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John W. Elder
Canterbury University College

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TITLE

THE ELECTRONIC MECHANISM OF THE OPTICAL PROPERTIES
OF ALKALI HALIDE PHOSPHORS, ACTIVATED BY NEGATIVE
HALIDE IONS.

ABSTRACT

Gyropoulos grown samples are used in an investigation
of absorption, emission and electrical properties of
crystalline phosphor of alkali halides, activated by
negative halide ions. Zero photoconductivity, the
form of half width temperature dependence, and asymmetric
line shape justify the use of a configurational
coordinate model. Trivial dependence of peak position
on temperature, or the solvent anion, show that the electronic
levels involved are associated with the activator ion.
CONTENTS

Table of Figures and Tables.
Notation.
Acknowledgments.
Summary.

CHAPTER I. Introduction

PART I.
THE DESIGN OF EQUIPMENT AND THE
ANALYSIS OF EXPERIMENTAL TECHNIQUES.

CHAPTER II. Crystal Growth. Page 12

2.1 Methods. 2.2 The furnace. 2.3 Temperature control. 2.4 Raising mechanism. 2.5 Annealing mechanism. 2.6 Crystal growth. 2.7 Crystal shaping.

CHAPTER III. The Optical Instrument. 22

3.1 The Photometer. 3.2 Ultraviolet sources. 3.3 Slit range. 3.4 Loss of Resolution due to finite slits. 3.5 Scattered light.

CHAPTER IV. The Detection System. 43

4.1 The Photometer. 4.2 The Photomultiplier. 4.3 The detecting system. 4.4 The mechanical coherent detector. 4.5 The electronic coherent detector. 4.6 The signal to noise ratio. 4.7 Comparison with other instruments.
<table>
<thead>
<tr>
<th>chapter</th>
<th>title</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>V.</td>
<td>Accessory Equipment</td>
<td>56</td>
</tr>
<tr>
<td>5.1</td>
<td>The hot cell.</td>
<td>57</td>
</tr>
<tr>
<td>5.2</td>
<td>The dark cell.</td>
<td>59</td>
</tr>
<tr>
<td>5.3</td>
<td>Fluorescence.</td>
<td>60</td>
</tr>
<tr>
<td>5.4</td>
<td>Photoconductivity.</td>
<td>61</td>
</tr>
<tr>
<td>5.5</td>
<td>Gaussian Analysis.</td>
<td>63</td>
</tr>
</tbody>
</table>

**PART 2.**

**EXPERIMENTAL RESULTS AND THEIR THEORETICAL DISCUSSION.**

<table>
<thead>
<tr>
<th>chapter</th>
<th>title</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI.</td>
<td>Experimental Results.</td>
<td>65</td>
</tr>
<tr>
<td>6.1</td>
<td>Background absorption.</td>
<td>66</td>
</tr>
<tr>
<td>6.2</td>
<td>Vibrational Broadening.</td>
<td>69</td>
</tr>
<tr>
<td>6.3</td>
<td>Photoconduction.</td>
<td>73</td>
</tr>
<tr>
<td>6.4</td>
<td>Emission.</td>
<td>74</td>
</tr>
<tr>
<td>6.5</td>
<td>Absorption.</td>
<td>77</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>chapter</th>
<th>title</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII.</td>
<td>Theory. The Model.</td>
<td>81</td>
</tr>
<tr>
<td>7.1</td>
<td>The Frank-Condon Principle.</td>
<td>82</td>
</tr>
<tr>
<td>7.2</td>
<td>Williams' calculation.</td>
<td>83</td>
</tr>
<tr>
<td>7.3</td>
<td>Conclusion.</td>
<td>86</td>
</tr>
</tbody>
</table>

**APPENDICES.**

<table>
<thead>
<tr>
<th>section</th>
<th>title</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Slit functions.</td>
<td>89</td>
</tr>
<tr>
<td>2.</td>
<td>Conversion tables. Angstroms to electron volts.</td>
<td>90</td>
</tr>
</tbody>
</table>

**REFERENCES.**

| | | 93 |
TABLE OF FIGURES AND TABLES.

Figures | Following.
--- | ---
1. Furnace control system. Block diagram | 2.7
2. Control unit. Circuit. | "
3. The raising mechanism. Photo. | "
4. The annealing drive. Photo. | "
5. Support, ball-joint, chuck and stud. | "
6. Front view of the furnace. Photo. | "
7. Back view of the furnace. Photo. | "
8. Crystal growth. Photo. | "
10. Crystal pieces. Photo. | "
11. Hg-arc and Hp6 output. Stray light. | 3.2
12. Dispersion and slit range. | 3.3
13. Range slit approximation. | 3.4
14. Sagitta correction. | "
15. Finite slit effect on an absorption maximum. | "
16. Finite slit corrections. | "
17. Analysis of stray light. | 5.3
18. Stray light mechanism. | "
19. D.C. null detection system. | Chpt.IV.
20. A.C. detector using a commutator. | "
22. Detector and square wave generator. Circuit. | "
23. Shot noise influence factor. | "
25. Commutator and pickup coil. Photo. | "
26. The detector. Photo. | "
27. The hot cell. Diagram. | 5.1
28. The hot cell dismantled. Photo. | "
29. The hot cell assembled. Photo. | "
30. Photoconduction arrangements. | 5.4
31. The dark cell. Photo. | "
32. Background. Absorption and reflection. | 6.1
33. Variation of surface absorption. | "
34. Absorption of thick samples. | "
35. Half-width against temperature. | 6.2
36. Emission spectrum. KBr:Cl | 6.4
37. Emission spectrum. RbCl:Br | "
38. Emission spectrum. KI:Cl | "
39. Absorption spectrum. KCl:Br | 6.5
40. Absorption spectrum. RbCl:Br | "
41. Absorption spectrum. NaCl:Ir | "
42. Absorption spectrum. KBr:I | "
43. Absorption spectrum. NaCl:F | "
<table>
<thead>
<tr>
<th>Tables</th>
<th>Following.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Colour centres in alkali halides.</td>
</tr>
<tr>
<td>2</td>
<td>Wavelength calibration. Hg-lines</td>
</tr>
<tr>
<td>3</td>
<td>HF6 stray light ratio.</td>
</tr>
<tr>
<td>4</td>
<td>HF6 stray light correction.</td>
</tr>
<tr>
<td>5</td>
<td>PM, current to intensity factor.</td>
</tr>
<tr>
<td>6</td>
<td>Emission energies and widths.</td>
</tr>
<tr>
<td>7</td>
<td>Emission existence.</td>
</tr>
<tr>
<td>8</td>
<td>Absorption energies and widths.</td>
</tr>
<tr>
<td>9</td>
<td>Absorption and emission. Approximations.</td>
</tr>
<tr>
<td>10</td>
<td>Williams calculation.</td>
</tr>
<tr>
<td>11</td>
<td>Gauss curve slit width functions. Appendix</td>
</tr>
<tr>
<td>12</td>
<td>Conversion of A to ev. 4000-7000A Appendix</td>
</tr>
<tr>
<td>13</td>
<td>Conversion of A to ev. 2000-5000A Appendix</td>
</tr>
</tbody>
</table>
### NOTATION

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Angstroms, Area.</td>
</tr>
<tr>
<td>AC, DC</td>
<td>Alternating, direct current. Dark current.</td>
</tr>
<tr>
<td>B</td>
<td>Band width in cps.</td>
</tr>
<tr>
<td>D, d</td>
<td>Optical density.</td>
</tr>
<tr>
<td>e</td>
<td>$Y_{\text{ideal}} = (1 + e) Y_{\text{observed}}$</td>
</tr>
<tr>
<td>E</td>
<td>Energy in ev, transition energy.</td>
</tr>
<tr>
<td>erf(t)</td>
<td>$\int_0^t \mathcal{N}(u) du$</td>
</tr>
<tr>
<td>ev, mev</td>
<td>Electron volts, milli-ev.</td>
</tr>
<tr>
<td>exp (_Y)</td>
<td>$10^Y$</td>
</tr>
<tr>
<td>f</td>
<td>Focal length.</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Phase angle.</td>
</tr>
<tr>
<td>h</td>
<td>Slit range / observed $\delta$-width.</td>
</tr>
<tr>
<td>HP6</td>
<td>Hydrogen arc.</td>
</tr>
<tr>
<td>i</td>
<td>Current.</td>
</tr>
<tr>
<td>I</td>
<td>Intensity or flux.</td>
</tr>
<tr>
<td>IK</td>
<td>Infra red.</td>
</tr>
<tr>
<td>K</td>
<td>Kilo - ohms.</td>
</tr>
<tr>
<td>I; l; e</td>
<td>Observed and ideal $\delta$-width.</td>
</tr>
<tr>
<td>m</td>
<td>$s/\sigma$. Absorption coefficient.</td>
</tr>
<tr>
<td>M</td>
<td>PM gain, Megohms.</td>
</tr>
<tr>
<td>$\mathcal{N}(t)$</td>
<td>$(2\pi)^{-\frac{1}{2}} \exp(-t^2/2)$</td>
</tr>
<tr>
<td>P</td>
<td>Time constant.</td>
</tr>
<tr>
<td>P(E)</td>
<td>Transition probability.</td>
</tr>
<tr>
<td>PM</td>
<td>Photomultiplier IP26.</td>
</tr>
</tbody>
</table>
Q

Revolutions.

RC

Resistance capacity.

rms

Root mean square.

s,a

Slit range, a - for a single slit.

σ

Standard deviation.

t

kt = zero-point energy.

T

Transmission = 10^{-D}.

UV

Ultraviolet.

v

Frequency.

V

Potential.

w(t)

t erf(t) + n(t)

x,x'

First and second nearest neighbour distances.

Reference to F. Johnson (1951) and D. Johnson (1952)
is by page number.
ACKNOWLEDGEMENTS

The writer greatly appreciates the privilege of working in the Physics Department, C.U.C., and in particular the offer of the late Professor F.C. Chalklin for the writer to commence research work in 1954.

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All other design and construction has been performed by the writer.

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SUMMARY.

Studies of negative halide ion activated, alkali halides begun by F. Johnson and D. Johnson are continued. The first stage of this problem is completed, a mechanism having been established. A detailed investigation of the experimental technique and results of these workers is reported.

The following equipment has been built.

1) A furnace and associated control gear, raising and annealing mechanism, for growth from the melt by the Kyropoulos method. A new technique of growth on a nickel stud is described. Several boules may be grown in a day.

2) A phase-sensitive coherent null detector and constant amplitude square wave generator for use with a Spekker photometer for absorption and intensity measurements. The detection limit is 1000 quanta/sec. Optical densities are reproducible to the nearest 0.002 for densities of 0.2 to 2.0 over the spectral range 2150 to 6500A.

3) A vacuum, hot cell capable of maintaining crystal samples at temperatures up to 500°C for absorption measurements at elevated temperatures.

4) A dark cell for use in fluorescent and photoconductive studies.

5) A projection system for analysis of curves into Gaussian components.
A number of calculations and theoretical derivations have been made.

1) The calculations of Brodersen and Runge are extended and simple practical rules deduced to allow for loss of resolution due to finite slits.

2) The error introduced by noise into a density measurement is deduced for a Spectrophotometer limited by shot noise.

3) A table for conversion of Angstroms to electron volts is given.

Various instrumental techniques and limitations have been investigated.

1) A simple temperature control system is discussed.

2) An investigation of Ultraviolet sources shows the superiority of a hydrogen discharge for absorption measurements.

3) Prism instruments, using a prism with a ground base, produce a stray light background at a level of 10^-3.

4) Commutators in coherent detectors are unreliable.

A repetition of the Johnsons' work and studies of background absorption, vibrational broadening, photoconduction, fluorescence, absorption and line shape, shows that the electronic levels are associated with the activator ion and describable in terms of a configurational coordinate model.
CHAPTER I.

INTRODUCTION

In April, 1951, Dr. Ferd Williams published the details of the first calculation, from first principles, of absorption and luminescent spectra in a crystal phosphor. This paper probably ranks among the most important contributions to the theory of solids in the last 20 years, being the first step away from a purely phenomenological theory.

Interest in phosphors stems from the insight provided into electronic processes and their rapidly increasing commercial use (Leverenz 1950). As a tool phosphors have the double advantage of the ability to effect an efficient direct conversion of a primary excitation ranging from 1 to over $10^7$ ev into visible photons, and the ability to store potential radiation energy for times of $10^{-7}$ to over $10^7$ sec.

In day to day use they are found in fluorescent lamps - 200,000 kg/year, electroluminescent lamps, television and radar cathode ray tubes - 100,000 kg of phosphor used during World War II, x-ray screens, infra-red image converters, lay-light fluorescent posters and scintillation counters.

Special applications are found as flow indicators, temperature indicators, cascade transformers, using contrast compression with $t^{-n}$ phosphors for solar observations in the icaroscope, and as time delays for storing information and controlling electronic timing devices. Luminescence is however, such a convenient and sensitive indicator of changes of composition, structure and atomic interactions that further research will overshadow the above tangible results.
Interpretations of crystal phosphor phenomena have been based on the band theory model or of the configuration coordinate model. These are in no way incompatible but are complementary—Johnson F (1921), Williams (1940).

