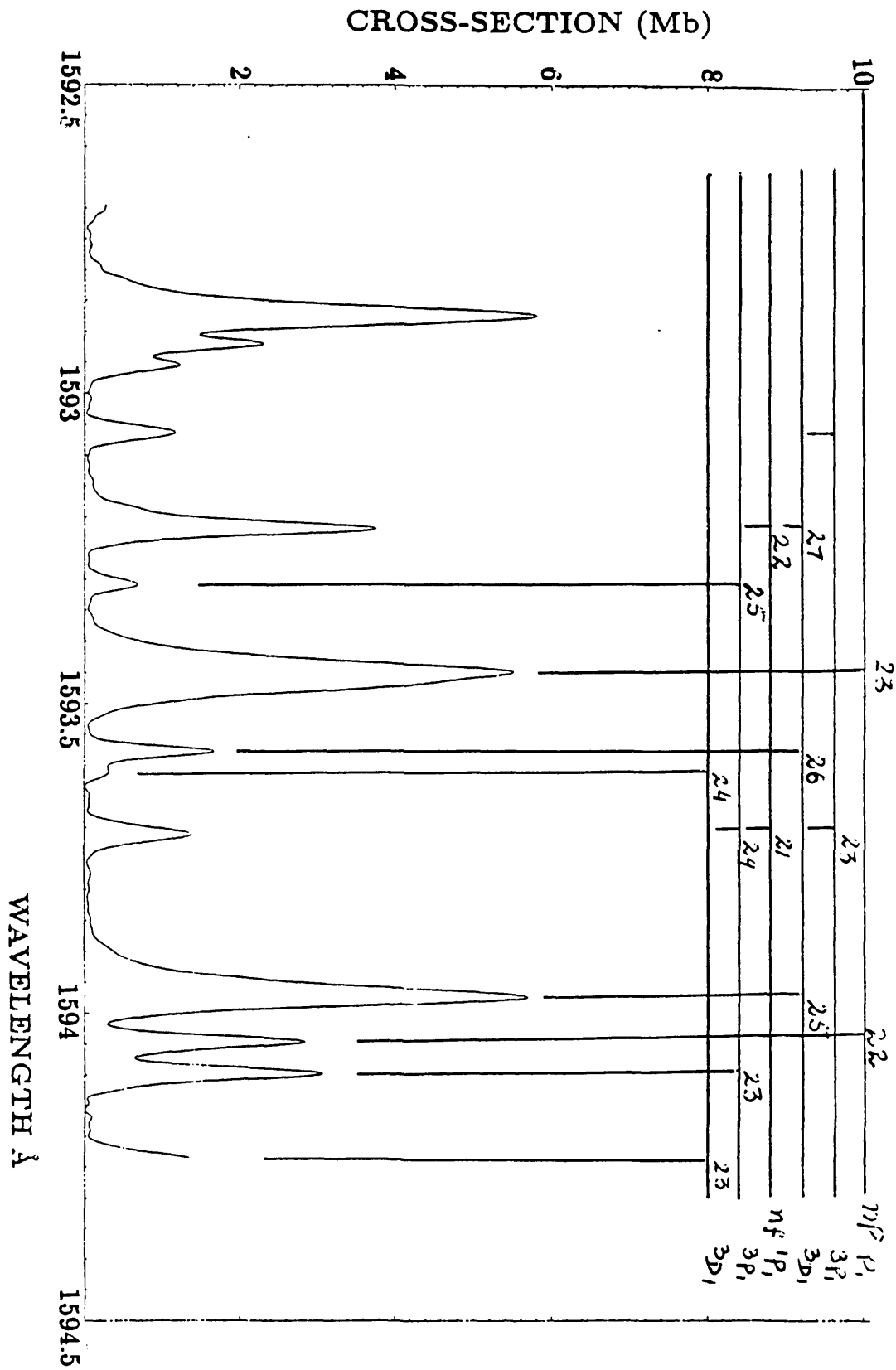


Figure 13.14: Absorption spectrum of the doubly excited series in Ca I below the 3d threshold

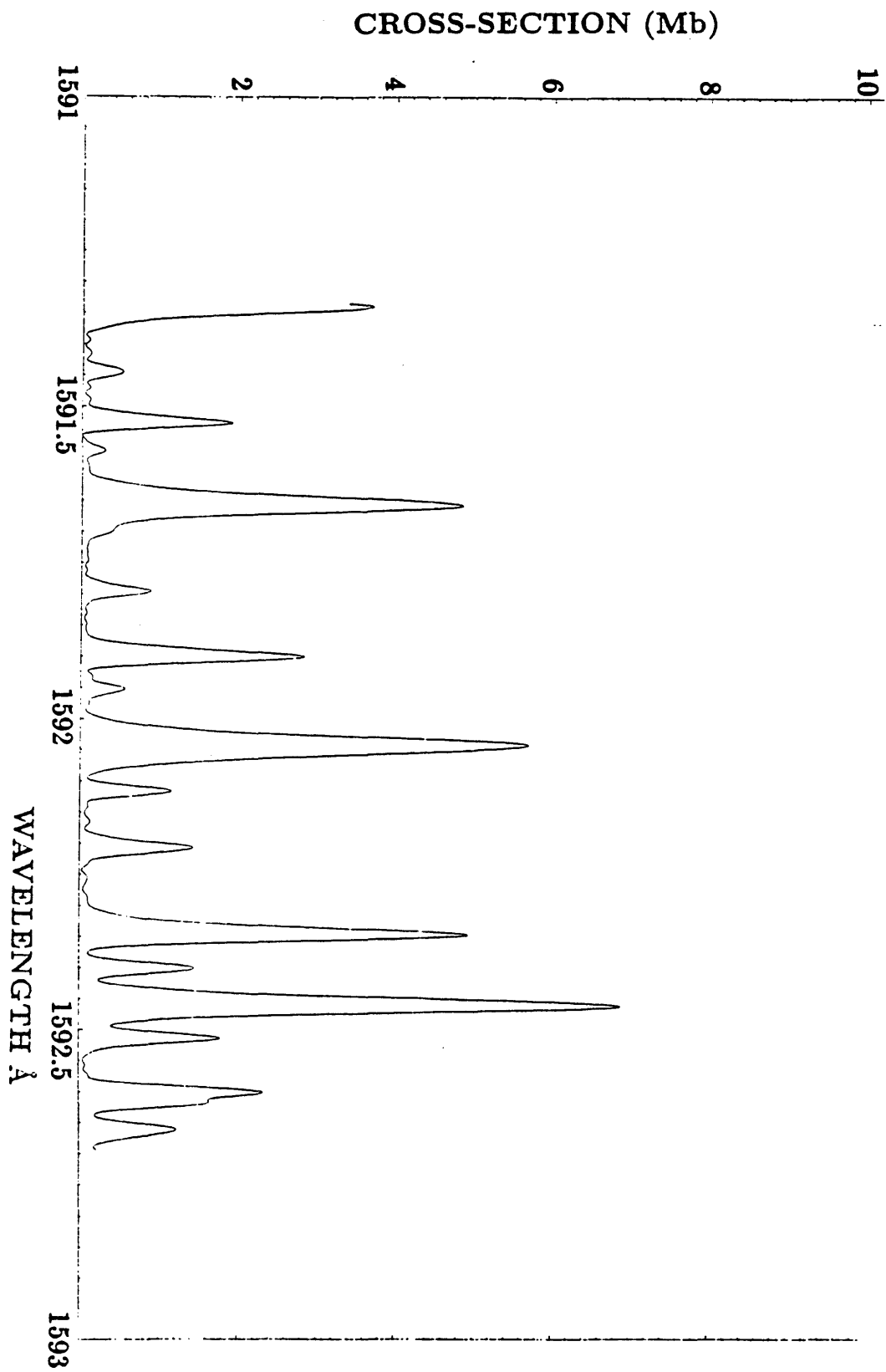


Figure 13.15: Absorption spectrum of the doubly excited series in Ca I below the 3d threshold

extends from $n=6$ to $n=34$, and are in agreement with the identifications by Brown *et al* (1973). We were able to identify one more member in this series beyond $n = 33$, as observed by Brown *et al* . According to Brown *et al* , this series initially approaches the $2D_{3/2}$ limit, but, after an avoided crossing with the $3dnf\ ^3P_1^o$ levels at $n=16$, the series finally converges on the $2d_{5/2}$ limit. For low n values, these levels appear very close to the $3dnp\ ^1P_1$ resonances and are very strong, confirming the fact that the states are a mixture of the members of the interacting basis sets. The levels are very asymmetric; this is due to interaction of these levels with the background continuum and with the nearby broad $3dnp\ ^1P_1$ levels. As remarked earlier, the two triplet levels at the either side of the broad $3dnp\ ^1P_1$ levels have their q reversed. This according to K-matrix approach, is due to the weak coupling between the broad and narrow features, as q reversal is the hallmark of the weak-coupling. A q reversal appears between the $3d11p$ and the $3d12p$ levels of this series. The spectrum of this series, as observed from the present experiment, shows a rapid decrease in the oscillator strength in the region of the maximum perturbation, and in fact, the $3d17p$ level is not observed in the present experiment. As n increases, so does the separation between these triplets and the singlet states (of the same n value). The asymmetry also fades away but not completely. Another q reversal is observed between $n = 15$ and $n = 16$ members of this series; $n = 17$ member could not be observed and $n = 18$ has q reversed with respect to $n = 16$. As this region is very complicated, it is difficult to point out a single resonance responsible for these reversals. Peculiarly, the $3d18p$ level is very strong, while the next two members are again weak. Beyond this region of maximum perturbation, the series once again gains in strength. The series is traced up to $n= 34$.

13.1.3 The $3\text{dnp } ^3\text{D}_1^o$ series

The lines for the $4s^2 \text{ } ^1\text{S}_0^o\text{-}3\text{dnp } ^3\text{P}_1^o$ series observed in the present experiment for $n=6\text{-}59$ are generally very sharp, narrow, and asymmetric. Previously, this series was observed up to $n = 58$, so we have observed one new member at the high energy end of the series. For the low n values, these transitions are weaker than the $3\text{dnp } ^1\text{P}$ and ^3P transitions (for the same n values), but at higher n value these become strong and are second to only the $3\text{dnp } ^1\text{P}$ levels in intensity. Altogether six q reversals are observed in this series. The normal series sequence is followed up to $n=12$, then the series enhances in strength from this level. All of the q reversals take place in this region of strong mixing. In terms of the K-matrix formalism, asymmetries and q reversals are due to the interaction of these levels with the broad singlet levels. For lower n values, the levels are very close in energy to the singlet p levels, and strong interaction takes place. As they are narrow, hence according to Connerade and Lane (1988, see also the review in chapter 3) these are type 1 profiles, which, in the isolated line limit, tend to the typical Fano shape.

13.1.4 The 3dnf series

The $4s^2 \text{ } ^1\text{S}_0\text{-}3\text{dnf } ^1,^3\text{P}_1, ^3\text{D}_1$ transitions play an important part in the calculation of the calcium spectrum in the range of interest (below the $3\text{D}_{3/2,5/2}$ series limit). Kim and Greene (1987 II), have used a simple frame transformation, from LS to jj coupling, to take into account these narrow and weak

features, and they were able to generate a complete spectrum.

The $3dnf\ ^1P_1^o$ levels are sharp, narrow, and asymmetric in general. They are the strongest in the $3dnf$ channels (i.e. as compared to the triplet series). In the present study the series has been observed up to $n=44$, adding five more members in the previously observed list. The $3d4f$ is the first member of this series above the $4s$ continuum, and it is q reversed with respect to the $3d5f$ member of the series (in between the two lies the broad intruder level, $5s4p\ ^1P_1$). Altogether 5 q reversals are observed in this series. Most of them appear in the region of strong mixing where either the levels overlap or they are very close in energy to the broad levels.

The $3dnf\ ^3P_1$ series, observed in this experiment, extends from $n=4-38$. The lines are narrow, sharp, and asymmetric. The first q reversal is observed between the $3d4f$ and $3d5f$ levels. In the region of strong mixing these lines are very weak and it is hard to make any judgement on their line profiles. The series improves in strength after this region. A total of two q reversals are observed.

At low n values, the $3dnf\ ^3D_1$ series appears on the high energy shoulder of the $3d(n+1)p\ ^1P$ levels, with the exception of the $3d6p$, where the broad intruder level pushes the $3d5f$ levels to the high energy side. These levels are narrow, asymmetric and sharp. The series has been followed up to $n=30$.