The band theory model is based on a quantum mechanical treatment of the interaction of the valence electrons with the periodic lattice potential. Neglecting electron exchange forces, produces broad allowed energy bands separated by forbidden bands. In the ground state of an insulator or semiconductor one of these bands is filled. The more precise Heitler-London approximation allows narrow bands in the above forbidden bands. Here the excited electron and its associated positive hole—an exciton—move together, transporting no charge. If the absorption and emission process involves states peculiar to an activator ion, and the energy bands of the lattice are not involved, this model is not particularly applicable. The band model is especially suitable for interpreting mechanisms involving the transport of electrons.

The configuration coordinate model emphasizes atomic rearrangements. Defining a 'centre' as the ion undergoing electronic transition plus the group of neighbours participating in the rearrangements and specifying to a first approximation the co-ordinates of the centre by a single co-ordinate, energy against co-ordinate contours can be constructed. Absorption consists of a transition to an excited state, maintaining the configuration by the Franck-Condon principle.
A redistribution of electronic charge follows, reducing the system to a new equilibrium position of minimum energy, the excess energy being propagated as elastic waves. Emission occurs, maintaining the atomic configuration, and another rearrangement follows. This model emphasises the rearrangement energy as the difference in excitation and emission energy, that atomic configurations other than that of lowest energy have finite probabilities, producing temperature dependent broadening, and draws attention to activated rearrangements and radiationless processes.

The history of the understanding of the properties of crystalline solids has occurred in four main steps, Seitz (1953), the macroscopic study of anisotropic properties, culminating in the discovery of the 52 classes of crystal symmetry, the understanding of the lattice properties of crystals, climaxd by the discovery of X-ray diffraction by crystal lattices, the analysis of the behaviour of atoms and particularly the valence electrons in perfect crystals, achieving its limit in the analysis of ionic crystals by Madelung and Born. The fourth and present phase centres about those phenomena which can be explained only in terms of imperfections.

An attempt to regard the various types of crystal imperfections from a uniform viewpoint has been suggested by Seitz (1952). There are six types of primary imperfections; phonons, electrons and holes, excitons, vacant lattice sites - Schottky and Frenkel defects - and interstitial atoms, foreign
atoms, and dislocations. In addition there are three transient imperfections, light quanta, charged radiations, and uncharged radiations. It is stressed that the interactions of these imperfections should be regarded as an essential part of their behaviour pattern, and that the imperfections are not independent of one another.

Since the majority of inorganic phosphors of commercial and research interest are obtainable only in the form of microcrystalline powders, Garlick (1949) has emphasised the need for study of phosphors available in the form of large single crystals. Thus alkali halides have received considerable attention because of their ease of growth and theoretical simplicity. Ionic binding, however, has the experimental disadvantage that the bond is destroyed when an electron is ejected from an anion, or supplied to a cation. The affected atoms may be irreversibly displaced and during an experiment the original simple crystal becomes increasingly complex. This is often the case with high energy photons or charged particles. Leverenz (1953) therefore also urges studies of crystals with non-ionic components in their bonding energies.

Simplicity of alkali halides in ionic binding, cubic structure, and binary composition is in contrast to the increasing variety of colour centre phenomena - Seitz 1946, 1954. Vacancies and vacancy clusters play a prominent role in alkali halides. Principle forms are, positive ion
vacancies, negative ion vacancies, coupled pairs of vacancies of opposite sign, a substitutional divalent ion associated with a positive ion vacancy, and two positive ion vacancies and a negative ion vacancy. The various colour centre phenomena may be discussed broadly under three headings; those absorption bands arise from a centre with an electron surplus - F, F', II centres; electron deficient bands - V centres; and crystals containing foreign ions or atoms. A summary of the centres and mechanisms so far discovered is given in Table (1). This summary has been largely based on the review article by Seitz (1954), and where necessary the original papers. It is intended to be a guide in the increasing complexity and diversity of colour centre phenomena, and to show the place of the work performed in this department.

Table (1).

Colour centres in alkali halides.

Energy of absorption peaks are in ev.

α-band. Negative ion vacancy, rises in proportion to F' band, (Selbee, Fringsheim and Huster 1951, 1952), previously called U' by Pohl.

<table>
<thead>
<tr>
<th></th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>AI</td>
<td>5.15</td>
<td>5.40</td>
</tr>
<tr>
<td>KBr</td>
<td>6.11</td>
<td>6.41</td>
</tr>
</tbody>
</table>

β-band. High energy band of an F centre.
F - centre. Excess electron near a negative ion vacancy - de Boer model. From addition of excess metal to a halide followed by quenching, or ionizing radiations, when other bands also appear. Characteristic of the crystal, not of metal vapour used.

<table>
<thead>
<tr>
<th>Metal</th>
<th>NaF</th>
<th>KF</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>RbCl</th>
<th>CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>3.63</td>
<td>2.73</td>
<td>3.20</td>
<td>2.64</td>
<td>2.19</td>
<td>2.00</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Illumination in F-band bleaches it, produces photoconductivity, and at low temperatures produces F' centres.

F' centre. F centre with a second electron.

M centre. After Molnar, F centre combined with a pair of vacancies occurs at 1.52ev in KCl, 1.72 in NaCl, 1.90 in LiCl. From ionization of an F centre by F- light at room temperature and transport of the vacancy thus formed. This also produces R1, R2, A, B, N bands in the near IR.

R1 centre. One excess electron near two negative ion vacancies.

R2 centre. Pair of bound F centres.


N centres. Cluster of three halogen ion vacancies, 1.5ev in KCl.

$V_1$ centre. Antimorph of F centre, hole and positive ion vacancy. From bombardment with high energy radiation - as are other V bands. Unstable above -100°C.

$V_3$ centre. Two positive ion vacancies with one hole, analogous to $R_1$ centre. $V_2$, $V_3$ observed by Mollwo in crystals containing excess halogen.

$V_2$ centre. Two positive ion vacancies with two holes, analogous to $R_2$ centre.

$V_{4,5,6,7}$ Mechanism uncertain. Results by Borendorf (1951).

$$
\begin{array}{cccc}
V_1 & V_2 & V_3 & V_4 & H \\
NaCl & 3.59 & & & 3.76 \\
KCl & 3.48 & 5.37 & 5.83 & 4.67 & 3.59 \\
KBr & 3.02 & 4.67 & 5.35 & 4.50 & 3.26
\end{array}
$$

H band. V bands at liquid helium temperatures.

Tl centres. Configuration co-ordinate model. Fundamental theory by Williams (1951a).

Divalent halides in alkali halides. Discovered by Pick. Visible bands. \( E_1 \) at 2.10 eV in KCl, by capture of a photoelectron liberated from an F centre by a divalent ion. Further structure at low and high temperatures.

**Mixed systems.** Studies of F, V centres in systems of form \( MX:MY \), \( MX:NX \). Pioneer work by Gnaedinger (1953).

**Halogen ion centres.** Pioneer work by F. Johnson (1951). Suggests absorption due to exciton levels of impurity.

- \( \text{NaCl}:F^- \), \( \text{NaBr}:Cl^- \), \( \text{NaCl}:Br^- \), \( \text{KCl}:I^- \)
  - \( 4.93, 4.82, 4.87, 4.47, 4.64, 3.8 \)

F. Johnson (1952) showed absorption temperature dependent, discovers emission.

- \( \text{KCl}:Br^- \), \( \text{RbCl}:Br^- \)
  - \( 4.82, 4.53 (0.21); 4.85, 4.67 (0.30) \)

Elder (1955). Form of temperature dependence, line shape, emission, zero photoconductivity, and doublet structure, shows validity of Williams' configurational coordinate model.
This field is at present at a peak of activity and likely to continue so for a considerable time. Let us pause a moment. This frenzied activity of searching for further interactions and phenomena is rather like building a house on sand. What is the ultimate aim of any such work? Is it to fill libraries with partially undigested facts! Surely it is to increase our knowledge and understanding of basic principles. Most workers in this field agree that many of the explanations and mechanisms of apparently well established facts are vague and unsatisfactory. Dr. Ford Williams has provided the first step towards a reliable basis for a detailed understanding of colour centre and crystal phosphor phenomena. This is the only detailed theoretical calculation made in a field which has been well established for nearly thirty years. There is nothing essentially novel or difficult in his calculation. He has merely applied well-known quantum mechanical principles to a model. Let us hope that future workers will follow in Dr. Williams footsteps.

The work performed in this department sprang from the need for detailed study of simple crystal systems. Alkali halides containing negative halogen ions were chosen as a tool. The contribution up to the present time is summarized in the last section of Table (1). F. Johnson discovered the absorption peaks in NaCl:F, NaBr:Cl, NaCl:Br, NaCl:In, obtained the absorption energies, made an empirical calculation of the levels of halide ions, and attempted to correlate
these levels with exciton levels formed by incorporating the the halide ions in a perfect crystal lattice. It was suggest-
ed that the double peaks in NaCl:Br and NaCl:I− were associated with the doublet ground states of the halide ions, and that the shift of peak absorption to lower energies was due to coulombic overlap interaction energy. It is the writer's belief that this theory is in no way fundamentally different from that of Dr. Ferd Williams for KCl:Ti. D. Johnson obtained the absorption energy for KCl:Br and NaCl:Br, showed that the bands were temperature dependent, discovered the luminescence of KCl:Br and pointed out the similarity of the absorption peaks with those found in the vapour. His work did not advance the subject.

In January 1954, the late Professor Frank C. Chalklin offered the writer the opportunity of carrying on the research begun by the Johnsans. During the regrettably short time he was my supervisor he was especially clear on two points. Firstly, that a thorough analysis be made of the experimental technique and the results of previous workers, and secondly, that an alternative technique of crystal growth be investigated.

From the beginning it was realized that a detailed experimental and theoretical investigation of the problem was more than could reasonably be performed in the year's research expected of an M.Sc. student. Throughout the emphasis has been on the analysis, design, construction, and testing of equipment and techniques, so that future workers in this
Department will be able to proceed as quickly and as efficiently as possible. Equipment has been built to allow studies of crystal growth, annealing processes, absorption and emission spectra, photoconduction, and the effects of temperature on the spectra. Several crystals can be grown in one day and their properties measured the next. In the course of this development, however, sufficient results have been obtained to establish the nature of the electronic mechanism, and at present a paper is being prepared for publication. It is the writer's hope that in some small way the work to be described will help our ultimate understanding of electronic processes.

The work in this thesis was performed over a total period of 44 weeks, involving 3500 hours, during 1954 - February, April to August, December - and 1955 - January, March to June.
PART I.

THE DESIGN OF EQUIPMENT AND THE ANALYSIS OF EXPERIMENTAL TECHNIQUE.

CRYSTAL GROWTH.

THE OPTICAL INSTRUMENT.

THE DETECTOR.

ACCESSORY EQUIPMENT.
CHAPTER II

CRYSTAL GROWTH.

(2.1) CRYSTAL GROWTH.

Useable crystals of convenient size are usually grown from the melt, by various techniques many of which are discussed by Verfoss, Johnson and Egli (1949).

1) The moving crucible method of Bridgman. A crucible containing the melt is lowered through a fixed thermal gradient.

2) The stationary crucible method of Stober and Stockbarger. A crucible containing the melt is cooled in a slowly changing thermal gradient.

3) The Kyropoulos technique of drawing a seed from the melt.

4) Eutectic melt growth, relying on special properties of a low temperate phase.

5) The Verneuil Technique. Powder passing through an oxyhydrogen torch is collected as a molten drop on a refractory rod.

6) Growth from the vapour phase.

7) Briquetting method. The powdered material is hot pressed under pressures of 20 tons / sq in. (Ryeason 1953).

All but (4) (5) or (6) could be used with convenience for the growth of alkali halides. Technique (7) appears especially promising. It was not investigated since equipment built by Johnson E (36) existed for method (1). It appears capable of producing optically excellent crystals and has two very great advantages. Firstly the technique is very simple, involving the most elementary principles of die casting.
technique. An hydraulic car jack, cylindrical die and ring gas burner being all the equipment required. Secondly, for work involving impurities no determination of the impurity content would be necessary since all the impurity will incorporate into the lattice. Investigation of this technique would be very valuable.

Johnson F (37) chose the Bridgman method because it is automatic. This is its main disadvantage, it is too automatic. One has to wait a week to know whether a satisfactory crystal has grown or not, or the crucible has leaked. If the crystal is unsatisfactory it is necessary to start again. In the method to be described a useable crystal can be grown in 4 hours and the furnace ready to grow another.

Techniques (1) (2) (3) are in principle identical for they rely on the relative motion of a thermal field and the crystal. Choice between them rests on the technological ease of supplying the conditions suitable for growth. Strong (1930) summarizing the experience of many workers lists five conditions which ensure growth.

1) Crystallization must start at a single point, otherwise the crystal may be multicrystalline.

2) There must be a strong thermal gradient in the molten salt. This helps orientation and prevents twinning.

3) Temperature isothermals within the crucible should be as nearly horizontal as possible to prevent convection currents in the melt. The melting isothermal must move
relative to the crystal slowly and uniformly so that the crystal laid down at this surface will be sound and flawless.

4) When the crystal has been formed the bottom and top of the crystal must be brought to the same temperature to avoid strains. During growth the crystal is in a thermal gradient of about 200°C/cm, and if the gradient is preserved as the temperature is lowered, as in the Johnson technique, considerable strains will be set up due to the unequal cooling rates, especially near room temperature. Above 200°C alkali halides are fairly plastic so that immediate removal of the gradient after growth produces no strain.

5) The crystal must be removed from its container or holder before cooling to eliminate strains from contraction of the holder.

A comparison of the Bridgman and Kyropoulos methods is given by Menzies and Skinner (1949). The outstanding advantages of the Kyropoulos method are ease of gradient control and the process can be interrupted during growth. The existing equipment was rebuilt to allow growth by the Kyropoulos method, but the lowering mechanism used by Johnson for the Bridgman method can be easily attached if required. The furnace and control gear were made to be versatile as it was hoped to perform studies of the annealing process and the possibility of using the technique for purification.
(2.2) THE FURNACE. The furnace need not be as large as it is. Since heat loss is proportional to area, the power to be controlled varies as the square of a typical linear dimension. Crucibles used by past workers and during the present work were 2" in diameter or less whereas the internal diameter of the furnace is 4". A reduction in size to \( \frac{1}{2} \) would have been convenient. This was appreciated only after the furnace had been entirely reconstructed, when it was realized, evidently not by Johnson F, that useable crystals need be only 1 x 1 mm in section, for this is the effective beam area of the Spekker Photometer where the absorber is placed.

(2.3) TEMPERATURE CONTROL. Although two independent circuits providing both proportional and integral response control, as described by Johnson F (42), are incorporated in the controller, for the work to be described it has been found sufficient to use a simple on off device. A light beam reflected from a mirror galvanometer, placed in a potentiometer circuit with the thermocouple, was either incident on a photocell or not, dependent on the galvanometer indicating above or below balance. Through an amplifier and D.C. relay a spring connected a resistance into or out of the furnace supply circuit, Figure (2). In the previous work the thermocouples were merely dangled in the radiation field of the furnace, and with the above simple controller control was inadequate, evidently due to the poor efficiency of radiation transfer to the thermocouple in a ceramic block, supporting

For on imbedding the thermocouple
the crucible, when the thermal contact of furnace wall and thermocouple is good, the simple controller was found to be adequate. It would appear advantageous in such a servo-mechanism to have only one controlling time constant, and since the controller delay cannot be removed the furnace response should be made as rapid as possible. This would be assisted if the furnace were smaller.

In practice it has been found sufficient to place the block holding the crucible in the middle of the upper winding; to switch on both heaters till the salt melted; start the controller and switch off the bottom heater. Both the elaborate and simple controllers suffer one disadvantage. Should the furnace temperature fall below that necessary for the controller to switch on the power—due to a temporary power failure, etc.—the furnace runs down. Temperatures were read to 1°C on a Cambridge unipivot 0-10 microamp meter or by watching the galvanometer spot.

(2.4) RAISING MECHANISM. It would appear that growth will occur over a range greater than 1 - 25mm/hour (McFee 1947) with optimum rates of 3mm/hour for pure halides. A convenient range of speeds is given by a mechanism using the block and tackle principle, Figure (3). A 40 rph synchronous motor drives the 40 : 1 worm attached to an A.S. A. screw. Hence a block on this screw moves at 1mm/hour. A ball bearing pulley and a clamp are fixed to the moving block and the base plate. This is wound with nylon dial chord. If a 'loop' is a
complete circuit of chord around the fixed pulley the raising rate in mm/hour is the number of 'loops'. A microswitch on the base plate, operated by the moving block, switches a changeover relay which switches off the raising motor and starts the annealing mechanism. A manual raising control is provided and various clamps to allow change of the number of loops. The raising mechanism was not used very often. Menzies (1952) points out that since the solid is denser than the liquid the level in the crucible automatically falls. This is very convenient.

(2.5) Annealing Mechanism. A 1hp synchronous motor through a 1:10 gear drives a 1" rubber ring on a 3" aluminium disc surfaced with glasspaper. This disc runs on a shaft attached to a 50 ohm wirewound potentiometer and may be firmly attached to this shaft by screwing up the 'clutch' nut which forces a concentric cylinder to bear on the disc. When in circuit the mechanism will lower the furnace temperature at any set rate from 10-60 hours; Figure (4). With this it was hoped to study the effect of various cooling rates on the crystals.

In the present work the crystal has been broken off the stud on which it grew and placed in a preheated box of asbestos powder. This appears to have no ill effect on the crystal since it is fairly plastic above 200°C.
(2.6) CRYSTAL GROWTH. A ceramic plug was made to fit neatly within the furnace, the crucible sitting in a hollow in the top. Various crucible materials have been used by other workers - platinum, silica glass, porcelain, iron. Vitreous silica has been found convenient provided that after growth has terminated the remaining melt is tipped out before it cools, else it adheres to the silica and the crucible cracks. Such crucibles are readily cleaned by heating or soaking in water.

The cooling mechanism is provided by nickel coated brass chuck with easy-flow joints, and water cooled; Figure (5). This has shown no deterioration after many hours of use. The department's water supply can send up to 200 cc of water/second through the chuck, so there is no difficulty in cooling the chuck. Normally it is run at 50-60°C.

One of the apparent difficulties of the Kyropoulos method is the need for a seed crystal. Menzies (1952) melts some of the material and after it has cooled picks out a suitable piece from the solid mass. This is an excellent method. In point of fact from each such mass there are usually 2 or 3 pieces which could be used immediately for measurements, since a piece 1 x 1 mm only, is required. It is however quicker to proceed as below. Some workers have evidently tried growth directly on to platinum. So various shaped nickel studs were fitted into the end of the chuck. Growth proceeded very easily. Since the head of the stud
is fully imbedded in the crystal excellent thermal contact is maintained. With this stud a pure NaCl boule of 2cm diameter has been grown at the rate of 10cm/hour. A simple analysis indicates that a rough guide is, length of crystal is proportional to the square root of time.

(2.7) CRYSTAL SHAPING. Lord, McDonald and Miller (1952) give many practical details of the fabrication of alkali halides. The cleavage planes are readily found by rather quickly forcing a corner of the boule on to the edge of a rough grinding wheel - the ordinary lab. grinder is excellent. The crystal tends to shatter at this point and the cleavage planes are clearly indicated. A sharp razor blade held in an ordinary glass scraper given a light tap, readily cleaves the crystals. There may be some advantage to perform this under water or parafin. The surface characteristics of all such crystals including some seen in other laboratories are rather variable due to many fine lines on the surface. Hence throughout this work all surfaces have been polished immediately before measurements, of absorption.

Occasionally when only a small boule is grown it is more convenient to grind a piece to shape rather than cleave it. A 3" fine grinding wheel mounted in the drill press run at top speed and water moistened was used. Contrary to expectation these crystals may be handled quite roughly, and may even be cut if a 1/64" milling cutter is mounted in the
lathe chuck and kept wet... this requires care, but would be, readily done if a diamond impregnated steel disc of similar thickness were available.

Polishing is performed in two stages. A grinding blank is prepared by grinding between two pieces of plate glass a drop of water and a trace of 600 emery. When washed and dry one breathes on the ground surface and begins polishing. As soon as the plate begins to feel sticky the crystal is quickly slid off and the plate cleaned. After 2 or 3 such operations the crystal surface will be quite clean and is then rubbed lightly and quickly on a soft cotton cloth tightly stretched over a piece of plate glass and moistened with a trace of alcohol. This produces uniformly optically excellent surfaces, in a very short time. If the surface should deteriorate it only is necessary to rerub it on the cloth.

A technique pointed out by Glowinski (1954) requires considerably more skill but produces slightly better surfaces. After the crystal has been rough ground on the plate glass grinder it is rubbed on a pitch lap slightly moistened with brine. The final polish is given with the lap barely moistened with water.

Views of the furnace, etc., are shown in Figures 6-10.
FIG. 1 Block diagram of the furnace control system.
FIG. 2 Integral and Proportional response control unit.
FIG. 3   THE RAISING MECHANISM. This is described in the text. From the left is the automatic control, microswitch and manual control. Lay shafts are of silver steel and the coupling is of rubber. The dimensions are half real size.
FIG. 4  THE ANNEALING MECHANISM.  This is described in the text.  Clutch nut and knob are on the right of the panel, the top of which appears out of focus.  Reproduction is full size.
FIG. 5 Sections of the water cooled Chuck, and Ball-joint centering attachment; and the Support, shown in the free position.

B = Bronze weld
E = Eutectic weld - take apart here.
O = Oil-well
R = Silver steel rod.
FIG. 6  Front view of FURNACE and CONTROLLER.

On the left is the raising mechanism. The chuck, stud and thermocouple are in position on the centre of the furnace, but the illuminating lamp is swung up, as is the viewing mirror, seen behind the chuck. The lower unit of the controller is the power unit and the upper the controller proper. Leads to the galvanometer and photocell run above the sink, where thermometers are placed to measure the inflow and exflow water temperatures.
FIG. 7  Rear view of FURNACE and CONTROLLER.

The annealing drive may be seen to the left rear of the sunvics, in the lower unit of the controller. Photo-cell and lamp are on a shelf to the rear.
FIG. 8 CRYSTAL GROWTH. A photograph taken in the viewing mirror near the completion of growth of Br\textsuperscript{-} in KCl. Dimensions are approximately full size. The glow of the furnace can be seen between the ceramic block and the furnace wall. The chuck support shaft - direct image - is out of focus. Notice, that by achieving radially symmetrical heating and cooling, as suggested by Menzies, no raising is required. In the figure radial growth has stopped.
FIG. 9 Nickel studs and some sample boules. Notice the multicrystalline nature, composed of large monocrytalline units.
FIG. 10  Some pieces of crystal used in this work.
CHAPTER III

THE OPTICAL INSTRUMENT.

Four sources of error. Two possible procedures of
adjustment. Lamp position.
Ultraviolet sources. Difficulty of achieving
stability. Various sources. Hg-arc superior
intensity. Large intensity change across the
spectrum. ML lamp for calibration. Use of a
phosphor.

Slit range. Optimum slit settings. Resolving
power. Neglect of $S_0$. Dispersion.
Loss of Resolution from finite slits. Earlier work.
Brodersen's calculation. Gaussian absorption curve.
Approximation from Brodersen's result. Superposition
principle. $\lambda^2 = \lambda_1^2 + \epsilon^2$. Modification of
Runge's work. Sagitta correction. Practical guide.
Spectral analysis of stray light. Triple reflection
scattering mechanism. Energy argument. Polarization
(3.1) THE PHOTOMETER. This unit is briefly described by F. Johnson (58). It is, however, the heart of the measurements and several important factors will be mentioned.

The flux attenuator of the Spekker Photometer, placed immediately behind the Fresnel Rhomb beam splitter, consists of a fixed upper aperture of width 0.500 cm, and a variable lower aperture fed by a screw of pitch 16 threads/cm, carrying at its lower end an aluminium cylinder, attached to which is a sleeve, calibrated in terms of density log $\frac{A'}{A}$. The fixed aperture, $A$ the variable aperture, the 8 revs. giving a 100 cm scale calibrated 0 - oo. Since the source is approximately 20 cm from the photometer a deviation of less than $0.5^2 / 20^2 = 1/1600$ from uniform intensity is achieved. Let this flux be $I'$ and $A$ be adjusted so that the upper beam emerging from an absorber has the same flux as the lower.

$$I'/I = A'/A$$

$$\log_{10} I'/I$$

A density reading involves four sources of error.

1) The screw may not be true. An accurately graduated circle was set into the drum cylinder with a turned wooden plug. Readings were taken, at various circle settings, of the position of the moveable slit, with a Pye travelling microscope, of quoted accuracy better than 0.0005 cm, and found to be a linear function of the circle setting.

2) The d-calibrations may not be consistent. Here, using the same graduated circle, log (circle setting) was a linear
function of $d$. Any error in these two is less than the error in reading the $d$-scale.

(3) The screw may be incorrectly zeroed at an aperture $A = A' + a$.

(4) The drum sleeve has been misplaced by a $q$ revs with reference to the above false origin.

Measuring $q$ revs, around the sleeve from $d = 0$, the true drum reading

$$R = -\log (1 - \frac{1}{2} (q - q))$$

$$= \log \frac{A'}{A}$$
as calibrated by the makers.

The true density, however $\theta = \log \left(\frac{A' + a}{a}\right)$

$$D = R + \log \left(1 + \frac{a}{A'}\right)$$

and $\theta = (1 - 10^{-d})$ since it is measured from $d = 0$.

Substituting in $R$,

$$D = \log \left(1 + \frac{a}{A'}\right) - \log (10^{-d} + \frac{1}{2}q) \quad \cdots (1)$$

When fixing the sleeve to the drum there are two possible procedures.

(1) Set $A(d = 0) = A'$ using a travelling microscope. This requires dismantling the photometer, and is tricky to set to better than .001 cm. In (1) if both $D, d = 0$ there remains $\frac{1}{2}q = a/A'$ and errors from the second term become large at large $d$.

(2) Close aperture - light finger pressure, - i.e., $D = \infty$ and set $d$ against the $\infty$ mark, giving from (1) $q = 0$

Then $D = d + \log \left(1 + \frac{a}{A'}\right)$
and the error term is a constant. Modifying this to allow for $I (d = 0) \neq I'$

$$D = d + \log \left(1 + \frac{a}{A'}\right) \frac{I}{I'}$$

In adjusting the lamp, $d$ is set to $0$, and the lamp adjusted till $D = 0$; i.e., $I' / I = (1 + a / A')$ - with this procedure $a / A'$ is $0.01$ - giving $D = d$; to an accuracy set by the screw and the maker's calibration. Since the sleeve calibration and screw is accurate this procedure is reliable with an error less than that of reading the $d$ - scale.