Conclusion

The doubly excited 3dnp spectrum in Ca I has proved to be much more complicated than was initially thought. The present, detailed experimental study has revealed the fact that the series is badly perturbed. More than one q reversals are observed. Because of the complexity of the spectrum, the theoretical analysis by Connerade and Lane regarding the number of q reversals in a Rydberg series is not applicable. No single point in energy is observed where all the profiles are reversed in symmetry, i.e. the point where the Cooper minimum lies. However, the existence of the Cooper minimum cannot be discounted and further *ab initio* R-matrix calculations for Ca I are clearly called for in order to determine its whereabouts more precisely.

Apart from this, the series are extended further by identification of a few new members at the high energy end of the spectrum which were not observed previously. Digital joining of the data files has proved to be very difficult job. The cross-section estimates are bound to some errors. This is due to certain joints at the background level, and addition of the synchrotron data to bridge the gaps. Since this work was mainly to study the profile structures, the energy range where no structures were reported was not scanned. This saved a lot of experimental work. The semi-empirical R-matrix calculations show a reasonable agreement with the experiment. The theory has successfully predicted the levels and their profiles especially at the low energy end of the spectrum, though the theoretical cross-sections for transitions are, in general, larger than those experimentally observed. At the high energy end, near the series limit, only the 3dnp 1P_1 series can be

traced up to $n=31$. This overall agreement with the experiment suggests by implication, that the interpretation which attributes the width fluctuation to the influence of the $4p5s\ ^1P$ perturber is the most plausible.

13.2 Barium experiment

The doubly excited autoionising resonances in barium are investigated. The transitions $6s^2\ ^1S_0-6p_{1/2}\ ns, nd$ converge on the $6p_{1/2}$ series limit at $62296.46\ \text{cm}^{-1}$ ($1605.2\ \text{\AA}$). There is also a gross perturber level $6p_{3/2}10d$, which belongs to a series converging on the $6p_{3/2}$ series limit. There are altogether eight open channels in the energy range of interest, i.e. $6s\epsilon p_{1/2}$, $6s\epsilon p_{3/2}$, $5d_{3/2}\epsilon p_{1/2,3/2}$, $5d_{3/2}\epsilon f_{5/2}$, $5d_{5/2}\epsilon p_{3/2}$, $5d_{5/2}\epsilon f_{5/2,7/2}$. The general schematic diagram of this $J=1$ odd parity spectrum of barium is as shown in Fig. 13.16. Levels have a typical asymmetric Beutler-Fano profiles.

As explained in chapter 6, this spectrum has been previously investigated by Garton and Tomkins¹, Garton *et al*², and Hudson *et al*³. Brown and Ginter⁹⁰ reinvestigated the 177-156 nm wavelength range with higher spectral resolution. The spectrum (see chapter 6) shows a strong variation in the Rydberg fluctuations with a minimum near the minimum of the gross structure caused by the broad level. There can be two possible situations when the fluctuations tend to zero. First and fairly obvious is the situation near the limit of a Rydberg series where the spectral fluctuations tend to zero as the limit is approached (Gailitis averaging). Another situation where experimental fluctuations in the cross-section tend to zero is when

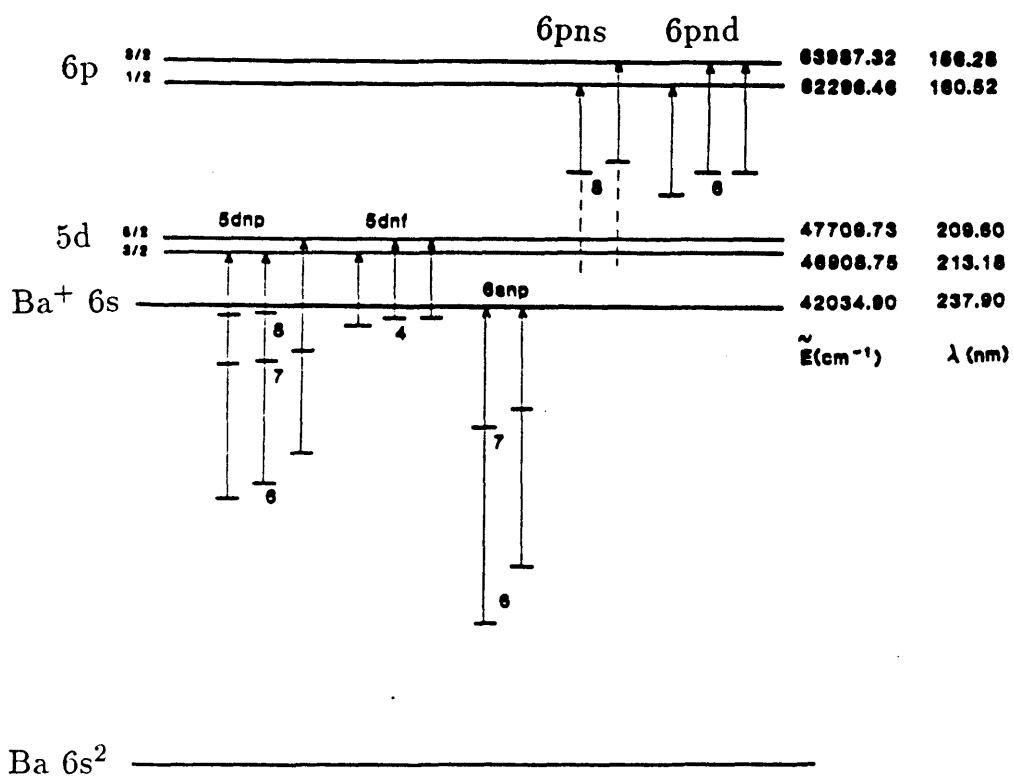


Figure 13.16: The schematic diagram of the J=1 odd-parity spectrum of barium

a vanishing width occurs¹⁰³ and the instrumental resolution is finite. This situation is more interesting, since the fluctuations then pass through zero at an energy which does not coincide with the series limit. However, the vanishing width effect occurs with one open channel, whereas fluctuations may exhibit variations even if many channels are open. However, Brown and Ginter themselves raised doubts about the genuineness of the minimum in the fluctuations, by saying that instrumental interference effect can occur amongst the high members of Rydberg series when the spacings between adjacent lines gradually approach the resolution limit of a classical spectrograph. Another interesting point is that, although two series are expected to the $^2P_{1/2}$ limit at 1605.2 Å and three to the $^2P_{3/2}$ limit at 1562.8 Å, in fact only four series (two to each limit) were detected experimentally. However, Brown and Ginter found evidence of very strong mixing in the range further studied here, and therefore suggested that the missing fifth series might be present in this region.

Lane¹¹ (1985) made a theoretical study of this spectrum using K-matrix formalism. As a result of his analysis that the number of parameters needed in this example is large, so that a zero-point in the fluctuations might prove unlikely, he raised the question of the genuineness of the observed minimum. Recently, calculation of the same spectrum using the LS-coupled numerical eigenchannel R-matrix method has been performed by Aymar¹². This spectrum also reveals the same fluctuations. The numerical approach is similar in energy resolution to the experiment of the Brown and Ginter, and hence the differences between the predictions for the high members of the series are hard to assess. The energy resolution in all the work previously cited

is inadequate to reveal the true behavior of the resonances in the vicinity of the vanishing fluctuations. Specifically, it remains unclear whether the fluctuation is purely due to intensities or to variations in the widths of the resonances.

The present experiment was aimed to establish the genuineness of this vanishing of the fluctuations, because if it is genuine, then it gives rise to the following question: can a point of zero fluctuations be similarly detuned from the associated series limit without occurrence of a vanishing width, i.e. do points of vanishing fluctuation exist as an independent property resulting from a perturbation by an intruder state?

The spectrum recorded in the present work is as shown in Fig. 13.17 and 13.18. Present results confirm the experimental observation of Brown and Ginter: the fluctuations vanish at a definite point near $1609.20 \pm .20$ Å. Secondly, it is observed that the widths of the resonances tend to zero smoothly as the $6p_{1/2}$ series limit is approached, i.e. that the minimum in the fluctuations is not due to a vanishing width effect. Third, changes in the shapes of the line profiles are observed as the vanishing point is traversed. A fourth point is that there may indeed be further structure present in this region that can be accounted for from the fourth most prominent series. However, the noise level on the present spectrum is still too high for an unambiguous conclusion to be reached.

Figures 13.17 and 13.18 show the regular progression of the Rydberg spacings and widths, which ensures the constancy of $\mu^2 = \Gamma_n/H_n^2$ where Γ_n is the particle width and H_n^2 is the interaction strength between the

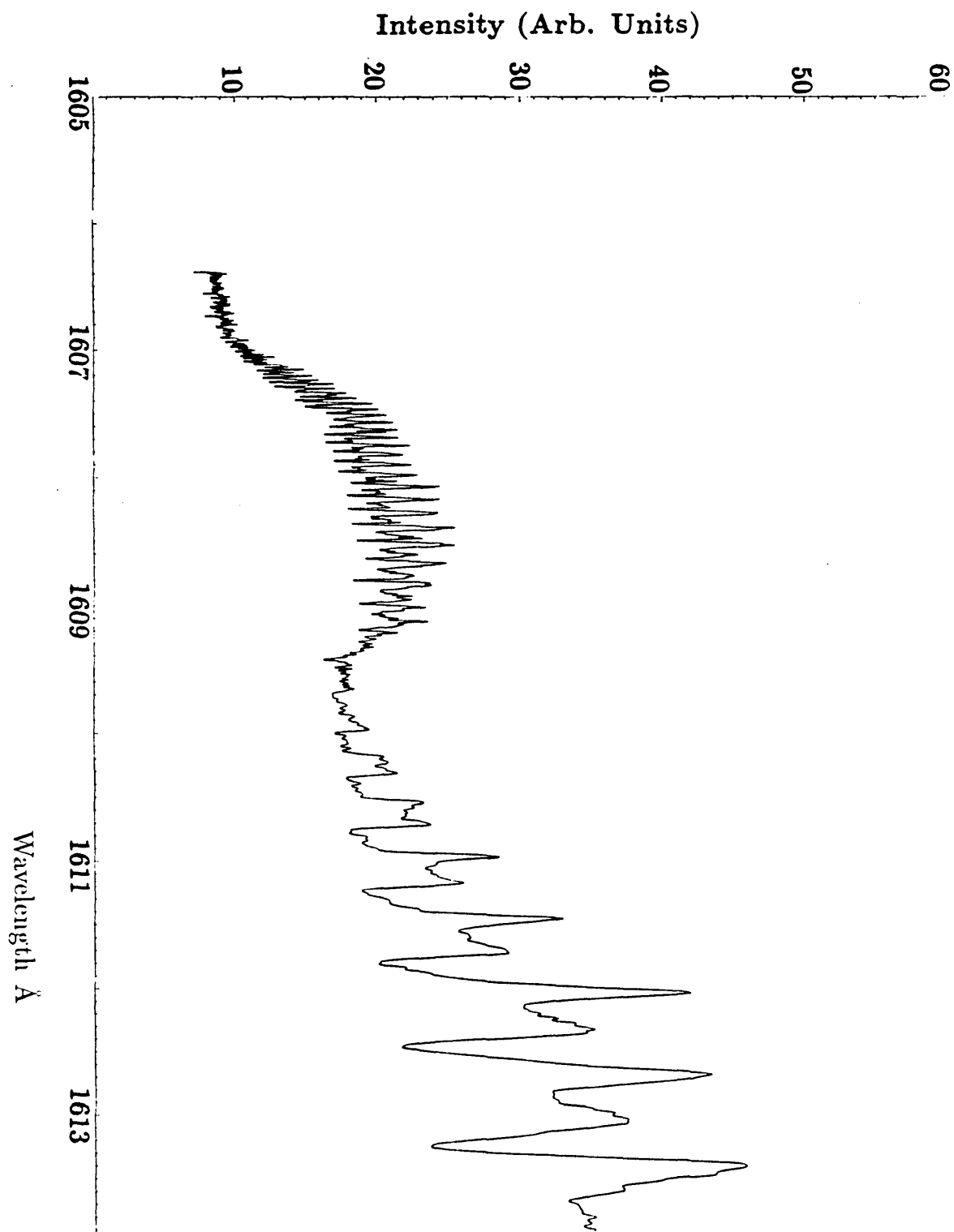


Figure 13.17: Absorption spectrum of Ba I below the $6p_{1/2}$ threshold, showing the vanishing of fluctuations.