The lamp position is critical, especially in a vertical direction when an $0.1$ mm shift changes the density by $0.04$, due to the rapid divergence from parallelism of the two beams as the source moves off the axis of the instrument, and the consequent more rapid vignetting of one beam than the other. The transverse and longitudinal positions are $5$ and $50$ times less critical. The lamp is positioned by a screw driven support.
(3.2) ULTRAVIOLET SOURCES.

It is known that the two previous workers experienced considerable difficulty in achieving stability and reliability in their measurements, as was the case with MacDonald (1953), (unrecorded). As is pointed out elsewhere, these difficulties centre around:
1) The use of a D.C. measuring technique.
2) Low H- arc output, and the predominating influence of variable dark current.
3) Considerable stray light with the Hg- source, and random intensity variations.

Johnson F (65), with reference to the Hg- arc, implies that the method used had sufficient sensitivity only on an emission line, and in fact his measurements were made photographically. In using an HF6 Johnson D (49) admits the need for wide slits. Hence an investigation of various sources was run at 2400 Å.

1) A hydrogen lamp, type HF6, though stable had low intensity.
2) An ordinary D.C. arc had fair intensity at an arc current of 5 amp. The arc was unstable and wandered over the carbons. A perpendicular arrangement of the carbons was used so as not to obstruct the radiation from the positive crater.
3) A box type MB lamp, 250 Å Hg-arc was convenient, had reasonable output, but the arc wandered.
4) A high intensity carbon arc using copper coated high
intensity carbons (6 mm.) was similar to the ordinary arc for currents below 15 amp. Above 15 amp the radiation increased considerably both at 2400 A and also in the visible region. The arc became quite stable, but the perpendicular carbon arrangement caused the positive carbon to crater diagonally, and most of the radiation was lost. The burning rate became alarmingly high above 15 amp.

5) Tungsten electrodes gave high intensity with a current of 3 amp. However, the arc was very unstable and would not burn for more than a minute at a time. The positive electrode burned rather quickly and clouds of tungsten oxide were deposited on all nearby objects.

6) A tungsten positive and a carbon negative gave similar results but the arc was a little more stable.

7) A tungsten negative and a carbon positive gave a fairly high intensity and reasonably stable arc which would run for several minutes without adjustment. Tungsten oxide was still troublesome but not nearly as bad as before.

From these tests the Hg-arc would appear superior from the point of view of intensity and convenience, as the air operated arcs are tricky to use and unreliable. For work in the 2000 - 2500 A region a tungsten source enclosed in an inert atmosphere would be worthy of investigation. All such sources, however, have the grave difficulty of large intensity variation across the spectrum enhancing stray light effects q.v. A detailed investigation of output is
shown in Figure (11) for the Hg-arc and the HP6. As shown
later the HP6 was used for all absorption measurements.
A number of other Hg-arcs were investigated and the
discharge tube from a 160 W blended type ML lamp was
found to be most convenient for wavelength calibration, with lines
at:

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5770</td>
<td>5461</td>
</tr>
<tr>
<td>4992</td>
<td>4358</td>
</tr>
<tr>
<td>4080</td>
<td>4047</td>
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<td>2967</td>
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<td>2894</td>
<td>2805</td>
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<td>2663</td>
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<td>2643</td>
<td>2537</td>
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<td>2494</td>
<td>2464</td>
</tr>
<tr>
<td>2400</td>
<td>2380</td>
</tr>
</tbody>
</table>

Those underlined being strong and suitable in the UV for use
with the fluorescent eye piece to check the wavelength
 calibration.

The use of a phosphor was considered as a means of
overcoming the poor response below 2300 Å. Since an
interrupted light beam is used, the phosphor decay time has
to be short, so that a 40 cps square wave would be transmitted
with little loss. Zinc Sulphide has a high conversion
efficiency but excessive decay time. Various oils and
vaselines were tried, and although their decay times appeared
short enough their conversion efficiencies were so low that
loss of output resulted. It would appear that sodium
salicylate applied to the PM by dissolving in Methyl alcohol
would be worthy of investigation since it has the advantage
of constant quantum efficiency 1000 - 3000 Å. - Watanable
and Inn (1953).
FIG. 11

IP28 CURRENT

Current gain $10^6$, 0.1 mm slits

-LOG current

ME 250 W

HF6

WAVELENGTH

2000 3000 5000 6000A
(3.3) SLIT RANGE.

Throughout the experimental work entrance and exit slits have been set the same - the optimum position. For, if the slit widths are a, b the energy reaching the detector varies as \(ab\), and the slit range as \(a + b\). If \(ab\) is constant, \(a + b\) is a minimum for \(a = b\). This was verified by traversing the broadened Hg-line 4050A. The variation of resolution for \(\frac{1}{2}b < a < 2b\) is small.

Brodersen (1954) shows that a quantity conveniently describing the actual resolving power of a monochromator is the effective slit range \(S_e\) related to the minimum value of \(S_e\), \(S_0 = S_0(v)\) a quantity characteristic of the monochromator, and \(S_g\) the geometrical slit range by \(S_e^2 = S_0^2 + S_g^2\).

The optimum slit width is of the order \(\lambda f/a\) where \(f\) is the focal length of the collimator mirror and \(a\) is the width of the beam leaving the prism, Forsythe (1937). For the Hilger UV monochromator \(a > 0.5\text{cm}\), \(f\) is 27.5cm. Hence, for \(\lambda \sim 3000\ \text{A}\), this is less than 0.01 mm, whereas the work reported here is with slit widths 10-20 times greater, so \(S_0\) can be neglected and \(S_e = S_g = S\) say.

The \(\lambda\) scale of the Hilger instrument has been checked against the Hg-arc and found to be accurate to about 1A from 2000-4000 A. Hence, take the calibrated \(\lambda\)-sleeve as correct and use it to calculate the angular dispersion \(d\Theta/d\lambda\) Figure (12); giving the slit range for 2 equal slits \(2d\lambda = 2\frac{d\lambda}{d\Theta}d\Theta = \frac{S^2 \lambda}{d\Theta f}\), which is to be expressed in terms of
\( E = \hbar \alpha / \lambda \).

Hartmann's formula may be written

\[ n = n + c(E^{-1} - E_0^{-1})^{-1} \]

\[ \therefore \frac{dn}{dE} = cE_0^2 / (E - E_0)^2 \]

and \( dx = f d\theta \cdot dn \cdot dE \)

\[ \therefore dE = K (E - E_0)^2 \]

since \( d\theta \) varies slowly with \( E \). Hence in Figure (12) we plot (slit range) \( \frac{1}{2} \) against \( E \).
FIG. 12

Hilger UV Monochromator,
Slit range and dispersion.
(3.4) LOSS OF RESOLUTION IN AN ABSORPTION SPECTRUM DUE TO FINITE SLITS.

Previous work on slit width errors was largely concerned with spectral lines. Only recently Hardy and Young (1949) gave a rigorous treatment of slit width errors for the general case of a continuous absorption curve, but their result is too complex for practical purposes. Again other workers, such as Eberhardt (1950), who fits the absorption curve at the maximum by a parabola, make rather crude approximations. The main objection, however, to many of these practical point of view approaches is that they discuss absorption in terms of transmission - e.g., Willis (1951) - whereas the physically significant quantity is related by a factor to optical density.

It would appear that the trend in modern instrumentation is to calibrate the intensity comparator in optical density - Daniell and Brackett (1953) - as on the Spekker photometer. Many of the results for correcting, for the effect of finite slits on emission lines could be used if density were converted to intensity, corrected and reconverted. This would be a tedious process even for one curve and as will be shown, unnecessary.

Broderen (1954) takes a middle course and derives results of practical value and very general validity, for emission lines, absorption lines and continuous absorption; a linear absorption curve only, being considered. He does not realize, however, that his results are of much wider
generality. As he himself admits, absorption lines are especially rare in ultraviolet absorption spectra. Let us consider a continuous absorption curve as a very wide absorption line. A typical case for an alkali impurity is, peak absorption at 4.8 ev, half-width 0.4 ev, slit range 0.1 ev. Although it is known that an absorption curve is not necessarily Gaussian - e.g., that due to F centres; Seitz, Theory of Solids (663) - Richards and Burton (1949) found that for solid and liquid specimens, even with wide slits, absorption curves may be closely fitted by a Gauss curve. Indeed, since in our case corrections to be derived will be less than 5%, in general about 2%, the correction will not be critically dependent on the assumed ideal shape, and the Gauss form is of mathematical convenience. Hence Brodersen's analysis for absorption lines may be used as it stands.

From D ideal \[ D_{\text{ideal}} = D_0 \exp \left( -\frac{(V-V_0)}{2\sigma^2} \right) \]

the observed intensity \( I_{\text{obs}} = \int_{V_s-s}^{V_s+s} Z_{\text{ideal}} \, dv \) where

\[ Z = s \left( 1 - \frac{(V_s-V)}{s} \right) \] the triangular slit function.

and \( I_{\text{obs}} = I_0 \cdot s^2 \)

\[ D_{\text{obs}} = -\log \frac{I_{\text{obs}}}{I_0} \]

\[ = -\log \frac{1}{s} \int_{V_s-s}^{V_s+s} \left( 1 - \frac{(V-V_0)}{s} \right) \exp \left\{ -D_0 \exp \left( \frac{(V-V_0)^2}{2\sigma^2} \right) \right\} \, dv \]

(1)
For \( D = 0.2 \), there is 20\% error in using \( 10^D = 1-2.3D \) (2)

when writing \( \frac{X}{\sigma} = x, \delta = \delta \)

\[ D_{\text{obs}} = D_0 \left( \frac{2\pi^{\frac{1}{2}}}{m} \right) \left( w(m+x) + w(m-x) - 2w(x) \right) \]

where \( w(t) = t \text{erf}(t) + N(t) \)

At \( x = 0, \frac{D_{\text{obs}}}{D_0} = 2 (2\pi)^{\frac{1}{2}} \frac{w(m)}{m^2} \)

From Brodersen’s numerical data (His Fig. 3) we derive

Figure (15). Notice, that though \( D_{\text{obs}}/D_0 \) is dependent on \( D_0 \) the results are given for \( m = 1, 2, 4, 6 \) whereas in UV absorption spectra values of \( m \) will be \( \leq 1 \) — in the case above \( m \) is 0.25, and in this range the curves differ by less than 10\%. Hence we calculate the curve for \( D \) sufficiently small so that the approximation (2) is valid and all the curves will be within \( \pm 10\% \) of this. This is reasonable since a density measurement will be regarded as significant only to 0.01 and if \( D_0 = 1, \frac{1}{20} \cdot \frac{1}{4} D_0 = 0.005 \) in the worst case.

Since we have shown for a Cauchy curve that it is legitimate to use \( 10^D = 1-2.3D \) the integral (1) is linear in \( D_{\text{ideal}} \). Hence the superposition principle holds. That is we may find the effect on a multiple curve by evaluating the effect on the single curves and adding the result ... or vice versa. This also follows from our modification of Runge’s work, as the result is independent, to the first order, of the form of \( D_{\text{ideal}} \).

It also follows at our level of approximation that Brodersen’s result for emission lines hold. \( L^2 = I^2 + s^2 \).
L, l observed, ideal half-width. This is an extremely valuable guide, as is the fact that for m:l the ideal and observed curves cross at x = ± 1.

The functions \( w(t), \frac{1}{2} \frac{d}{dt} \left( t + w(t) - w(t) \right) \) have been tabulated for various values of \( t \) in the Appendix, and the correction \( e \) such that \( D \) = \((1 + e)D\), for the maximum value, is graphed in Figure (16) against \( h \), where

\[
h = \text{slit range/observed \( \frac{1}{2} \)-width.}
\]

Note from

\[
\left[ \frac{1}{8} \right]^2 = \left[ \frac{2}{3} \right]^2 + 1
\]

\[
h = (1 + b)^2
\]

where \( b = \frac{6}{1} = \frac{6}{2.35} = \frac{m}{2.35} \)

To use (3) in practice would be impossibly tedious, and would not be justified by the small correction necessary. The following provides a practical solution. The method is a modification of that due to Runge and Paschen (1897). Let the optical density at the spectral position \( v \) — usually frequency or ev — be \( D = D(v) \). Consider a source with a slowly varying intensity distribution — e.g. an H-arc — such that over the \( v \)-ranges considered below its distribution may be taken as a constant, unity. Hence the intensity distribution after the absorber is \( f(v) = \exp (-D) \). This is a very minor approximation for the intensity distribution of the H-arc below 4000Å is very nearly linear and the form of \( f(v) \) is not required in the following analysis.

Consider equal slit ranges, \( a \), q.v., centred on \( x \). At \( x + v \) the image of the entrance slit has intensity \( f(x + v) \) of which the fraction \( \frac{a-v}{a} \) is collected at the exit.
slit. Note that this implies a triangular slit function, area \( a^2 \), base \( 2a \), in agreement with Brodersen (1953). See Figure (13).

For all pts \( v \) lying on one side of \( x \), the collected energy is

\[
\int_0^a \frac{a-v}{a} f(x+v) \, dv
\]

For all pts \( v \) lying on the other side of \( x \), the collected energy is

\[
\int_0^a \frac{a-v}{a} f(x-v) \, dv
\]

\[ \therefore \text{Total energy } F(x) = \int_0^a \frac{a-v}{a} (f(x+v) + f(x-v)) \, dv \] \hspace{1cm} (5)

Note the similarity between this and (1).

The total energy collected from the comparison beam is \( a \).

(5) may be solved for \( f(x) \) by expanding as a Taylor difference series in \( v \), performing the integration, and inverting by Newton's method, giving

\[ \Delta f(x) = F(x) - \frac{1}{6} F_1(x) + \ldots \]

where

\[ F_1 = \left( F(x+a) + F(x-a) \right) - F(x) \] \hspace{1cm} (6)

\[ \therefore \frac{F}{a} = f + \frac{1}{6a} F_1 \text{ to the first order} \] \hspace{1cm} (7)

The observed density \( D_{\text{obs}} \) is obtained by comparing the signal through the absorber to that in the comparison beam.

\[ D_{\text{obs}} = -\log_{10} \frac{F}{10a} \text{ by (4)} \] \hspace{1cm} (8)

\[ = D_1 -\log_{10} \left( 1 + \frac{F_1}{6a} \right) \text{ using (4), (7)} \]

\[ \therefore D_1 = D_{\text{obs}} + \frac{\log_{10} e}{6} \cdot \frac{1}{1} \cdot \frac{F_1}{1} \] \hspace{1cm} (9)
Now \( 10^{D_{\text{obs}}} \frac{F_1}{a} = i \left( \exp_{10} \left( D_{\text{obs}}(x) - D_{\text{obs}}(x+a) \right) \right) \)
\( + \exp_{10} \left( D_{\text{obs}}(x) - D_{\text{obs}}(x-a) \right) \) - 1

But for a small, \( D(x) - D(x + a) \) is small, expanding

\[ 10^{D_{\text{obs}}} \frac{F_1}{a} = \log_{10} \left( D_{\text{obs}}(x) - \frac{1}{2} (D(x+a)+D(x-a)) \right) \]
\[ = \log_{10} \cdot D \text{ say, which we will call the sagitta.} \]

Substituting for \( \frac{F_1}{a} \) in (9) and noting \( f \equiv \frac{F_1}{a} = 10^{-D_{\text{obs}}} \), as in Newton's method.

\[ D_{\text{ideal}} = D_{\text{obs}} + \frac{\log_{10} e}{6} \cdot 10^{D_{\text{obs}}} \cdot 10^{-D_{\text{obs}}} \cdot \log_{10} \cdot D \]
\[ = D_{\text{obs}} + \frac{1}{6} D \]

In Figure (14) \( D_1 = AB \)

In Figure (15) we show the undercorrection as a % of

\( D_{\text{ideal}}, \) when using the sagitta correction; as derived

from numerical calculations of the required correction for

the maximum point, at which the correction is largest, using

the previous results for a Gauss curve. Notice:

1) The result is independent of the meaning of \( x \) and the

form of \( D. \)

2) The method undercorrects, as is to be expected since

we have made only a first order approximation.

3) Below 0.25 the error is negligible.

4) With a density significance level of 0.01 the corrected

curve will not differ significantly from the ideal for

\( h \leq \frac{1}{2}. \)

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curve will not differ significantly from the ideal for

\( h \leq \frac{1}{2}. \)
FIG. 13 Runge triangular slit approximation.

FIG. 14 Sagitta correction for an absorption curve in terms of density.
FIG. 15

Effect of a finite slit on the maximum of an absorption peak.
\[ e = \% \text{ correction to } D_{\text{obs}} \]

**FIG. 16**

Slit width corrections.

\[ h = \frac{\text{slit range}}{\text{obs } \frac{1}{2}-\text{width}} \]
(3.5) SCATTERED LIGHT.

It was decided to use a thin microscope cover glass as a standard absorber for testing sensitivity of the absorptiometer and comparing the Hg6 and the Hg-arc; because of its convenience and suitable d-range from 2500-3500 A. Using the Hg-arc source, low d-readings were obtained below 2700 A. The glass was tested on the Chemistry Department's Uvispek, a photoelectric instrument. Comparing results:

<table>
<thead>
<tr>
<th>100A's</th>
<th>35</th>
<th>32</th>
<th>30</th>
<th>29</th>
<th>28</th>
<th>27</th>
<th>26</th>
<th>25</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uvispek</td>
<td>03</td>
<td>04</td>
<td>24</td>
<td>47</td>
<td>84</td>
<td>1.4</td>
<td>2.0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Spekker</td>
<td>03</td>
<td>04</td>
<td>25</td>
<td>47</td>
<td>85</td>
<td>1.4</td>
<td>60</td>
<td>1.3</td>
<td>12</td>
</tr>
</tbody>
</table>

This indicates considerable "stray light" in the region less than 2700 A.

The following steps were taken in the hope of removing the trouble.

1) The chopper disc and the internal walls of the monochromator, collimator tube, and PM housings were painted with a matt black paint having a reflection coefficient of about 2% as determined using a Weston exposure meter.

2) Numerous diaphragms of matt black card were placed in the collimator tubes, along the axes of the spherical mirrors and shields placed across the faces of the prism and mirrors so that only a very narrow beam passing along the collimator axis could pass out of the exit slit.

3) A small piece of surface silvered mirror was set at
various positions within the monochromator, in particular near the slits with the hope of making the effect worse.  
4) Runs were made in the dark, with the fluorescent lights on and the cover removed, and at various slit widths. None of these gave a detectable change of the above result, indicating that the effect was not due to the walls, mirror or reflections at the faces of the prism, or the surroundings.  
5) Measurements were made with a galvanometer directly connected to the PM. The results were the same. Hence the effect is not caused by the detecting system.  
6) A piece of black UV glass transmitting radiation below 4000 A only, was placed directly in front of the Hg-arc. The result was unchanged. However, with the HPG source the stray light effect disappeared and the Uvispek results were reproduced. In the region 3000 - 4000 A the incident radiation passes freely through both the glass and the UV glass and in this region the Hg-arc output is very high. Hence the effect is associated with the prism and the high Hg output from 3000 - 4000 A. Further, the only conceivable untested effect is multiple reflections or scatter within the prism.

Assuming that this scattering process is not selective, all wavelengths will be scattered to a certain extent, and the PM current therefrom should be fairly independent of prism setting. A thick glass slab, of similar material to the microscope slide and 100 times thicker, was used as a
standard absorber. This passes 3000 - 4000 Å radiation fairly freely, but in the region in question has a density greater than 200. Hence the measured density is a direct measure of the scattered radiation. Let \(i_0\) be the intensity of the standard beam. \(i\) ................. after the absorber. \(i_s\) ............... of the scattered beam. The signal after the absorber, \(i + i_s = i_0 10^{-D} + i_s\) The comparison signal is \((i_0 + i_s) 10^{-d}\) where \(D, d\) is the true, measured density. \(\therefore (i_0 + i_s) 10^{-d} = i_0 10^{-D} + i_s \tag{1}\) In this case \(D > 200,\) hence neglect \(10^{-D}\). Now \(i_0 + i_s = r\) say, is the quantity measured in a determination of the PM output for a given source against wavelength. \(\therefore i_s = r 10^{-d}\) The results are shown in Figure (11) and indicate that the assumption is reasonable. Associating \(i_s\) with the 3000-4000Å region the ratio of the intensities is of the order \(10^{-3}\). At this stage a Bellingham and Stanley UV monochromator with Littrow mounting became available. This allowed an analysis of the radiation leaving the exit slit - Figure (17). The Hilger instrument was set on 2350, 2483 Å and the exit radiation analysed by the BS instrument using the coherent
detector to measure intensity. The slit range at 3000A was 50, 100A respectively for the double monochromator. Note:

1) the peaks and hollows may be indentified in a rough way with those in the Hg-arc at 2700, 3100-3200, 3400, 3600, 3800, 4350A.

2) stray 2483 / signal 2483 order 10^{-4}

" 3100 / "  " " 10^{-5} which is of the right order to give a total stray level of 10^{-3}.

3) Though the peaks of the curve may be indentified with similar peaks in the Hg-arc spectrum they are much broadened the indicating that stray light mechanism is a scattering process.

Though the assumptions have been verified; what is the scattering mechanism which operated within the prism? Einhorn and Cohen (1953) discuss the stray light caused by a triple internal reflection in a polished 60° prism and conclude that all such stray light is refracted into a single line which appears at the position of minimum deviation. Though the prism in the Hilger instrument has a ground base, a similar mechanism could occur with scattering at the ground face. The prism was removed from the instrument and set up in the path of a parallel beam from the Hg-arc, with dimensions duplicating those in the monochromator. Using the PM and a galvonometer as detector, the reflection coefficient of quartz was found to be approximately 5%, and 2% of the energy incident on the ground base was scattered into the collecting mirror of the PM. The experimental arrangement for the ground base measurement is shown in Figure (18).
The ratio of PM current with the collecting mirror at A, B was 2%. Thus with 2 quartz reflections and the scatter at the base, the stray signal should be of the order of $5 \times 10^{-2}$.

$5 \times 10^{-2} \times 2 \times 10^{-2} = 5 \times 10^{-5}$ which is in reasonable agreement with previous results.

Further, since the degree of polarization for an internal reflection, at incidence angle of $30^\circ$, in quartz is found to be 0.91 using Morgan's (1953) result; with two such reflections and being scattered by the ground face, the stray signal should be almost completely polarized; as was found to be the case. A thick piece of polaroid glass mounted on a goniometer tube was placed in the path of a beam from the Hg-source, and PM current measured against angle of rotation with the monochromator set at 2300A. Polarization effects in the PM may be neglected since Clancy (1952) has shown that there is only a 1.7% effect, independent of wavelength, for an IP28.

To summarize:

1) Use of a ground base prism produces stray light at a level of $10^{-3}$.

2) The Hg-arc is an extremely unsuitable source if work is done from 2000-3000A because the great intensity variation from 2000-5000A enhances the stray light effect in regions of low intensity, and below 2700A - except near the 2483 peak - the stray signal is of the same order as the real signal, producing completely erroneous results.
Similar techniques as described above were used to determine the ratio of stray radiation to signal for the HF6, and is expressed in parts /1000 in the table.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>2400</th>
<th>2250</th>
<th>2300</th>
<th>2200</th>
<th>2150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio x</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 3.

These results are what would be expected from the work on the Mg-arc and though small, indicate a small correction. Using equation (1) with \( D \) the true density, \( i_b = x_i_o \times i_o \)

\[
D = d - \log (1 - x \cdot 10^d)
\]

\[
= d + x \cdot 10^d \quad \text{for} \quad d < 2, \quad x = 10^{-3}
\]

For \( x = 1 \) the correction is tabulated below.

<table>
<thead>
<tr>
<th>( d )</th>
<th>0</th>
<th>.5</th>
<th>.7</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>correction</td>
<td>.001</td>
<td>.003</td>
<td>.005</td>
<td>.01</td>
</tr>
</tbody>
</table>

No correction is used above 2400A or at densities below 0.3; otherwise the correction is applied as the \( d \)-scale is read.

All this, as far as the present work is concerned, is to derive the last two tables, and indicate the use of the HF6, since it has the advantages of:

1) Superior intensity stability.
2) Superior output below 2350A.
3) Almost negligible stray light effect.
4) Effectively a point source and does not suffer from wandering of the arc, which is the main disadvantage of the Mg-arc in its region of usefulness.
5) A linear continuous output below 4000A, permitting use at all wavelengths, and not continual adjustment of the slits.
6) Ease on the eyes of the operator.
FIG. 17
Analysis of stray light.
Output expressed for a 0.1 mm slit.

-LOG current

- Range

Set on 2483A
Set on 2350A

Range

WAVELENGTH

2000 3000 4000A
FIG. 18
Monochromator optical path, showing the stray light mechanism.

FIG. 18
Ground base scatter coefficient determination.

Mirror A, PM and slit on a common bench.
CHAPTER IV.

THE SPECTROPHOTOMETER AND
COHERENT DETECTOR.

(4.1) THE PHOTOMETER.

In the usual case of manual recording three readings are taken, sample in the optical path, standard in the path, and one with the radiation cut off. For the solids involved in this work it is more convenient to use air as an intermediate standard.

Octjen and Roess (1951), in considering the ideal design of a Photometer unit for IR spectrographs, conclude that the instrument should have a double beam photometer unit, in which the optical paths from the radiation source to the entrance slit of the spectroscope are symmetrical, a dispersing unit which employs a single optical path, and a single detector which by an appropriate mechanism operates an intensity control in one of the photometer paths. The Spekker bar, Hilger Monochromator and IP28 PM used by the previous workers satisfy these requirements.

(4.2) THE PHOTOMULTIPLIER.

The heart of the detector is the RCA type TP28 PM, housed in a Corning 9741 high silica glass, with a sensitive region, 2mm wide and 10 mm long, with a maximum sensitivity of 23000amps/watt with 100 volts per stage, at a gain of 10^6. Engstrom (1947) has shown that the output is linear over the range 10^-12 to 10^-3amp, and has been verified for the tube used in this work. Dark current and noise limit the ultimate sensitivity.

Studies of dark current have been made by Engstrom and Marrinan (1953). Dark current is usually 10^-8 to 10^-9amp,
though in our tube it has values as high as $10^{-7}$ amp, of which a fraction 0.2 to 0.7 is due to ohmic leakage. Marrinan's conclusion that over short intervals variations of up to 50% in dark current can be expected was verified. As shown by Taylor (1949) the DC and its variations can be reduced by keeping the envelope at cathode potential by means of a graphitic coating such as Aquadag, though this has not been investigated. Hence Johnson D (40) in quoting the sensitivity of his measurements at $2.10^{-10}$ amp, which corresponds to a 1mm reflection at 2.5m on his instrument, does not give a realistic estimate. It is low by at least a factor of 10.