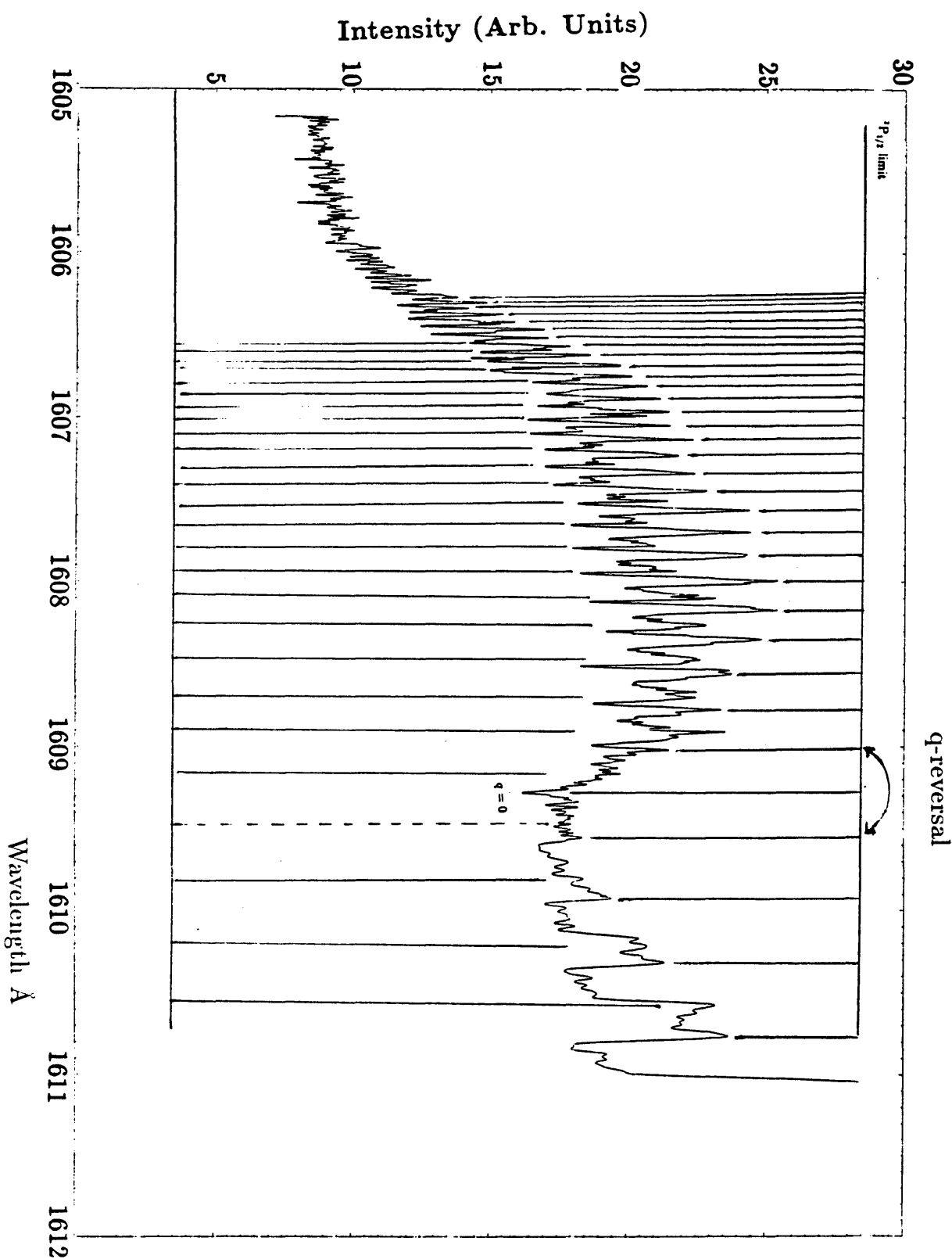


Figure 13.18: High energy end of the absorption spectrum of Ba I

Rydberg levels $|n\rangle$ and the broad intruder state $|B\rangle$. Fig 13.17 and 13.18 also show the presence of a transmission resonance, about which a q-reversal occurs¹⁰³. This is a crucial new observation, which is useful in the analysis of the spectrum in the K matrix formalism. Another instance where a q-reversal straddles a $q = 0$ window resonance was discussed by Connerade *et al*¹⁰⁴ in the spectrum of Tl I. Connerade and Lane¹⁰³ also found a theoretical example in calculations of a Rydberg series of sharp lines weakly coupled to a broad resonance: in the latter case, the form of the variation of q was shown to be (see also the review in chapter 3, Eq. 3.51):

$$q = \frac{1 - \bar{\delta}\bar{\Delta}}{\bar{\delta} + \bar{\Delta}} \quad (13.1)$$

where $\bar{\delta}$ is a background, essentially constant phase shift due to the underlying continuum, and $\bar{\Delta}$ is the phase shift due to the broad intruder level (see Eq. 3.47). Hence $q = 0$ when $\bar{\Delta} = 1/\bar{\delta}$, which also turns out to be the condition for a maximum to occur in the cross-section the intruder level would possess at zero coupling strength. This condition is satisfied at energy (Eq. 3.51)

$$E_0 = E_B - \left(\frac{\Gamma_B}{2}\right) \tan \delta \quad (13.2)$$

About this value, $\bar{\Delta}$, and therefore q , change sign, i.e. a q-reversal occurs. The present data exhibits this behavior quite clearly, close to the point where the fluctuations disappear: one line (marked 'X') has $q \sim 0$ and, about this line, a q-reversal of the associated series does indeed occur (see Fig. 13.17).

Connerade and Lane¹⁰¹ (1987a) had performed their calculations with a

single open channel, and they had found a vanishing width at an energy

$$E_{vw} = E_B - \mu_a^{-1} \Gamma_B^{1/2} = E_B - H_n \Gamma_B^{1/2} / \Gamma_n^{1/2} \quad (13.3)$$

Even if the ratio of the widths $\Gamma_B^{1/2} / \Gamma_n^{1/2}$ is large, E_{vw} still comes close to E_B provided the interaction strength H_n remains very small. Although there is no vanishing width in the present data, as noted above, for finite resolution, a vanishing width would also lead to vanishing fluctuations: in the presence of eight open channels, if one supposes that only one of them (the dominant channel) contains the vanishing partial width, one expects that coupling to the remaining open channels introduce a non-fluctuating width, producing an effect similar to finite resolution.

The situation can be further explained by considering first fluctuations in the presence of a single open channel, treated in the general case by Lane¹¹. According to this treatment fluctuations vanish at an energy $E_{vf} = E_B - (\Gamma_B^{1/2} H_n^2 / \Gamma_0)$. The quantity Γ_0 itself is the mean of Γ_n and since $\mu^{-1} = \frac{H_n^2}{\Gamma_n}$ is a constant, Eq. 13.3 is recovered with E_{vf} in place of E_{vw} .

Thus the present data show that the vanishing point lies close to one specific intruder energy E_B , signalled by a q-reversal in one series (which is the hallmark of weak coupling)¹⁰⁴. It is therefore reasonable to assume that the influence of one intruder state dominates in the vicinity of E_{vf} and that coupling to the other has become negligible close to E_{vf} . As regards the presence of second series, it is noted that the ns and nd states built on the same core and with the same total J are anyway strongly mixed: it is therefore entirely reasonable that they should possess parallel properties.

13.2.1 Conclusion

Present data points to the idea that the effect described as a vanishing width in the case of a single open channel becomes a vanishing fluctuation in the presence of several open channels, i.e. the two effects are connected. The data also demonstrates that the influence of a single perturber is responsible for the disappearance of fluctuations, as witnessed by a single q-reversal close to the same energy.

13.3 Strontium experiment

This work presents detailed experimental study of the absorption spectrum of Sr out of the $5s^2\ ^1S_0$ ground state. The autoionisation region between the $4d_{5/2}$ and $5p_{1/2}$ thresholds is investigated. The structure is due to transitions to the five $5pns, nd$ levels ($J = 1$). These closed channels can couple with the open continuous (open) $J = 1$ channels built on $5s\ ^2S_{1/2}$, $4d\ ^2D_{3/2,5/2}$. Thus the series that converge on the $5p_{1/2}$ limit, can interact both with the continua (open channels) and with series converging on the $5p_{3/2}$ threshold. Fig. 13.19 and Fig. 13.20 show the present results. Cross-sections are arbitrary. The present results demonstrate the extent of resolution achieved. The $5p_{1/2}ns$ levels are identified up to $n = 70$. According to the level identification by Brown *et al* (1983), the $5p_{1/2}ns$ and $5p_{3/2}ns$ levels correspond to the sharpest features while the shoulders or broad resonances between the $5pns$ peaks are associated with $5p_{1/2}nd$ or $5p_{3/2}nd$ levels. According to Aymar (1987), the strongest mixing corresponds to the $4d_{mf}$ - $5p_{md}$ one

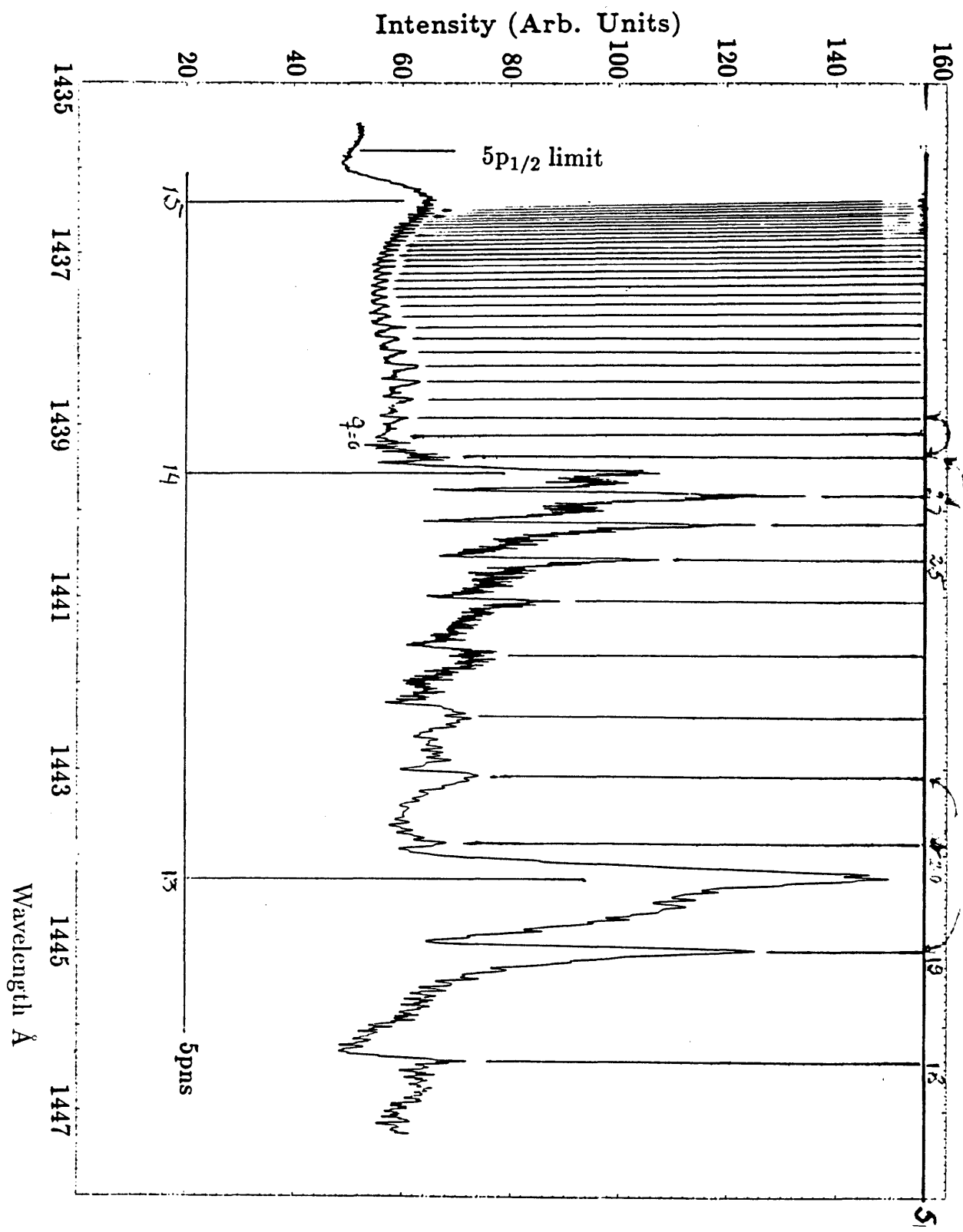
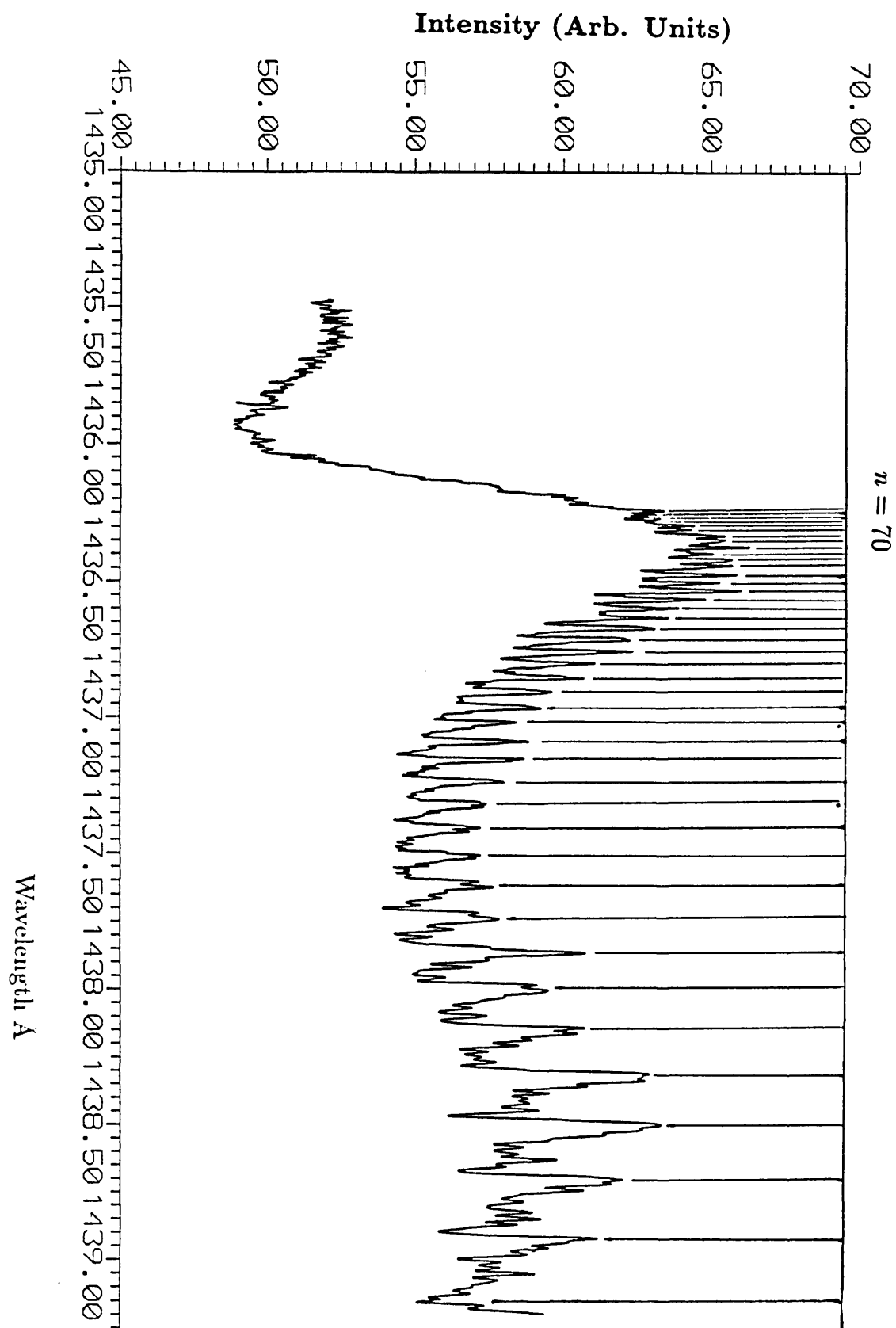