Engstrom shows that the rms noise current $V$ is predominantly due to shot effect at the first cathode, and given by $V^2 = 2eU_0^2B$; $U$, PM gain; $B$, Band width of detector; $i$, total anode current. Neglected in this equation is the shot effect at the secondary dynodes - an effect which increases the noise by about 20%.

This is markedly different for a phototube in which the limiting factor is Johnson noise in the load resistance. The RCA tube manual quotes a UV equivalent noise input of $6.10^{-15}$ watt at unit signal to noise ratio and unit band width. This corresponds to a current of $10^{-10}$ amp. For a band width of 0.03 cps this would imply an AC method an increase of sensitivity over the Johnson DC method of more than 100, and assuming a quantum efficiency of $10^5$ at the first cathode.
gives a detection limit of about $10^3$ quanta per second. It would appear that the detector to be described approaches this limit. A very full discussion of Photomultipliers is given by Rodda.

(4.3) THE DETECTING SYSTEM.

Before a satisfactory detector can be realized the entire measuring technique must satisfy a number of requirements.

1) The surface characteristics of the crystals change with time due to their mildly hygroscopic nature. Hence the need for measurements to be performed in the shortest possible time consistent with the required accuracy.

2) Again this requires a design with few adjustments for a reading. Such a design is desirable in a point by point technique as opposed to a scanning technique to ensure that in changing the independent variable the output meter should indicate in a clear fashion the approximate change in the dependent variable.

3) Also the fatigue, dark current, drift and noise effects of the PM should be minimized.

To measure accurately the equality of the two beams, any deflection method involves a loss of sensitivity at deflections greater than the scale length, since to accommodate the deflection on the scale the sensitivity must be lowered. Therefore a back balancing, or a null method is required. The operation of changing beams could be avoided by using a slowly turning chopper disc of frequency of the order $1/t$ where $t$ is the time constant of the galvonometer.
Further the rapid random variations in output could be removed by means of an RC integrating circuit. A typical arrangement would be as shown in Figure 19.

It is found by experiment that a convenient compromise between speed of response and noise is an anode resistance of 100K, R = 5K, C = 2000mfd, the largest available. For a signal of $10^{-8}$ amp the galvanometer current will be $10^{-6}$ amp, corresponding to a 50cm deflection using the Johnson galvanometer set up. This would allow transmission measurements to be made to 1% if it were not for DC, and its irregular variation. Direct use of a galvanometer was slow and one was never completely sure that equality had been reached due to the slow but irregular drifts. This is accentuated by any attempt at DC amplification, such as a PE galvanometer, since the dark current rises in proportion.

The input blocking condenser of an AC amplifier removes the dark current and if the frequency is chosen above a few cps the slow irregular changes of dark current will be avoided. However, the problem of noise remains. This may be dealt with by choosing a narrow band width, $B$, since noise voltage varies as $B^5$. Convenient frequencies would be about 30cps, in the range of commercial motors.

Band width may be reduced in two ways:

1) a sharp cut off band pass amplifier. An example is Etzel's (1953) Spectrophotometer using feedback through a twin – T network (Scott 1938). This method is expensive as
it requires a motor of extremely constant frequency. Miller (1949) solves this problem in his Raman Spectrophotometer by operating synchronous with the mains.

2) A phase sensitive detector is a simpler and more economical system. Among phase sensitive detectors are two distinct types - mechanical (Gunn 1938, Sear 1940, Liston 1946, Kron 1952) and electrical (Schafer 1954). The bandwidth of such a system is set by the indicating device. The great advantage of a coherent phase detector is that for a null method components are not critical, for its operation is independent of variations of lamp intensity, amplifier linearity and gain, angular velocity of the chopper motor, and power supply voltages. The method is cheap and extremely reliable.

(4.4) THE MECHANICAL COHERENT DETECTOR.

Because of its apparent simplicity the mechanical method was tried first, being similar in principle to the Department's Microdensitometer (Tait and Chalkein 1952). There is in principle little change from the previously mentioned DC detector except that the method is a null one and the ease of AC amplification allows the use of a robust galvanometer. (Figure 20).

If the two beams in the photometer are of unequal intensity the PM sees the signal as a square wave modulated at the chopper frequency of 40 cps and of height proportional to the intensity difference. The chopper was designed to be of such size that the square wave rise time was less than 0.01
cycle. The commutator, being rigidly attached to the chopper motor shaft, is synchronous with the amplified AC signal applied to its brushes. Hence a rectified, DC signal results.

The grid current and stability of the preamplifier places a lower limit upon the currents measurable. Nielson (1947) points out that several commercial valves, operated under reduced potentials, can equal the performance of specially designed electrometer valves. Crawford (1948) and Gilespie (1953) find that the Philips' tube EF37 has excellent electrometer and noise characteristics. Specially selected EF37's are available labelled MP 1400. The recommended operating conditions are:

\[ V_f = 4.5 \; V, \; V_g2 = 45 \; V, \; V_g1 = -2 \quad \text{when} \]

\[ I_s = 80 \mu A; \; V_g1 < 10^{-11} \text{amp}; \quad g_m = 240 \mu A/V \]

The design of the amplifier is standard and is in Figure (22). Considerable care was taken to ensure adequate shielding of the preamplifier. Self bias is used since the grid is effectively earthed, and hence earthing the shield provides a guard.

PERFORMANCE. Though the commutator (DPDT) was carefully designed and fabricated it was erratic and difficult to keep in order due to the difficulty of obtaining good brushes - shim brass made the best brush material.

(4.5) THE ELECTRONIC COHERENT DETECTOR SYSTEM.

A ring type modulator (Waveforms p210) using EB34's was substituted and performed well. To provide switching signals for the ring a scale of two (Waveforms p604) was built and
triggered by a magnetic pickup coil system near the disc.
Two steel nails were attached to the disc so as to give two
symmetrically spaced pulses every revolution. These
triggered the scale of two giving a square wave whose funda-
mental frequency was the same as the disc speed. The EBJ4's
were later replaced by crystal diodes, type 6612B and the
output coupling was changed to transformer coupling to provide
a better impedance match between the output stage and the ring.
These modifications increased the sensitivity considerably.

The system performance was still poor at short wavelengths
due to a very poor signal to noise ratio, so a filter was
designed and built to go at the input to the amplifier.
Noise which had no component at the filter frequency would
not pass on to the amplifier, and secondly a large 100cps
component from the lamp would not overload the amplifier. A
distinct possibility of this existed as with the null method
of detection used there would be no signal frequency in the
amplifier at balance but large amplitude 100cps, pulses would
still occur. The filter was not fully successful for
several reasons.

1) When the $\phi$ of the filter was sufficiently high to give
useful noise reduction it became impossible to keep the motor
speed accurately adjusted to the filter frequency. The
filter design values were, Centre frequency 40cps and
bandwidth 5cps, giving a $Q$ of 8. This meant that $2\frac{1}{3}$ cps
off resonance the output was 0.707 of its resonance value,
and because of the coherent detector this had to be multiplied
by \( \cos \phi \) where \( \phi \) is the phase shift of the filter. At 2\,\text{cps}
off resonance \( \phi = 45^\circ \) and \( \cos \phi = 0.7 \) giving a final output
of 0.5 of the resonance value.

2) A noise impulse with a 40\,\text{cps} component would pass through the filter, producing a wave train at the output. The
detector would see this as a coherent signal lasting perhaps for up to two seconds. These wave trains had random phase
relationship to each other, some causing the meter to deflect to the left and others causing it to deflect to the right.
Each deflection lasted for approximately two seconds making it impossible to detect the null position. This effect
always occurs when the predetector bandwidth is smaller than the post detector bandwidth. The post detector bandwidth
could be made small by using a long period meter, so the filter was abandoned and the lamp run on DC to remove the
100\,\text{cps} pulses. Several galvanometers were tried but a sufficiently long period could not be obtained. A meter was
made centre zero, and filled with a mixture of glycerine and alcohol to damp the movement to a suitable value. Glycerine
gave a time constant of 45 seconds by itself. The value chosen (about 5 second) was a compromise between speed of
operation and performance with weak signals in noise. By sacrificing speed of response such small signals could be
used but the lag between shifting the density drum and obtaining a meter deflection was not convenient. Using a Tinsley Box
Type galvanometer of high sensitivity, 100\,\text{mm/\mu A} allowed an
RC integrator to be used. This has a time constant \( P \) of \( \frac{1}{2}RC \),
and with \( RC = 12 \) performed extremely well. Bandwidth,
B = \frac{1}{2\pi T} = 0.03 \text{ cps}. \quad \text{Thus the system finally used is}
\text{exactly the same in principle as the IR Recording Spectrophotometer of Liston and White (1950).}

To make intensity measurements it was thought desirable to use the null coherent system. A constant amplitude square wave generator was designed to be triggered off by the scale of two, with an 85A1 as the source of the reference voltage, through a 6H6 as catching diode. The system may be regarded as an AC potentiometer, generating a signal 180° out of phase with the light signal. Thus the comparison beam used for absorption work is replaced by an electrical signal. It functions very satisfactorily, a change of 1ohm in the output control producing a substantial meter deflection. This corresponds to a current sensitivity of the order of 10^{-11} \text{amp.}

It is especially convenient to have one detector for both intensity and absorption measurements since to convert from absorption to intensity measurements requires nothing more than placing the emitter in front of the chopper on the axis of the instrument.

(4.6) THE SIGNAL TO NOISE RATIO.

Following a similar derivation for Johnson noise in IR spectroscopes by Brodersen (1953) we derive an expression for the performance of a spectrophotometer limited by shot noise.

The rms noise voltage at the output of the AC amplifier is

\[ e^2 = 2eM^2i_0B^2s^2T \]

where M is the PM gain, \( i_0 \) total PM current = \( i_0s^2T \), \( s \) slit
width, \( T \) transmission of the sample, \( R \) anode load, \( B \) detector band width, and \( G \) is the amplifier gain.

At half power, \( B = \frac{1}{2\pi P} \) where \( P \) is period of output filter.

\[
\therefore E_n = (\frac{G}{2\pi P})^{\frac{1}{2}} \cdot MRCST^{\frac{1}{2}}
\]

Introduce \( q \) a characteristic of the detector and amplifier defined as rms noise at \( P = 1, T = 1 \) and maximum gain.

\[
\therefore E_n = q \cdot \frac{P}{2} \cdot (\frac{G}{2\pi})^{\frac{1}{2}}
\]

With this we compare the signal

\[
E_S = MRC i_0^4 e^{2T} \text{ where } i_0^4 \text{ is the signal current.}
\]

Introduce \( s_0 \) a characteristic of the apparatus, the slit width necessary to obtain unit signal output, without the sample, at maximum gain.

\[
E_S = (\frac{s}{s_0})^2 \cdot (\frac{G}{2\pi})^{\frac{1}{2}}
\]

\[
\therefore \frac{E_S}{E_n} = \frac{1}{q s_0^2} \cdot s^3 \cdot P \cdot T \text{ which differs in the factor } s^3 \text{ from the result for Johnson noise, where the factor is } s^2.
\]

Instead of characterizing the experimental conditions by the signal to noise ratio it is more advantageous to speak of the random errors caused by noise in the determination of optical density \( D \).

\[
D = \log I_0 - \log I
\]

:. relative error

\[
\frac{\Delta D}{D} = 0.433 \left( \frac{\Delta I_0}{I_0} \right)^2 + \left( \frac{\Delta I}{I} \right)^2
\]

associating \( \frac{\Delta I}{I} \) with \( E_n \) and noting \( T = 10^{-D} \)

\[
\frac{\Delta D}{D} = 0.433 s_0^2 \cdot \frac{(1 \cdot 10^D)^{\frac{1}{2}}}{s^3 P^{\frac{1}{2}}}
\]
The influence factor is shown in Figure (23) and indicates an optimum range of 0.2 to 2.0. It would appear that this analysis is more realistic than treatments such as that of Cole (1951) who avoids a detailed study of the measuring technique. Note further that since resolution is proportional to \( s \) and the relative error to \( s^{-3} \) there is considerable advantage in wide slits at low light levels. Since \( P \) occurs as \( P^2 \) no great advantage is gained by changing \( P \) from its optimum value.

(4.7) COMPARISON WITH OTHER INSTRUMENTS.

Considerable study has been made of a means of testing the photometric scales of spectrophotometers. For work in the UV, solutions in cells with quartz end plates prove superior to solid filters. In particular, Haupt (1952) advocates an aqueous solution of potassium chromate

\[ K_2CrO_4, 0.04 \text{ gm/l in 0.05 N KOH}. \]

This has been used by Brüde, Gould, Whitney and Wyman (1953) to compare the Cary and Beckmann instruments. For the Beckmann DU instrument, which should produce reasonably similar results to our instrument, they find in the region 2200-3500Å a standard deviation of the data of 0.05 in terms of density. Using such a solution against distilled water in matched 1cm quartz cells gave agreement with the published data, providing density was measured to two decimal places only. This still left minor discrepancies in the second place, which is to be expected if the Beckmann instrument gave a standard deviation of 0.05.
Though densities on our instrument can be reproduced over short intervals to 0.002, we will regard densities as significant to two decimals only.

Various details of the Spectrophotometer may be seen in Figures (24) to (26).
FIG. 19 A direct current null detector.

FIG. 20 Alternating current coherent detector using a commutator.
FIG. 21 Block diagram of the operation of the coherent detection system.
FIG. 22 Phase sensitive coherent detector and square wave generator.