Figure 13.19: Absorption spectrum of Sr I below the 5p_{1/2} limit

Figure 13.20: Absorption spectrum of Sr I just below the $5p_{1/2}$ limit

($\sim 56 - 52\%$) between the 4d and 5p thresholds. This results in the very large autoionisation widths of the 5pnd resonances. Other channel interaction strengths are weaker. It has been observed that each time an intruder level (in this case the $5p_{3/2}ns$ levels) is traversed, q of the $5p_{1/2}ns$ levels is reversed. This happens between $n = 19$ and $n = 20$, and between $n = 27$ and $n = 28$. Another point is that q is reversed between $n = 28$ and $n = 30$ levels, and between them is a transmission window for $n = 29$. This situation is more clear in the theoretical R-matrix calculations as shown in Fig. 13.21 (Aymar, private communication)³. This is similar to the case we have just discussed in barium, but because the number of channels involved in the present spectrum is more than those in barium, the analysis becomes more difficult. As said before (see ch.1) the K-matrix formalism is not very appropriate for this type of situation, and one has to resort to the numerical calculations. The present results show some disagreement with the theory over the general shape of the gross perturber. However, in general, the agreement is satisfactory and the theory has done a very good job in reproducing this complicating spectrum.

In the present experimental results, some narrow features are observed, modulated on the otherwise smooth Beutler-Fano profiles of the 5pnd levels. Though the signal to noise ratio in this spectrum is not very good, yet it appears (by comparison of the different files recorded in the same energy range) that many of these features reproduce themselves. Their genuineness has to be established.

³The calculated spectrum is convolved with our laser bandwidth of 5 GHz

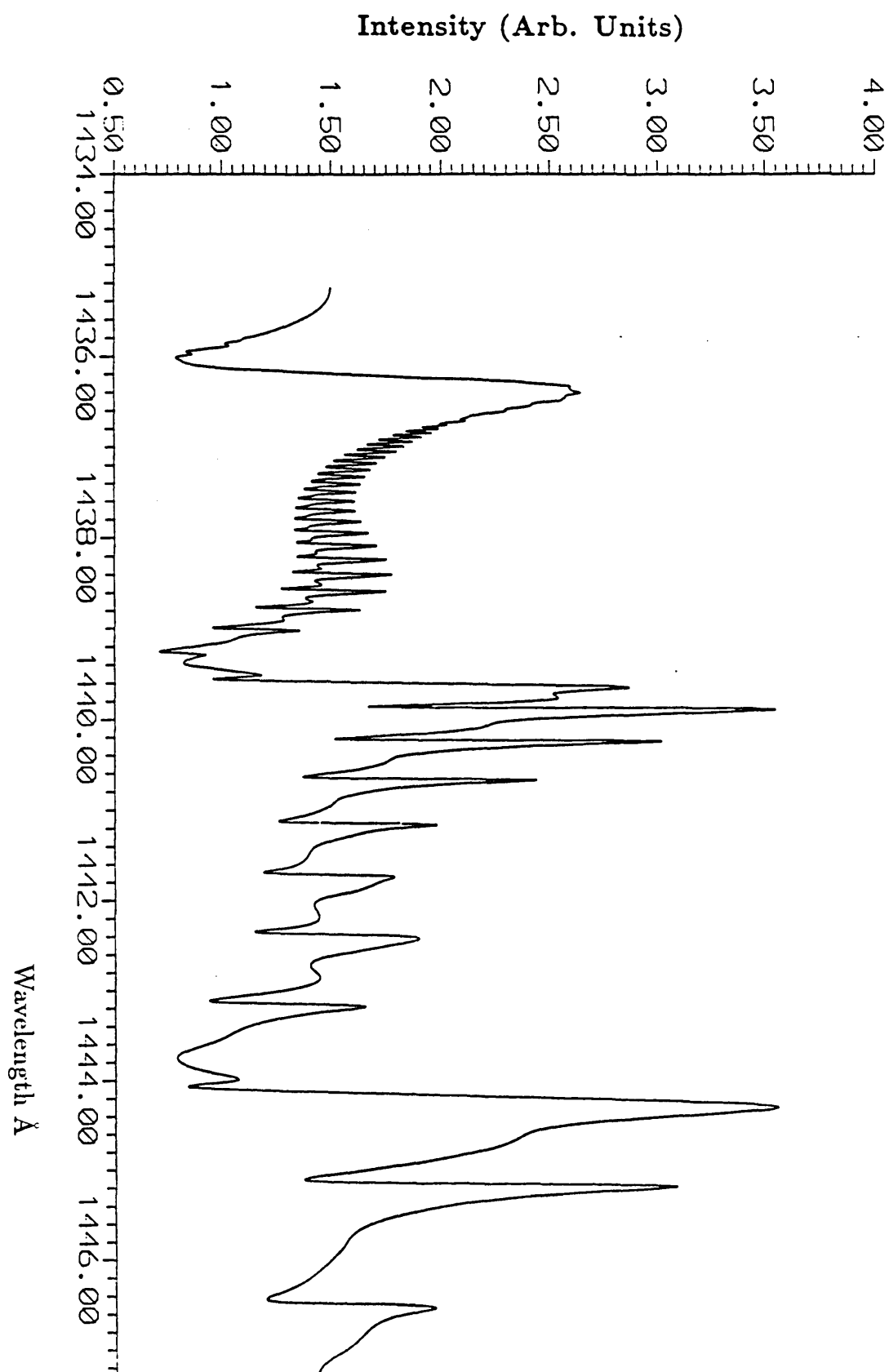


Figure 13.21: Theoretically predicted absorption cross-sections of Sr I below the $5p_{1/2}$ limit

13.3.1 Conclusion

The situation in the case of strontium is a bit complicated as a total of thirteen channels are involved. As explained in the introduction (chapter 1), K-matrix formalism is simple to use when few channels are involved. In the case of many channels, one has to rely more on the numerical approach. Nevertheless, q reversals are observed whenever a broad perturber ($5p_{3/2}ns$) level is traversed. The two channels ($5p_{1/2}ns$ and $5p_{3/2}ns$) are weakly coupled with each other (Aymar 1987), hence the prediction of the K-matrix formalism is fulfilled. The narrow features observed in the present experiment need to be confirmed independently. In terms of resolution, the results, in general, are much better than the previous experiments.

13.4 Suggestions for further work

The thermionic diode detectors, due to their linear detection over many decades of intensity, freedom from opacity effects and very high intrinsic gain, are ideal for photoabsorption spectroscopy. Currently these are employed for the study of elements for which a maximum furnace temperature up to 900 °C is required. The limitation is due to the stainless steel tube (which acts as an anode) which can be safely heated up a maximum temperature of 1000 °C . Thus it is limited to the study of a few elements and gases. However, it is possible to extend the temperature range by using a ceramic tube as an oven. In fact a similar scheme is under way at our group, in which an alumina tube is used as an oven, and a tantalum sheet

as an anode. This detector is expected to stand up to a temperature of 1400 °C , thus extending the application of this linear detector for the absorption spectroscopy (employing thermionic diode detector) of those elements which were limited by temperature.

As discussed previously, a grating monochromator was employed to separate the generated VUV from the fundamental radiations. The coating of the grating was very sensitive to the total radiation intensity, so a compromise was made by choosing a narrow inlet slit opening, i.e., fewer VUV photons were available for the experiment (this was a sad situation, because, due to the limitation of the monochromator, maximum number of the VUV photons could not be directed in to the detector). This limitation has now been removed (after the completion of present work) by employing a home made prism monochromator. For the high energy VUV photons (less than 1750 Å), the VUV flux directed in to the detector has increased by almost an order of magnitude. However, for the low energy VUV photons the selectivity is at risk: as the fixed laser (see VUV generation) output is in the UV (212.55 nm), the prism monochromator can not fully resolve the two beams. The solution is a further compromise, i.e. use of the grating monochromator at the low energy side of the VUV, and the prism monochromator for the high energy VUV experiments.

This experimental setup (i.e. the laser system and the thermionic diode detector) has also been used for the inner-shell spectroscopy of atoms by multiphoton excitation technique (Ding *et al* 1988).

In the present experiment, especially in calcium, a wide energy range

has been scanned, and the data was recorded over many computer files. For this type of detailed study of a complete spectrum, it is very important to have it initially scanned by synchrotron radiation, so that the broad and well resolved features should not be repeated by the laser, but instead they should be plugged in to make a complete spectrum. This has been done in the present experiment.

References

1. Garton W R S and Tomkins F S
1969 *Astrophys. J.* **158** 1219
2. Garton W R S, Grasdalen G L, Parkinson W H, and Reeves E M
1968 *J. Phys. B: At. Mol. Phys.* **1** 114
3. Hudson R D, Carter V L, and Young P A
1969 *Phys. Rev.* **180** 77
4. Breuckner K A
1955 *Phys. Rev* **97** 1353
5. Goldstone J
1957 *Proc. R. Soc* **A239** 267
6. Kelly H P
1963 *Phy. Rev* **131** 684
7. Connerade J P, Garton S W R, Mansfield M W D and Martin M A P
1976 *Proc. R. Soc.* **A 350** 47
8. Kapur P L and Peirels R E
1938 *Proc. Roy. Soc. Ser A* **166** 277
9. Lane A M and Thomas R G
1958 *Rev. Mod. Phys.* **30** 257
10. Wigner E P and Eisenbud L
1947 *Phys. Rev.* **72** 29
11. Lane A M
1985 *J. Phys. B: At. Mol. Phys.* **18** 2339
12. Aymar M
1990 *J. Phys. B: At. Mol. Phys.* **23** 2697

13. Mansfield M W D and Connerade J P
1978 Proc. R. Soc. A **359** 389
14. Altun Z, Carter S L and Kelly H P
1983 Phys. Rev. A **27** 1943
15. Kelly H P
1968 Adv. Theor Phys **2** 75
16. Brown C M, Tilford S C and Ginter M L
1973 J. Opt. Soc. Am. **63** 1454
17. Carter V L, Hudson R D and Breig L L
1971 Phys. Rev. A **4** 82
18. Newsom G H
1966 Proc. Phys. Soc. London **87** 975
19. Ditchburn R W, and Hudson R D
1960 Proc. Roy. Soc. London Ser A **256** 53
20. Scott P, Kingston A E and Hibbert A
1983 J. Phys. B At Mol Phys **16** 3945
21. Burke P G and Taylor K T
1975 J. Phys. B At Mol Phys **8** 2620
22. Connerade J P, Baig M A, Garton W R S and Newsom G H
1980 Proc. Roy. Soc. **371** 295
23. Fano U
1961 Phys. Rev. **124** 1866
24. Fano U and Cooper J W
1965 Phys. Rev. A **137** 1364
25. Bates D R
1947 Proc. Roy. Soc. A **188** 350

26. Seaton M J
1951 Proc. Roy. Soc. **A 208** 418
27. Cooper J W
1962 Phys. Rev. **128** 681
28. Newsom G H
1966 Proc. Phys. Soc. **87** 975
29. Fano U
1983 Rep. Prog. Phys. **46** 97
30. Fano U
1976 Proc. 9th Int. Con. on physics of electronic & Atomic collisions. ed. J.S. Risley and R. Geballe (Seattle: University of Washington Press) pp. 271 - 80
31. Greene C H
1981 Phys. Rev. **A 23**
32. Greene C H and Kim L
1987 Phys. Rev. **A 36** 2706
33. Sugar J and Corliss C
1979 J. Phys. Chem. Ref. Dat **8** 865
34. Seaton M J
1958 Mon. Not. Roy. Astron Soc. **118** 504
35. Ham F
1955 Solid State Phys. **1** 127
36. Green H S, Fano U, and Strianti G
1979 Phys. Rev. **A 19** 1485
37. New G H C and Ward J F
1967 Phys. Rev. Lett. **19** 556

- 38. Ward J F and New G H C
1969 Phys. Rev. **185** 57
- 39. Young J F, Bjorklund G C, Kung A H, Miles R B and Harris S E
1971 Phys. Rev. Lett **27** 1551
- 43. Bjorklund G C
1975 IEEE J. Quantum Electronics **QE-11** 287
- 45. Shenstone
1931 Phys. Rev. **38** 873
- 46. White H E
1931 Phys. Rev. **38** 2016
- 47. Fano U and Cooper J W
1968 Rev. Mod. Phys. **40** 441
1969 Rev. Mod. Phys. **41** 724
- 48. Connerade J P, Garton W R S, Mansfield M W D and Martin M A P
1976 Proc. R. Soc. **A 350** 47
- 49. Cowan R D
The Theory of Atomic Structure and Spectra.
1981 Berkeley, University of Californian Press
- 50. Langmuir I
1923 Phys. Rev. **21** 419
- 51. Shen N
1988 Ph.D Thesis, Blackett Laboratory Library
- 52. Porter J H, Franzen E and Wenstrup R S Jr.
1972 J. Appl. Phys. **43** 344
- 53. Niemax K
1985 Appl. Phys. **B 38** 147

54. Armstrong J A, Esherick E and Wynne J J
1977 Phys. Rev. **A 15** 180
55. Beigang R, Makat W and Timmermann A
1984 Opt. Commun. **49** 253
56. Badareu E Popescu I, Ghitta C and Zamfir O
1964 Brit. J. Appl. Phys. **15** 1171
57. Thompson D C and Stoicheff B P
1981 Rev. Sci. Instrum. **53** 204
58. Kingdon K H
1923 Phys. Rev. **21** 408
59. Mohler F L, Foote P D and Chenault R L
1926 Phys. Rev. **27** 37
60. Mohler F L and Boeckner C
1929 J. Res. Nat. Bur. Stand. **3** 303
61. Sansonetti C J and Lorenzen C J
1984 Phys. Rev. **A 30** 1805
62. Griesmann U, Shen N, Connerade J P, Sommer K and Hormes J
1988 J. Phys. B: At. Mol. Phys. **B 21** L83
63. Marangos J P, Shen N, Ma H, Hutchinson M H R, and Connerade J P
1990 J. Opt. Soc. Am. **7** 1254
64. Kaenders W G, Shen N, Marangos J P, Hutchinson M H R
and Connerade J.P.
1990 J. of Mod. Optics **37** 835
65. Ding R, Kaenders W G, Marangos J P, Shen N, Connerade J P
and Hutchinson M H R
1989 J. Phys. B: At. Mol. Phys. **B 22** L251

- 66. Williams F C
1941 J. Inst. Electr. Eng. **88** 219
- 67. Rado W G
1967 Phys. Rev. Lett. **11** 123
- 68. Vidal C R
1987 Tunable Lasers, Volume 55 Springer-Verlag Topics in Applied Physics, ed. by Mollenauer L.F. and White J.C.
- 69. Hilbig R, Hilber G, Lago A, Wolff B and Wallenstein
1986 Proc. Soc. Photo-Opt. Instrum. Eng **613** 48
- 70. Harris S E and Miles R B
1971 Appl. Phys. Lett. **19** 385
- 71. Bloom D M, Yardley J T, Young J F and Harris S E
1974 Appl. Phys. Lett. **24** 427
- 72. Hodgson R T, Sorokin P P and Wynne J J
1974 Phys. Rev. Lett. **32** 343
- 73. Leung K M, Ward J F and Orr B J
1974 Phys. Rev. Lett. **A9** 2440
- 74. Langer H, Puel H and Röhr H
1980 Opt. Commun. **34** 137
- 75. Hilbig R and Wallenstein R
1981 IEEE J. QE **17** 1566
- 76. Hilbig R and Wallenstein R
1982 Appl. Opt. **21** 913
- 77. Freeman R R, Bjorklund G C, Economou N P, Liao P F
and Bjorlhiolm J E
1978 Appl. Phys. Lett. **33** 739

78. Hansch T W
1972 Appl. Opt. **11** 895
79. Littman M G and Metcaff H C
1978 Appl. Opt. **17** 2224
80. Shoshan I
1978 J. Opt. Phys. **48** 4495
81. Brown C.M. Longmuir M.S. and Ginter M.L.
1983 Opt. Soc. Am. **73** 985
82. Garton W R S and Codling K
1965 Proc. Phys. Soc. **86** 1067
83. Kaiser T R
1960 Proc. Phys. Soc. **75** 152
84. Justum P J
1954 Proc. Phys. Soc. **A 67** 190
85. Ueda K
1987a J. Opt. Soc. Am **B 4** 648
1987b Phys. Rev. **A 35** 2484
86. Shore B W
1967a Rev. Mod. Phys. **39** 440
1967b J. Opt. Soc. Am. **57** 881
87. Parkinson W H, Reeves E M and Tomkins F S
1976 J. Phys. B: At. Mol. Phys. **9** 157
88. Shabanova L N
1963 Opt. Spectrosc. **15** 450
89. McIlarth T J and Sandeman R J
1976 J. Phys. B: At. Mol. Phys. **5** L217

90. Brown C M and Ginter M L
1978 J. Opt. Soc. Am. **68** 817
91. Ginter M L, Ginter D S and Brown C M
1980 Appl. Opt. **19** 4015
92. Aymar M
1990 J. Phys. B: At. Mol. Phys. **23** 2697
93. Greene C H and Aymar M
1991 Phys. Rev. (to be published)
94. Connerade J P and Lane A M
1988 Rep. Prog. Phys. **51** 1439
95. Pearson, 'Quantum Scattering and Spectral Theory' page 277
Academic press (1988), New York
96. Connerade J P and Lane A M
1987 J. Phys. B: At. Mol. Phys. **20** L363
97. Dubau J and Seaton J M
1984 J. Phys. B: At. Mol. Phys. **17** 381
98. Giusti-Suzor A and Fano U
1984 J. Phys. B: At. Mol. Phys. **17** 215
99. Soloman E B, Ebner S C and Hughey L R
1982 Optical Engineering **21** 951
100. Mark M, Greaves G N, Poole M W, Suller V P and Walker R P
1983 Nucl. Instrum. Meth. **208** 97
101. Connerade J P and Lane A M
1987a J. Phys. B: At. Mol. Phys. **20** L181
1987b J. Phys. B: At. Mol. Phys. **20** 1757
102. Connerade J P, Esteva J M and Karnatak R C

- (ed) 1987 Giant Resonances in Atoms Molecules and Solids
1986 Proc. NATO ASI (Les Houches) (New york: Plenum)
103. Connerade J P
1978a Proc. R. Soc. **A 362** 361
1978b Nucl. Instrum. Meth. **152** 271
1978c Contemp. Phys. **19** 415
104. Connerade J P, Lane A M and Baig M A
1985 J. Phys. B: At. Mol. Phys. **18** 3507
105. Richard P, Moore C F and Fox J D
1964 Phys. Rev. Lett. **A 13** 343
106. Garton W R S
1965 Scientific Rep. Harvard College Observatory, Cambridge, Ma
107. Rinneberg H, Jonsson G, Neukammer J, Vietzke K, Hieronymus H,
Konig G and Cooke W E
1985 Proc. 2nd. European Conf. on Atomic and Molecular Physics
(Amsterdam) unpublished.
108. Brown C M, Longmire M S and Ginter M L
1983 J. Opt. Soc. Am **73** 985
109. Connerade J P and Baig M A
1987 Handbook on Synchrotron Radiation vol 2, ed G V Marr
(Amsterdam: North-Holland)
110. Wick G C
1950 Phys. Rev **80** 268

Appendix A

Publications

LETTER TO THE EDITOR

Vanishing fluctuations in atomic spectra

J P Connerade and S M Farooqi

Blackett Laboratory, Imperial College, London SW7 2BZ, UK

Received 7 May 1991

Abstract. Spectral fluctuations are discussed in the context of the **K**-matrix theory of interacting autoionizing resonances. New measurements of the doubly-excited spectrum of Ba I in the vicinity of the $6p_{1/2}$ threshold provide unambiguous evidence for the disappearance of fluctuations at a specific excitation energy well below the associated series limit. We discuss the origin of this effect, we show that it occurs close to the resonance energy of one broad intruder level, and we suggest a more general connection between the vanishing width effect and the disappearance of fluctuations in atomic

Spectral fluctuations are a distinctive property of atomic spectra, but have rarely been studied in their own right. One instance involving fluctuations is the procedure of Gailitis averaging near a series limit (Seaton 1983), which emphasizes the fairly obvious result that the fluctuations tend to zero as the limit of a Rydberg series is approached. Another situation where experimental fluctuations in the cross section tend to zero is when a vanishing width occurs (Connerade and Lane 1985) and the instrumental resolution is finite (for an experimental example, see Connerade *et al* 1988). This situation is more interesting, since the fluctuations then pass through zero at an energy which does not coincide with the series limit. However, the vanishing width effect occurs with one open channel, whereas fluctuations may exhibit variations even if many channels are open. The more general question then arises: can a point of zero fluctuations be similarly detuned from the associated series limit *without* the occurrence of a vanishing width, i.e. do points of vanishing fluctuation exist *per se* as an independent property resulting from a perturbation by an intruder state?

In nuclear physics, fluctuations are studied directly through the variance:

$$\text{var } \sigma \equiv \langle \sigma(E)^2 \rangle - \langle \sigma(E) \rangle^2 \quad (1)$$

where the Dirac brackets denote an average performed over an interval of energy ΔE sufficiently wide to encompass local fluctuations, but sufficiently narrow for gross variations to be preserved.