Values generally in kilo-ohms and mfd's.
A = transformer phase correction.
RC = Integrator. 2000 mfd; 60, 25, 10, 5, 2 K.
FIG. 23 Shot noise influence factor S, for a Spectrophotometer with a detector limited by Shot noise.

\[ S = \frac{(1 + 10^D)^{\frac{1}{2}}}{D} \]
FIG. 24 A view of the SPECTROPHOTOMETER taken during the measurement of $\frac{1}{2}$-width against temperature. On the right is the HF6 source with its screw driven support; the chopper and pickup mounted on the Spekker bar, as is the hot cell. In the left foreground is the detector, behind which is the variac and transformer hot cell power supply, and the temperature measuring meter and its series resistance box. The backing pump, cooling and power leads are in the background.
FIG. 25  The COMMUTATOR, chopper and pickup. The pickup has been displaced low to the left for clarity. Note the alnico magnet and the balancing strip on the chopper.
FIG. 26 A rear view of the DETECTOR system. A front view may be seen in Fig. 24. From the left are the two electronic switch valves, the main amplifier with the lid removed from the ME 1400 preamplifier box, and the square wave generator, below which is the integrator. In the foreground is the PM housing and the preamplifier lid, showing the steatite switch and the perspex grid lead insulation.
CHAPTER V.

ACCESSORY EQUIPMENT.

The hot cell. Measurement of half-width against temperature. Size limits set by Spekker bar.
(5.1) THE HOT CELL.

To extend the results of Johnson D. (see his Figure 18) on the absorption curve half-width against temperature a hot cell has been constructed, to fit on the Spekker Bar and maintain the crystal at temperatures up to greater than 400°C. Details of the design are shown in Figures 27-29.

Two factors provided strict limits in the design. The size is limited by the dimensions of the Spekker bar, since the beams are only 3.5 and 7cm from the base of the bar, and for convenience in construction the cell should be cylindrical. The dimensions chosen are as large as possible. Secondly, the cell is close to both the operator and delicate optical parts. Its outer surface should therefore be cool. This implies low heat loss unless very fast cooling is provided. Further, dry air is essential if rapid surface deterioration of the crystal surfaces is to be avoided. A $\text{P}_2\text{O}_5$ tube would ensure this but the vacuum provided by a backing pump is more convenient. This has the advantages of preventing any possible surface effect of dry air and of removing the convection heat loss.

All exposed internal surfaces have been plated with Nickel, followed by Chromium, and polished, reducing radiation loss. Conduction loss has been minimized by making the main conduction path - the block supports - of two $\frac{1}{2}$" long $\frac{1}{4}$" diameter mild steel rods. Electrical connection is through glass to metal seals; joints are welded with easyflo - except the supports and the glass to metal seals, which are hard soldered for convenience in assembly; and seatings are
provided with O-rings. Power is from a Variac in the primary of a 12.5 volt transformer feeding the single layer, 7ohm, which 22 gauge Nichrome winding is insulated from the block with mica and held in place with Foradix porcelain cement. A radiation shield fits about the block. Temperatures were measured with a chromel - alumel thermocouple and a 0-10 microamp meter. A temperature of 500° C was maintained by the 12.5 volt input, and taking 5 minutes to reach half maximum temperature.

Temperature control which could have been provided by the controller, previously described, was unnecessary. The heat loss is small and observations sufficiently rapid to allow a sweep of the spectrum before the temperature had fallen by 3° C at the highest temperature, after the cell has been elevated to temperature and the power switched off.

The design has one defect. Replacing the block after putting in a crystal is tricky due to the limited space within the cell. This can be easily rectified. Weld a common tube into the central holes of the block and the removeable face on which two further glass to metal seals should be placed for the thermocouple leads. A spiral of copper tubing on the face would provide cooling.

In use the cell is placed in the upper beam of the instrument and two quartz plates placed in the lower beam to compensate for the transmission losses of the two cell windows. Six such windows were available and from these two matched pairs were chosen. Fortunately the windows were
sufficiently uniform to allow choice of pairs so that there was no detectable difference in their transmissions over the full range of the instrument. At the conclusion of the run a small metallic deposit was found on the cooler parts of the cell windows, the central parts being unaffected.

(5.2) THE DARK CELL.

To make an investigation of the fluorescence reported by Johnson D (78, Br⁻ in KCl) and a preliminary search for photoconductivity a dark cell has been constructed. This is an enclosure to hold the crystal sample, and is painted internally with matt black paint. It has been constructed to fit the exit slit of the Bellingham and Stanley UV monochromator, but may readily be mounted on an optical bench. The cover is provided, perpendicular to the incident radiation, with a side arm containing baffles so that the central portion only, of the sample may be viewed, thus avoiding the radiation scattered from the sides of the sample. Two ceramic ports are set in the cap to conduct wires out of the cell. The type Hg Mercury arc source is focused by a mirror on the monochromator slit, this unit being totally enclosed within a light tight box, with a small exit aperture butting against the entrance slit. Cell details and the optical arrangement are shown in Figure (30). Behind the chopper the system is light tight and all possible extraneous effects on the sample are removed. Runs, however, were made in total darkness.
FIG. 27
THE HOT CELL, Central Section.
Full size.
FIG. 28  THE HOT CELL DISMANTLED.  From the left is the front face and power leads, the block and crystal holder, radiation shield and the thermocouple plate.  Notice the glass to metal seals, the thermocouple glass shield and the water cooling.  In particular, notice on the block the power lead studs, and the end grooves to allow mounting on the semi-circular cradles — a portion of one of these can be seen through the rear hole in the furnace.
FIG. 29  THE HOT CELL ASSEMBLED. Within the cell the block can be seen, sitting on the front cradle. Notice the lack of space and the method of electrical connection. This photograph should be compared to Figure 28. Both photographs were taken after the temperature run.
(5.3) FLUORESCENCE. The arrangement was capable of quantitative measurements on one sample only, that of Br⁻ in RbCl for several reasons.

1) The bulk of the absorption occurs below 3000 Å and from 3000 Å down the effective source intensity drops by a factor of 10^5 (Fig. 11). Unfortunately a low pressure Mercury resonance lamp was not available.

2) The monochromators available are slow, having f numbers of the order of 10.

3) The Littrow type instrument is notorious for its high level of stray light, and although the perpendicular arrangement and baffling mentioned above are very effective the internal scattering within the body of the crystal was sufficient to provide stray energy as high as twice the least detectable signal.

4) Because of the need to chop the emitted radiation the sample could not be mounted at the entrance slit of the analyser, a preferable arrangement, and the collection efficiency is reduced in using a lens to focus the emitted radiation on the entrance slit. The radiation could be chopped just prior to the PM, but time did not allow a trial of this. This point is very minor compared to (1) (2) and (3).

To gain emission intensity some information must be sacrificed. There are two possibilities.

1) Loss of analyser information by focusing the emitted radiation directly on to the PM and not through the analysing
monochromator. Wavelengths of radiation necessary to excite emission and integrated emitted intensity would be obtained. The only new information over absorption measurements is the integrated output; and since in most studies, other than those involving the evaluation of process efficiencies, interest centres on relative output against a suitable variable, such as wavelength, and such is the case here, the information is of little value. The method was not investigated.

2) Loss of exciting radiation information by replacing the exciting monochromator by a simple filter. The emission spectrum is obtained. A low pressure mercury arc emitting chiefly 2537A would have been ideal. A suitable filter for the Hg type lamp was obtained from the bulb of a 'dark-light' lamp. The glass of this bulb appears black to the eye and is an extremely efficient filter, passing 3000-4000A with little loss and being practically opaque outside this region except above 6000A. The 10cm diameter bulb filled with distilled water makes a lens of high power. Figure (31) gives a general view of the source and spherical lens as set up for conductivity measurements. In spite of all the precautions quantitative measurements were possible on only three samples. It would appear that unless the emitted intensity is about twice the threshold intensity of the eye quantitative measurements with the existing equipment are impossible.

(5.4) PHOTOCONDUCTIVITY. Electrical connection to the crystal was made with two sheets of thin Aluminium foil pressed on to the crystal faces with two brass plates, ground
flat and polished, this being sandwiched between sheets of mica insulation in the dark cell clamp. Ideally the crystal surfaces should have been sputtered with Aluminium. Crystal sections were 1mm thick and 1x1cm in area giving a capacity of approximately 2pf. Various D.C. and A.C. bridge circuits of poor sensitivity were tried until it was realized that since the aim of the experiment was to show zero photoconductivity or from a practical point of view show that the conduction current is less than the least detectable current, then sensitivity would be lost by the elaboration of a bridge. A simple series arrangement of an 1800 volt D.C. supply, galvanometer of sensitivity 2000 µA per microamp at 1 metre, protective resistance of 100 Megohms and the cell was used. At 3 metres the galvanometer was sufficiently stable with a war - assets projection system to allow deflection changes of 0.25 µm to be significant. This corresponds to a current of 40 micromicroamp or, a maximum detectable resistance of $5 \times 10^7$ Megohms. Wires were dangled in the air else small leakage currents arose and remained even when the cell was disconnected.

This simple experiment while being suggestive is barely within the range of typical photocurrents. A considerable increase in sensitivity was made possible through the courtesy of Mr G.K. Roth, Dominion X-ray Laboratory, in lending a Lindemann electrometer and portable projector, and a Victoreen, vacuum sealed, high resistance. The circuit is shown in
Figure (30). For safety the electrometer was operated at half maximum sensitivity. Calibrated against a known voltage derived from an accumulator the deflection, projected at a 100:1 magnification, was 50 mm per volt. The voltage drop across a resistance of $2.15 \times 10^5 \Omega$ — by the previous results negligible compared with that of the sample — in series with the cell and batteries of 10, 30 and 160 volt, was applied to the electrometer needle. Noise produced deviations of 1mm from the mean positions, allowing differences in average needle position of less than 0.5mm to be noticed. This corresponds to a detection limit of $2.10^{-14}$ amp. The environment was warm $(25^0\text{C})$ and dry.

Cleanliness must be observed in this work and in that on fluorescence. Work was performed in cleaned rubber gloves, tools were washed in X3A and alcohol and finally inspected by UV, using the source and spherical lens. All surfaces of the crystal samples were freshly cleaved.

The possibility of a space charge effect must not be overlooked, in spite of the fact that the build up of an opposing space charge is at variance with the model to be proposed. For a simple calculation take,

Charge = \( i t = CV = 2.10^{-12} \times 100 \), and \( i = 10^{-14} \text{ am} \). Hence the time for a space charge build up is of the order of half an hour, and such an effect would be insignificant.

(5.5) GAUSSIAN ANALYSIS.

Analysis of a spectrum into Gaussian components is a long and tedious job usually not justified by average experimental accuracies of a percent or so. The graphical projection
method used in this work is convenient, rapid and introduces inaccuracies of about 0.5%.

Six Gauss curves of heights 20, 10, 4cm and widths 6, 2.5cm were carefully drawn on the same axes and photographed at a reduction of 8 on to a 5cm square process plate. The positive was placed in an alt-azimuth mounting with the horizontal and vertical axes in line with the axes of rotation, on an optical bench. Illumination by an opal bulb, and an achromatic projection lens of 15cm focal length allowed operation with normal sizes of graph paper, 20 x 25 cm, on a table or bench.

Height variation is provided by varying the degree of enlargement or by a horizontal rotation of the mount, and width variation by a vertical rotation of mount or screen. Accuracy loss was checked by fitting the original drawing. The only other worker known to the writer who has used a similar idea is Sinden (1937), for a numerical solution of equations. As a technique it is of wide application and should be more generally known. The above figures are given as a guide to a system which has proved convenient.
Optical arrangement for photoconduction studies.

The dark cell

Circuit for the Lindemann Electrometer.
FIG. 31  THE DARK CELL, set up for photoconductivity measurements, with the cover removed. Notice the spherical lens and the position of the crystal sample.
PART II

EXPERIMENTAL RESULTS

and their

THEORETICAL DISCUSSION.
CHAPTER VI.
EXPERIMENTAL RESULTS.


Theoretical half width. Extension of original measurements from 100°K to 700°K for KCl:Br. Previous omission. Least squares fit. Photoconduction. Comparison with other cases. No photoconduction. Band model not applicable.

(6.1) BACKGROUND ABSORPTION.

For an absorber of length $l$, absorption coefficient $m$ having two faces of equal reflection coefficient $r$,

$$I = I_0 (1-r^2) 10^{-ml}$$

and

$$I = I_0 10^{-d}$$

by experiment.

Hence $d = m l + t$, where $t = -2 \log (1-r)$ \hspace{1cm} \ldots (1)

Measuring $d, l$ for two samples $1,2$, two simultaneous equations are obtained having solutions,

$$m = \frac{d_2 - d_1}{l_1 - l_2} \hspace{1cm} t = \frac{l_1 d_2 - l_2 d_1}{l_1 - l_2} \hspace{1cm} \ldots (2)$$

Any attempt to use (2) for pieces with $l_1$ of the same order as $l_2$ fails, since the surfaces are not sufficiently uniform. If, however, $l_1$ is greater than 10 $l_2$ consistent results are obtained and approximate values for $m,t$ derived; those shown in Figure (32) being for pure KCl. Notice that the shape of the absorption curve of the thin sample follows the shape of the surface loss, and that of the thick sample follows the shape of the absorption coefficient.

It is possible to cleave slices as thin as 0.5mm.