Although the variance is strictly of fourth order in elements of the **S**-matrix, a useful theorem, due to Moldauer (1963) states that the fluctuation in the *total* cross section for a given entrance channel *a* is of second order in **S**-matrix elements:

$$\text{var } \sigma_a = 2\{ \langle |S_{aa}|^2 \rangle - \langle S_{aa} \rangle^2 \} = 2\langle \sigma_{aa}(fl) \rangle \quad (2)$$

Thus, $\text{var } \sigma_a$ behaves like a cross section. For example, continuity theorems apply across thresholds (Lane 1986) and the variance may possess interesting variations and

zeros, just as one finds when considering interferences between Rydberg series of resonances and broad intruder states (Connerade and Lane 1989).

A promising (but hitherto not quite conclusive) experimental example is cited by Lane (1985) who noticed a minimum in the variance of data for the $6p_{1/2}ns$ and nd series of Ba I recorded photographically by Brown and Ginter (1978)[†]. The observation, though promising, was inconclusive for two reasons. First, Ginter *et al* (1980) have themselves pointed out that instrumental interference effects can occur amongst high members of Rydberg series when the spacings between adjacent lines gradually approach the resolution limit of a classical grating spectrograph. Second, the resolution in the spectrum recorded by Brown and Ginter (1978) and their use of photographic detection may not be quite adequate to yield the widths and profiles of the lines near to and above the vanishing point of fluctuations.

Another interesting point is that, although two series are expected to approach the $^2P_{1/2}$ limit at 1605.2 Å and three to the $^2P_{3/2}$ limit at 1562.8 Å, in fact only four series (two to each limit) were detected experimentally. However, Brown and Ginter (1972) found evidence of very strong mixing in the range further studied here, and therefore suggested that the missing fifth channel might be present in this region.

Although inspired by the data of Brown and Ginter (1978) to consider the problem of fluctuations in atomic spectra, Lane (1985) became concerned, as a result of his analysis, that the number of parameters needed in this example is large, so that a zero-point in the fluctuations might prove unlikely. In his own words '... the strong minimum in the fluctuations in figure 1 is an exception to general expectation. In view of this, it may be just as well that there is some doubt about the effect in figure 1 being genuine...'.

Although not commented on in the context of spectral fluctuations a new indication that the minimum observed by Brown and Ginter (1978) must be a real effect came from simulated spectra obtained using the *LS*-coupled numerical eigenchannel R-matrix method (Aymar 1990, see figure 11) which revealed a minimum in the fluctuations similar (but not identical) to the photographic observations. More recent *jj*-coupled calculations (Greene and Aymar 1991) again reveal a similar fluctuation, with significant differences amongst the highest members from the earlier *LS* results. The numerical approach is similar in energy resolution to the experiment of Brown and Ginter (1978), and the differences between the predictions for the high members of the series are therefore hard to assess. The eigenchannel R-matrix method produces impressive agreement with experimental data and has the advantage of including all the relevant open channels, but unfortunately does not provide much clue as to which specific interaction can be responsible for the fluctuation. Also, it is clear by inspection of the published spectra that the energy resolution in *all* the work previously cited is inadequate to reveal the true behaviour of the resonances in the vicinity of the vanishing fluctuations. Specifically, it remains unclear whether the fluctuation is purely due to intensities or to variations in the widths of the resonances.

Recently, a high resolution coherent VUV four-wave mixing source has been developed in our laboratory (Marangos *et al* 1990) and has been applied to thermionic diode spectroscopy of alkaline-earth elements (Kaenders *et al* 1989, Farooqi *et al* 1991). It seemed appropriate to bring this new experimental technique to bear on

[†] This particular doubly-excited spectrum of Ba I has not been much studied: the structure was discovered originally by Garton and Parkinson (1974) and the only other observation prior to the present work appears to be that of Brown and Ginter (1978).

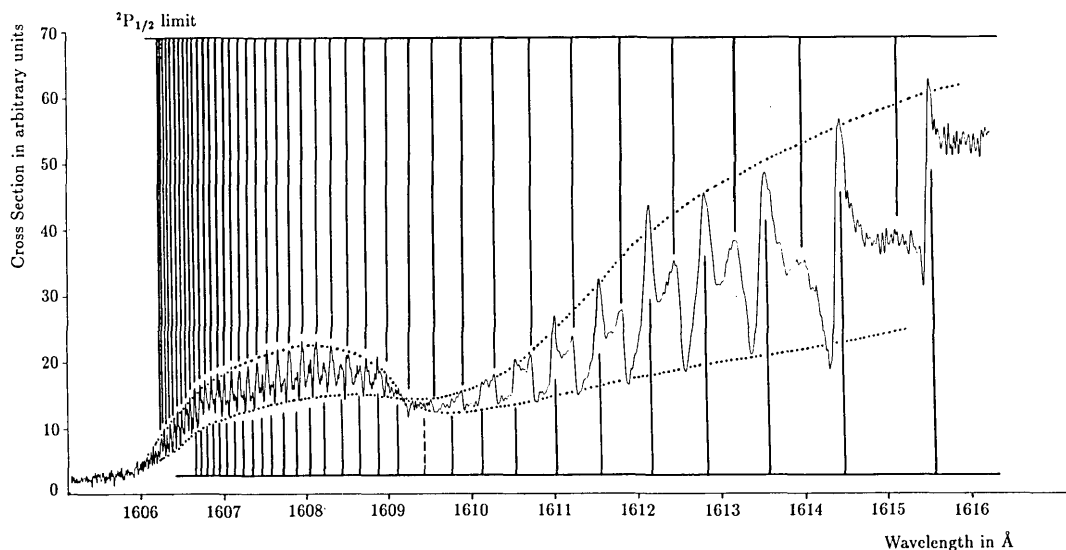


Figure 1. The Rydberg series converging on the $6p_{1/2}$ threshold of Ba I, as observed in the present laser-based thermionic diode experiments. Note the zero point of fluctuations, the window resonance and the q -reversal. The most prominent Beutler–Fano resonance at 1615.5 Å is assigned by Garton and Parkinson (1974) in JK coupling as $(6p^2P_{1/2} 22s[\frac{1}{2}]_1^0)$, but Brown and Ginter (1978) avoid giving precise designations in view of the heavy configuration mixing.

the aforementioned problem, and we present here (see figures 1 and 2) data, recorded using a linear detector, at a resolving power of about 5 GHz.

Our first result, based on the new data, is a much more detailed confirmation of the experimental observation: the fluctuations vanish at a definite point near 1608.80 ± 0.20 Å. Secondly, we find that the widths of the resonances tend to zero smoothly as the $6p_{1/2}$ series limit is approached, i.e. that the minimum in the fluctuations is *not* due to a vanishing width effect†. Third, we are able to observe changes in the shapes of the line profiles as the vanishing point is traversed, an important new observation to which we return below. A fourth point is that there may indeed be further structure present in this region than can be accounted for from the four most prominent series. However, the noise level on our spectra is still too high for an unambiguous conclusion to be reached.

The approach we will adopt is the same as Connerade and Lane (1989), namely within the framework of *analytic* K-matrix theory (which has the advantage of meromorphy in dealing with overlapping resonances—for a discussion of the formal connection between the S, R and K matrices, see Connerade and Lane (1990)). We seek the simplest description, bearing in mind that the algebra of the full problem including all possible channels becomes too forbidding to be useful. The conceptual framework of the analytic K-matrix theory (Lane 1985) is, we believe, valuable to uncover the origin of specific fluctuations in spectra, an approach complementary to detailed numerical simulations of spectra.

We assume radiative widths can be neglected, i.e. that the spectrum is dominated

† The Doppler width of Ba I is much smaller than the widths of the lines near the point where fluctuations disappear.

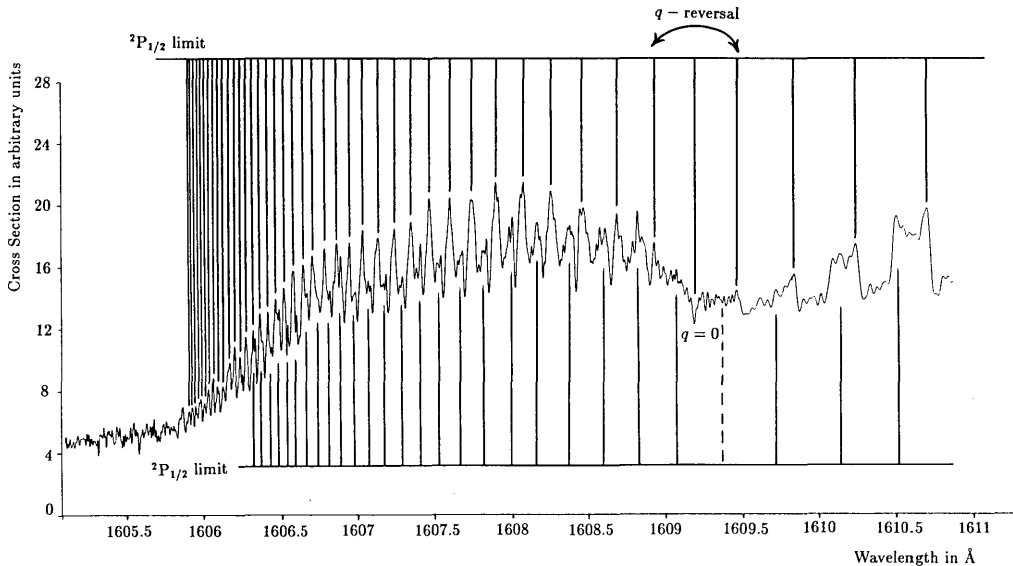


Figure 2. Upper members of the series converging on the $6p_{1/2}$ threshold of Ba I at greater dispersion than in figure 1, showing the line profiles more clearly. If we adopt the n values suggested by Garton and Parkinson (1974), then the series can be followed out to about $n \sim 65$ which is similar to values recently found for Ca I (Farooqi *et al* 1991).

by autoionization (particle widths, in the language of K -matrix theory). We thus work in the elastic scattering approximation. We further note the regular progression of Rydberg spacings and widths in figures 1 and 2 which ensures the constancy of $\mu^2 = \Gamma_n/H_n^2$ where Γ_n is the particle width and H_n^2 is the interaction strength between the Rydberg levels $|n\rangle$ and the broad intruder state $|B\rangle$ (i.e. Γ_n and H_n^2 both vary as n^{*-3} where n^* is the effective principal quantum number). This condition is of itself sufficient for an explicit inversion of the scattering matrix (Lane 1985) to be performed†.

Referring again to the data of figures 1 and 2, we also note the presence of a transmission resonance, about which a conspicuous q -reversal (Connerade 1978) occurs. This is a crucial new observation, which enables us to advance the analysis beyond the original discussion by Lane (1985). Another instance where a q -reversal straddles a $q = 0$ window resonance was described by Connerade *et al* (1985) in the spectrum of Tl I. Connerade and Lane (1987a) also found a theoretical example in calculations of a Rydberg series of sharp lines weakly coupled to a broad resonance: in the latter case, the form of the variation of q was shown to be:

$$q = \frac{1 - \bar{\delta}\bar{\Delta}}{\bar{\delta} + \bar{\Delta}} \quad (3)$$

where $\bar{\delta}$ is a background, essentially constant phase shift due to the underlying continuum, and $\bar{\Delta} = (\Gamma_B/2)/(E_B - E)$ is the phase shift due to the broad intruder resonance $|B\rangle$.

† This, incidentally, is a unique feature of atomic physics (a property of the asymptotically Coulombic potential) and atomic spectra are therefore the most favourable for detailed tests of K -matrix theory to be performed, especially as regards its meromorphic pole structure.

Hence $q = 0$ when $\bar{\Delta} = 1/\bar{\delta}$, which also turns out to be the condition for a maximum to occur in the cross section the intruder resonance would possess at zero coupling strength. This condition is satisfied at an energy E_0 given by

$$E_0 = E_B - \left(\frac{\Gamma_B}{2} \right) \tan \delta \quad (4)$$

about this value, $\bar{\Delta}$, and therefore also q , change sign, i.e. a q -reversal occurs. This type of q -reversal is the most stable (for a classification of types, see Connerade and Lane 1987b), and usually remains within the energy range of the intruder level under conditions of weak coupling, because it is tied to the energy E_B . The present data exhibit this behaviour quite clearly, close to the point where the fluctuations disappear: one line (marked 'X' in figures 1 and 2) has $q \sim 0$ and, about this line, a q -reversal of the associated series does indeed occur (see figure 1).

In their calculations, performed with a single open channel, Connerade and Lane (1987a) also found a vanishing width at an energy

$$E_{vw} = E_B - \mu_a^{-1} \Gamma_B^{1/2} = E_B - H_n \Gamma_B^{1/2} / \Gamma_n^{1/2} \quad (5)$$

Even if the ratio of the widths $\Gamma_B^{1/2} / \Gamma_n^{1/2}$ is large, E_{vw} still comes close to E_B provided the interaction strength H_n remains very small. Although there is no vanishing width in the data of figure 1, we have noted above that, for finite resolution, a vanishing width would also lead to vanishing fluctuations: in the presence of eight open channels, if we suppose that only one of them (the dominant channel) contains the vanishing partial width, one expects that coupling to the remaining open channels introduces a non-fluctuating width, producing an effect similar to finite resolution.

To make this connection more apparent, consider first fluctuations in the presence of a single open channel, treated in the general case by Lane (1985) section 3 (in what follows, we use his notation—see his paper for details). It emerges that, for $C^2 = 1$, fluctuations vanish at an energy $E_{vf} = E_B - (\hat{\Gamma} \Gamma^{1/4} / 4\pi s_0)^{1/2}$. For narrow resonances Γ_n such that $\Gamma_n / D_n \rightarrow 0$ (D_n is the inter-level spacing), we then have $y \rightarrow 0$ and so $\hat{\Gamma}^{1/2} \rightarrow \Gamma_B^{1/2}$, whence $E_{vf} = E_B - (\Gamma_B^{1/2} \bar{H}_n^2 / \Gamma_0)$. The quantity Γ_0 is itself the mean of Γ_n and since $\mu^{-1} = H_n^2 / \Gamma_n$ is a constant, we recover equation (5) above with E_{vf} in place of E_{vw} .

Lane (1985) has shown that, in the case of many open channels, an expression for $\text{var } \sigma_a$ is obtained which might plausibly vanish for a single series and a single intruder state in Ba I. However, the problem is rendered far more complex if there are two series and two intruders, and a vanishing point then becomes far less likely.

The present data show that the vanishing point lies close to *one* specific intruder energy E_B , signalled by a q -reversal in one series (which is the hallmark of weak coupling, see Connerade *et al* 1985). It is therefore reasonable to assume that the influence of one intruder state dominates in the vicinity of E_{vf} and that coupling to the other has become negligible close to E_{vf} . As regards the presence of a second series, we note that the ns and nd states built on the same core and with the same total J are anyway strongly mixed: it is therefore entirely reasonable that they should possess parallel properties.

In conclusion, our data point to the idea that the effect described as a vanishing width in the case of a single open channel becomes a vanishing fluctuation in the presence of several open channels, i.e. that the two effects are connected. Our

data also demonstrate that the influence of a single perturber is responsible for the disappearance of fluctuations, as witnessed by a single q -reversal close to the same energy.

With the development of laser-based high resolution photoelectron spectroscopy, the present series would appear to be an ideal candidate for further investigation, because of the possibility that the associated vanishing width might become observable in one of the partial cross sections.

Acknowledgments

The present research was performed with support from the SERC in the form of a rolling grant. One of us (SMF) is grateful to the Ministry of Education (Islamabad, Pakistan) for financial support in the form of a research studentship.

References

- Aymar M 1990 *J. Phys. B: At. Mol. Opt. Phys.* **23** 2697
Brown C M and Ginter M L 1978 *J. Opt. Soc. Am.* **68** 817
Connerade J P 1978 *Proc. R. Soc. A* **362** 361
Connerade J P and Lane A M 1985 *J. Phys. B: At. Mol. Phys.* **18** L605
— 1987a *J. Phys. B: At. Mol. Phys.* **20** L181
— 1987b *J. Phys. B: At. Mol. Phys.* **20** 1757
— 1989 *Rep. Prog. Phys.* **51** 1439
— 1990 *Aspects of Electron-Molecule Scattering and Photoionization* ed A Herzenberg (*AIP Proc.* **204**) (New York: AIP) p193
Connerade J P, Lane A M and Baig A M 1985 *J. Phys. B: At. Mol. Phys.* **18** 3507
Farooqi S M, Connerade J P, Greene C H, Marangos J P, Hutchinson M H R and Shen N 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** L179
Garton W R S and Parkinson W H 1974 *Proc. R. Soc. A* **341** 45
Ginter M L, Ginter D S and Brown C M 1980 *J. Appl. Opt.* **19** 4016
Greene C H and Aymar M 1991 *Phys. Rev.* In press
Kaenders W G, Shen N, Marangos J P, Hutchinson M H R and Connerade J P 1990 *J. Mod. Opt.* **37** 835
Lane A M 1985 *J. Phys. B: At. Mol. Phys.* **18** 2339
— 1986 *J. Phys. B: At. Mol. Phys.* **19** L601
Marangos J P, Shen N, Ma H, Hutchinson M H R and Connerade J P 1990 *J. Opt. Soc. Am. B* **7** 1254
Moldauer P A 1963 *Phys. Lett.* **8** 70
Seaton M J 1983 *Rep. Prog. Phys.* **47** 167

LETTER TO THE EDITOR

Laser-based VUV spectroscopy of doubly excited Ca I

S M Farooqi†, J P Connerade†, C H Greene‡, J Marangos†,
M H R Hutchinson† and N Shen†

† The Blackett Laboratory, Imperial College, London SW7 2AZ, UK

‡ Department of Physics and Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, CO 80309-0440, USA

Received 4 February 1991

Abstract. We describe a new study of the odd-parity doubly excited spectrum of Ca I, in which a tunable coherent VUV source was used to scan over an energy range previously investigated by classical spectroscopy using synchrotron radiation. A vast improvement in the quality of the data, especially as regards the available spectral resolution, results from the use of a four-wave mixing source and enables the comparison between theory and experiment to be pushed further than ever before for doubly excited states in alkaline-earth spectra. Some remaining limitations of the theoretical computations are brought to light and discussed.

The study of double excitations in the spectra of the alkaline earths has a long and varied history, which is intimately linked with the development of multichannel quantum defect theory (MQDT) (Seaton 1966). Recently, attention has concentrated on measurements using linear detectors and instrumentation of sufficiently good spectral resolution for comparisons between theory and experiment to be detailed and quantitative, i.e. to involve both the cross sections and the profile parameters (Karamatskos *et al* 1985, Griesmann *et al* 1988).

Perhaps the most interesting of the autoionizing doubly excited series occurs in Ca I, whose $3dnp\ ^1P$ series exhibits a fine example of fluctuating width (Connerade and Lane 1985, 1988) in a Rydberg series broadened by particle decay. Not only is the effect interesting *per se* (stabilization of states in the continuum by a perturbation is of course intrinsically a remarkable situation), but there has been some disagreement as to its cause in the specific instance of Ca I (Connerade 1990). Whilst many-body calculations (Altun *et al* 1982) and the eigenchannel *R*-matrix theory (Greene 1988) would both suggest that a perturber is responsible for the fluctuation in width, a direct *ab initio* Wigner-Eisenbud *R*-matrix calculation (Scott *et al* 1983) points towards a Cooper minimum in the underlying continuum as a more likely cause.

To date, the best agreement between theory and experiment has been obtained from the eigenchannel *R*-matrix theory by Kim and Greene (1987). Indeed, the agreement is so good (Griesmann *et al* 1988) that some doubt exists as to how much of the residual discrepancy might be due to finite instrumental resolution in the earlier experimental work. Also, Kim and Greene (1987) stressed the sensitivity of their calculations to the presence of transitions to the *nf* series, which are hardly detectable

in the spectra of Karamatskos *et al* (1985) and of Griesmann *et al* (1988)[†], but have a large effect on the appearance of the whole spectrum if omitted from the computation.

All these facts suggested that a new study of the Ca I spectrum, combining the advantages of linear detection and of high spectral resolution by exploiting a recently developed tunable vuv coherent four-wave mixing source (Marangos *et al* 1990) should be undertaken, the purpose being to check theory against experiment in the vicinity of the *nf* and other sharp features, and also to explore the high members of the doubly excited series, details of which are not readily included even in an eigenchannel approach because of computational limitations. Thermionic diode detection, as previously described (Griesmann *et al* 1988) provides a signal which remains linear over many decades.

In the present letter, we provide (figures 1 and 2) what is believed to be the most detailed and complete comparison between theory and experiment ever achieved in this range of the calcium spectrum. Both theory and experiment are on an absolute scale.

Experimental techniques are not described here, since details are given in earlier papers cited. However, we should remark that we have benefitted by access to earlier synchrotron data (Griesmann *et al* 1988) in order to join certain laser data files together: the main advantage of the synchrotron is its broad tunability, and it therefore provides a bridging reference over a wide wavelength span. This is particularly valuable when the structures are very broad.

The theoretical curves in figures 1 and 2 are the geometric mean of the length and velocity curves[‡] obtained from a *jj*-coupled eigenchannel *R*-matrix calculation described elsewhere by Greene and Aymar (1991) and Greene (1990). The major difference of this approach from previous *LS*-coupled calculations in calcium (Kim and Greene 1987, Greene and Kim 1987, Greene 1988), in strontium (Aymar 1987) and in barium (Aymar 1990) is that the *LS*-calculations ignored spin-orbit effects within the reaction zone, but included them in the final MQDT calculation through a frame transformation procedure. In contrast, the present *jj*-coupled approach includes the spin-orbit effects somewhat better. For an atom as light as calcium, however, the two methods should be nearly identical.

The predictive power of the *LS*-dependent calculations has already been demonstrated by two measurements carried out near the 4p thresholds (Lange *et al* 1989, Ueda *et al* 1990), both of which were able to make detailed comparison with MQDT calculations based on the short-range reaction matrix of Kim and Greene (1987). The far greater complexity of the spectrum below the 3d thresholds, including the possibility of a Cooper minimum discussed by Scott *et al* (1983), would indicate that this energy range allows for a new, sensitive test of such calculations. It should be remembered that all of the eigenchannel *R*-matrix calculations just mentioned incorporate experimental information about the singly charged positive ion to obtain an effective one-electron potential experienced by each valence electron of the neutral atom. The calculations of Scott *et al* (1983) similarly incorporate experimental information, but through small adjustments to Hamiltonian matrix elements rather than to the potential.

Overall, the agreement between theory and experiment illustrated in figures 1 and 2 is remarkably good, provided one allows for a systematic but wavelength-dependent

[†] The *nf* series and other sharp structure can be seen rather better in photographic data (Brown *et al* 1983), but of course one does not obtain quantitative cross section measurements in this way.

[‡] The use of the geometric mean is appropriate when length and velocity results do not differ greatly—see e.g., Pan *et al* (1987).

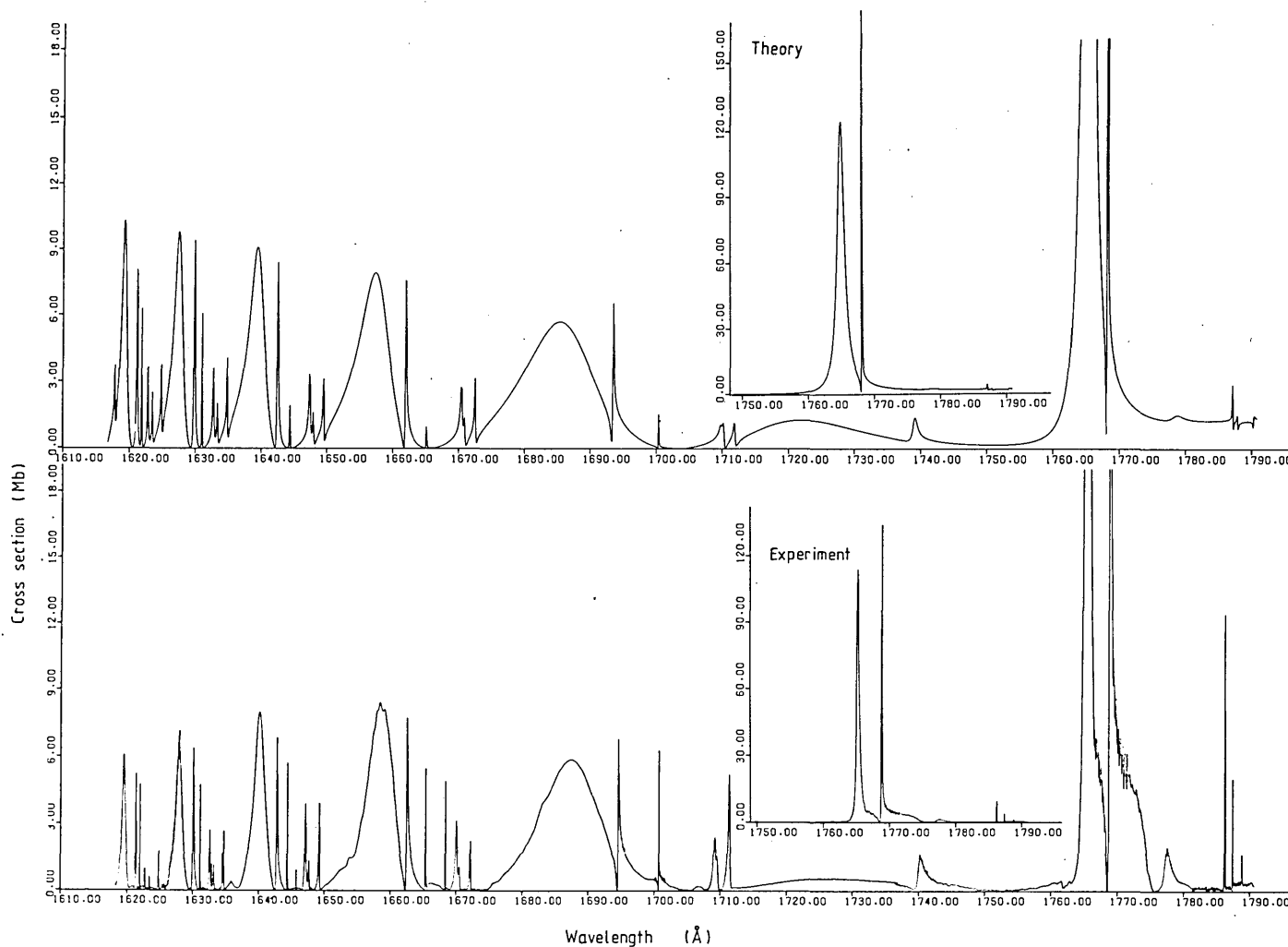


Figure 1. The doubly excited spectrum of Ca I from 1790 to 1620 Å. The sharp, very strong 3d6p resonances are shown on a ten times reduced scale of the ordinate the inset. The lower spectrum is experimental, and the upper one is the geometric mean of the present length and the velocity calculations.

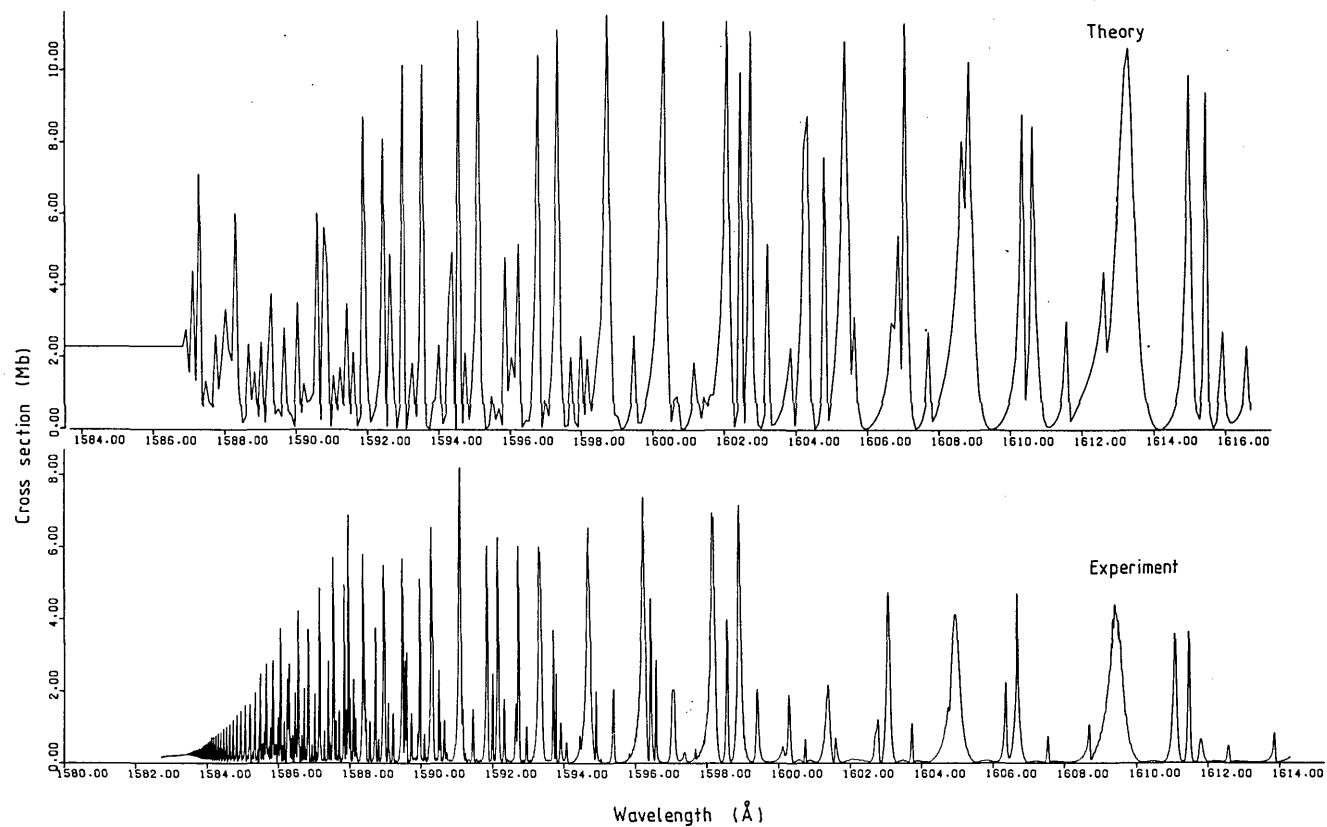


Figure 2. The doubly excited spectrum of Ca I between 1614 and the series limit at 1584 Å. Note the slight energy shift between the scales of the experimental and theoretical curves to bring the structures into full correspondence.

shift in wavelength rising to about 4 Å in figure 2 as the 3d thresholds are approached. Experimental transition energies are lower than the computed ones.

There are many new examples, both in the experiment and in the theory, of the *q*-reversal effect (Connerade 1978) in which the asymmetry of sharper resonances 'flips' over when a broad resonance is traversed. The effect is most clearly apparent in the theory around 1655, 1685 and 1720 Å, and reveals that the sharper states couple more strongly to the 3dnp 1P_1 members when the latter are themselves perturbed. However, one should note that the asymmetries of sharper lines in the spectrum, for example the group at about 1670 Å in figure 1, are sometimes a good deal less marked in the experiment than in the theory.

As the threshold is approached, an energy shift between experiment and theory occurs, as already noted, and the very fine and detailed structure close to the threshold at the higher energy end of figure 2 is quite different in the experimental data from the appearance of the simulated spectrum. In previous theoretical studies of the alkaline-earth atoms (e.g. Greene and Aymar 1991 and references therein), discrepancies of this type for very high Rydberg states have been largely removed if one uses exact experimental threshold energies, e.g. of $\text{Ca}^+(3d_{3/2}, 3d_{5/2})$ in the final MQDT calculation. The present study has used instead theoretical threshold energies, and the possibility of improving the spectrum in this fashion has not been investigated, since the calculation shown here was performed prior to the experimental measurements.

In figure 3, we show, on a more open scale, experimental data obtained close to the series limit. The doubly excited 3dnp series can be followed up to about $n = 65$. Again, this is not surprising, since the 3d states of Ca^+ are metastable, and the widths of the autoionizing series members fall off as $1/n^3$. Indeed, the observed halfwidth of about 15 GHz for high members (which involve blended lines) is reasonably close to the laser bandpass of about 6 GHz halfwidth combined with a Doppler width of about 6 GHz.

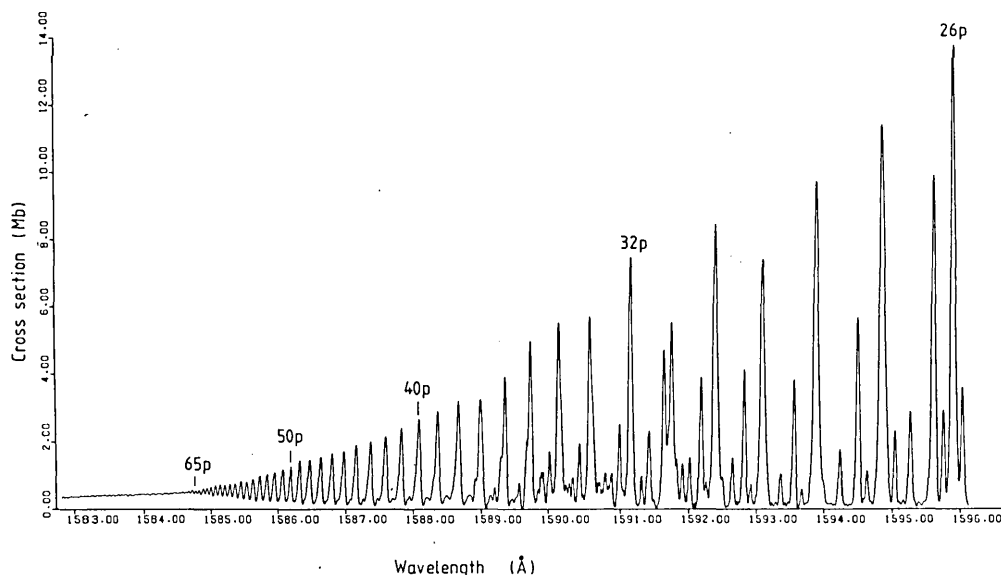


Figure 3. Uppermost members of the 3dnp series. The intrinsic resolution is close to the bandwidth of the laser for the uppermost members. Despite autoionization broadening, the series can be followed to $n \sim 65$.

Our conclusion is that the eigenchannel *R*-matrix calculations provide a very good description for most of the observations and, by implication, that the interpretation which attributes the width fluctuation to the influence of the 4p5s ¹P perturber (Connerade and Lane 1990) is the most plausible. The existence of the Cooper minimum discussed by Scott *et al* (1983) cannot, however, be discounted, and further *ab initio* *R*-matrix calculations for Ca I are clearly called for in order to determine its whereabouts more precisely.

The present research received financial support from the SERC (UK) under a rolling grant, and was carried out in the Blackett Laboratory Laser Consortium. One of us (SMF) is grateful to the Ministry of Education (Islamabad, Pakistan) for financial support at Imperial College during the present experiments. Also CHG was supported in part by the National Science Foundation (USA).

References

- Altun Z, Carter S L and Kelly H P 1982 *J. Phys. B: At. Mol. Phys.* **15** L709
Aymar M 1987 *J. Phys. B: At. Mol. Phys.* **20** 6507
— 1990 *J. Phys. B: At. Mol. Opt. Phys.* **23** 2697
Brown C M, Longmire M S and Ginter M L 1983 *J. Opt. Soc. Am.* **73** 985
Connerade J P 1978 *Proc. R. Soc. A* **362** 361
— 1990 *Atoms in Strong Fields (ASI Series B Physics)* vol 212, ed C A Nicolaides, C W Clark and M H Nayfeh (New York: Plenum) p 1
Connerade J P and Lane A M 1985 *J. Phys. B: At. Mol. Phys.* **18** L605
— 1988 *Rep. Prog. Phys.* **51** 1439
— 1990 *Aspects of Electron-Molecule Scattering and Photoionization (AIP Proc. No 204)* ed A Harzenberg (New York: AIP) p 193
Greene C H 1988 *Fundamental Processes of Atomic Dynamics (ASI Series B Physics)* vol 181, ed J S Briggs, H Kleinpoppen and H O Lutz (New York: Plenum) p 105
— 1990 *Phys. Rev. A* **42** 1405
Greene C H and Aymar M 1991 *Phys. Rev.* in press
Greene C H and Kim L 1987 *Phys. Rev. A* **36** 2706
Griesmann U, Shen N, Connerade J P, Sommer K and Hormes J 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** L83
Karamatskos N, Mueller M, Schmidt M and Zimmermann P 1985 *J. Phys. B: At. Mol. Phys.* **18** L107
Kim L and Greene C H 1987 *Phys. Rev. A* **36** 4272
Lange V, Eichmann U and Sandner W 1989 *J. Phys. B: At. Mol. Opt. Phys.* **22** L361
Marangos J P, Shen N, Ma H, Hutchinson M H R and Connerade J P 1990 *J. Opt. Soc. Am. B* **7** 1254
Pan C, Carter S L and Kelly H P 1987 *J. Phys. B: At. Mol. Phys.* **20** L335
Scott P, Kingston A E and Hibbert 1983 *J. Phys. B: At. Mol. Phys.* **16** 3945
Seaton M J 1966 *Proc. Phys. Soc.* **88** 801
Ueda K, Ito K, Sato Y and Namioka T 1990 *Phys. Scr.* **41** 75