For $l_2$ small, by (2) \hspace{1cm} $d_2 = t$

and \hspace{1cm} $m = (d_1 + t) / l_1$ \hspace{1cm} \ldots (3)

Further by (1) \hspace{1cm} $t = d_2 - m l_2$ \hspace{1cm} \ldots (4)

For $l_2 = 0.05$cm; $m$, 0.3 to 0.6; $ml_2$ = 0.02 to 0.03, and a 20% error in $m$ is required to affect $t$ by 0.01. Hence for $m$ we may use the values determined, finding the correction to be 0.02, and 0.03 at and below 3000A. Four such thin slices were measured and the results shown in Figure (33).
FIG. 32
Background absorption.
A, B 0.051, 0.789 cm KCl samples.
C, D Absorption, reflection coeff.

Density

0.5
B

0.2
A

Wavelength
2000A
6000A

Density

0.5

0.4

0.3

2000A
6000A

FIG. 33
Variation of surface absorption.
KCl.

Density

1.0

0.5

2000A
5000A

FIG. 34
Absorption of 3 thick samples.
KCl.
In the main they are of the same form but displaced vertically by ± 30% about the mean. Herein lies the explanation of the remarks by Johnson F. (67). It is important to notice the more rapid rise of surface loss below 4000A compared to that of the absorption coefficient, and the high surface loss which it is reasonable to explain in terms of absorbed water vapour. To use such measurements and (3) to determine \( m \) are futile since even for a sample 1cm thick the uncertainty of 30% in \( t \) involves a ± 0.1 uncertainty in \( m \).

A further difficulty arises as illustrated in Figure (34), where the densities of samples from two different boules of pure KCl are shown. Curves b, c are for slices from the same boule. All samples were cut approximately 0.3cm thick and densities are expressed in terms of this thickness. The curves differ markedly at low wavelengths. This is in agreement with the results of Ballard, Combee and McCarthy (1951) who found wide variations among sample of air and vacuum grown LiF; variations of density at 2050A of as high as 0.7 being determined.

An identical series of determinations of \( m, t \) were made with Br⁻ in KCl and the results were similar. The form of \( t \) was the same as that for the pure crystal, the presence of the new absorption peaks having no detectable affect. The accuracy of this statement, considering the above figures, implies that the refractive index of the material - related by the classical equation to \( r \), after allowing for the lack of perfection in the crystal polish - does not change by 10%.
A result of little value.

We are thus faced with the problem of allowing for a rather uncertain background which in a plot of a density spectrum manifests itself in three ways.
1) A vertical displacement of surface loss.
2) Variations in curvature of the surface loss curve at low wavelengths.
3) Variations in solvent absorption at low wavelengths due to lack of homogeneity.

Factors (2) and (3) may be lumped together. This problem is discussed by Johnson F (67) and Johnson D (48) who, however, do not mention points (2) (3). They suggest vertical displacement of the absorption curve for the pure crystal until the long wavelength tails match. This allows for point (1) only, unless the samples used are uniform, as is the case for the three curves given by Johnson F. (His Figs. 22,23) where the absorption has been measured below 2300A. Further results given by Johnson D (His Figs. 15,19) a common characteristic is the sharp rise in density at wavelengths just below the primary absorption peaks. Here the effect of (2) and (3) is very strong.

To provide, however, an independent experimental check of the above argument and also to investigate the method of background correction subsequently to be suggested, a further detailed investigation of pure KCl and Br⁻ in KCl was performed below 2400A to 2130A, the limit of the instrument. A long time constant was used in the detector. Five samples of
each were measured, four of thickness approximately 1cm and another of 0.05cm. There was no significant difference of behaviour.

Further, the actual procedure used by Johnson in removing the background is a little doubtful (see his Figure 19). Presumably, lacking data on the absorption of pure RbCl, in removing the background, he has merely reduced each density by a constant. This gives no absorption above 2800A. But as will be pointed out later Br⁻ in RbCl fluoresces strongly to radiation above 3000A and up to 3400A.

Thus background removal, as it stands is extremely unsatisfactory. To fit a background controlled by two effects requires a fit at two different portions of the spectrum. By extending measurements on both sides of the absorption peaks such a fit is possible. It is sufficient to do this by eye and for samples of the order of 1cm in thickness is accurate to ± 2%. This is a difficult problem and this appears to be the only reasonable solution. It is of interest to note that in this way the absorption of both the pure and impure salt is obtained in one determination.

(6.2) VIBRATIONAL BROADENING.

For electronic transitions between sharp levels of an activator system, involving highly localized wave functions, and describable by a configurational co-ordinate, Williams (1951a) shows that a classical distribution of atomic configurations, characteristic of the initial state, yields
theoretical absorption and emission spectra in satisfactory agreement with experiment, above 80°C.

Schen (1948) was the first to appreciate that for a luminescent centre the quantum mechanical zero-point energy must be considered at low temperatures (Williams 1951b). The system is then a harmonic oscillator, assuming that the normal modes of motion involving significant potential energy changes are approximated by an Einstein distribution of frequency 2kt/h. A calculation of the spectra involves a sum over the matrix elements for all initial and final vibrational levels with a Boltzmann weighting factor for the initial levels. This calculation derives P(E), the probability that an electron performs a transition of energy E from the ground to the excited state. From the properties of the Slater sum involved in this, Williams and Hobb (1951) derive:

\[ e = c \left( \tanh \frac{C}{T} \right)^\frac{1}{2} \]  

(1)

where \( e \) is the absorption or emission half width, the zero-point energy \( \hbar k = \frac{\hbar}{2} \), and \( C \) is a constant.

For \( T \) large \( e = cT^\frac{1}{2} \), Mott's expression.

and \( T \) small \( e = cT^\frac{3}{2} \).

It is important to realize that the absorption coefficient is of the same form as \( P(E) \). For monochromatic radiation the intensity is proportional to photon flux. Hence, if the flux is \( I \) at the point \( x \) through a crystal, of uniform activator electron density \( N \) per unit volume, \( d\varphi \) is proportional to \( I, P(E)d\varphi dx \).
The original measurements of Johnson D (his Figure 18) have been extended from 100°K to 700°K with the hot cell. Lack of a coolant better than liquid air prevented measurements at lower temperatures. Liquid Helium would have been ideal. The system chosen was Br⁻ in KCl since, the 4.5 ev peak is strong, is well separated from the rapid absorption rise of pure KCl above 5.2 ev, does not overlap other strong peaks - the effect of the weak companion at 4.8 ev being easily subtracted, and in particular, a detailed study of its shape shows it to contain only one component, it is symmetrical and fits a Gauss curve except in the tail. Johnson D. performed his experiments with slits of 0.25mm but applied no correction for the resulting loss in resolution. It is due to this neglect that he did not discover the effect subsequently to be discussed. His original measurements have been reanalysed and slit width corrections applied. Procedure has been to graph the experimental figures as density against electron volts, using the conversion table given in the Appendix, fit a background by hand, plot density difference, fit Gauss curves by the graphical projection system, previously described, measure the half width and correct it with the formula \( I^2 = I_0^2 + \sigma^2 \) previously derived. The results are shown in Figure 35. Temperature error is negligible compared to the half-width error, the maximum possible value of which is indicated by the radius of the plotted circles. The standard error, may be taken as a third of the radius. The
square root of temperature has been plotted against the width relative to that at room temperature.

The full curve is the best least squares fit of an expression of the form (1), regarding the temperature error as negligible and giving each point equal weight. The first approximation was determined by choosing $C_1t$ so that the calculated curve passed through the mean centre of the lower two points and that of the upper six. Each parameter was varied in turn by small amounts until the rms deviation was minimized at 0.033 width units for $t = 91^\circ K$. Changing $t$ by $10^\circ K$ either side of this value produced an average increase in rms deviation of 0.0044 units. A rough estimate of the standard deviation of $t$ is given by using Weatherburn's (137) result that the s.d. of the $s.d. = s.d. / \sqrt{2\pi} = 0.0083$, which is twice that produced by a $10^\circ K$ change in $t$. Therefore, $t = (90 \pm 20 s.d.)^\circ K$, and the zero point energy $= kT$

$= 0.0083eV \pm 20s.d.$.

The above analysis of the standard deviation of $t$ is intended as a guide only.

Though the accuracy in $t$ is low, the clear manifestation of the zero-point energy is beyond question and emphasises the need for a quantum dynamical discussion of such low temperature phenomena.
FIG. 35
Br⁻ in KCl.

SQUARE ROOT OF TEMPERATURE (°K)

RELATIVE WIDTH OF ABSORPTION BAND
(6.3) PHOTOCONDUCTIVITY.

From conductivity studies of Br⁻ in RbCl any photoconductive current was shown to be less than $2 \times 10^{-14}$ amp, corresponding to a specific conductivity of $10^{-17}$ ohm/cm. Known conductivities of insulators vary from $10^{-12}$ to $10^{-18}$ ohm/cm. Using pressed powders of 0.2mm thickness under a 200 volt potential Randall and Wilkins (1949) obtained photocurrents from $10^{-10}$ to $10^{-12}$ amp for samples of many crystal phosphors. A photocurrent of as low as $2 \times 10^{-13}$ amp has been reported by Moss (1952) for phosphorus, for similar fields. Pohl (1937) found that the photocurrent produced by F centres under a field of 25 volt/cm at 30°C was $2 \times 10^{-11}$ amp. It is clear then, that there is no photoconduction in Br⁻ in RbCl for excitation in the first absorption band. Other crystal samples were tested with similar results, but no conclusions should be drawn from them alone since their fluorescence is exceedingly weak.

From the Br⁻ in RbCl result it is reasonable to suggest that there is no photoconductivity in these mixed halide phosphors. It is now accepted that all crystalline materials are capable of electronic conductivity if free electrons can be produced in them. These electrons can then move freely through the crystal in a conduction band. Hence, the electronic levels involved in absorption and emission are not levels in a conduction band. This does not, however, refer to exciton levels. Of the two basic models used to discuss electronic processes in crystal phosphors, the Band and the
Configurational co-ordinate model, the former is therefore not applicable to the electronic levels so far discovered.

(6.4) EMISSION.

Quantitative measurements of Cl in KBr, Br in EbcI and Cl in KI are shown in Figures 36-38. The experimental points have been joined by a dotted line. Knowing the form of the transmission limits of the filter, shown as curves a, has allowed an analysis into Gaussian components, using the graphical projection method. Curves b, c are residual light passed by the filter and scattered by the sample, and were also found in pure samples of NaCl, KCl, KI and KBr. In Figure 37 components b, c have been left unasymmetrical. There was no difference in the fluorescence of EbcI:Br for excitation from the Bellingham monochromator or black light.

To convert PM current to units of intensity involves a factor, PM sensitivity/Dispersion. The PM was calibrated against a 6v, 35W tungsten bulb fed from a constant voltage transformer, using the known intensity distribution of this source. Figures expressing the above factor with that for 5000A defined as unity are:

<table>
<thead>
<tr>
<th>Wavelength (A)</th>
<th>3400</th>
<th>4000</th>
<th>4500</th>
<th>5000</th>
<th>5500</th>
<th>6000</th>
<th>6500A</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM Current</td>
<td>1.75</td>
<td>1.20</td>
<td>1.04</td>
<td>1.00</td>
<td>1.29</td>
<td>3.21</td>
<td>13.3</td>
</tr>
</tbody>
</table>

These values were reproducible over long periods. The intensity units used correspond to a PM current of 10⁻¹⁰ amp at 5000A.

Most crystals were grown from melts containing 1 mole%
of impurity. Of these the RbCl:Br\textsuperscript{−} sample grown from a 2 mole\% melt gave the only measurable fluorescence. To investigate the possibility of obtaining such phosphor samples in a simple way, melts of KBr:Cl\textsuperscript{−} and KI:Cl\textsuperscript{−} of 1 mole\% impurity were poured into flat fused silica dishes. The edges cooled quickly and remained clear while the central portion of the melt became cloudy, especially when the edges commenced freezing. At room temperature the masses were transparent apart from innumerable cracks. These samples fluoresced well in the centre but not in the outer annules corresponding to the clear portion during freezing. Hence, rapid rates of growth appear favourable for rejection of impurities and, a 1\% of impurity incorporated in the solvent lattice is necessary for a useful intensity of fluorescence.

Accuracy of an individual measurement of intensity is 1\%, of energy 0.3\%, and half widths 2\%. Within these limits the emission spectra measured are accurately represented by Gaussian curves, of position and width, corrected for the effect of finite slits:

<table>
<thead>
<tr>
<th></th>
<th>Energy in ev.</th>
<th>Width in ev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbCl:Br\textsuperscript{−}</td>
<td>2.38</td>
<td>0.46</td>
</tr>
<tr>
<td>KBr:Cl\textsuperscript{−}</td>
<td>2.45</td>
<td>0.39</td>
</tr>
<tr>
<td>KI:Cl\textsuperscript{−}</td>
<td>2.30</td>
<td>0.38</td>
</tr>
</tbody>
</table>

There is little doubt that all these crystals are phosphors, for by using the black light to give 5000-4000Å excitation and the Bellingham and Stanley monochromator 2000-2900Å, fluorescence, barely detectable by the eye, was seen for most samples.
At such low levels sense of colour is poor and great care
was necessary to avoid confusion with stray visible light.
These results, which should only be regarded as showing the
existence of fluorescence, were:

Table 7

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Strong emission</th>
<th>Very weak blue-green near 2.5 ev.</th>
<th>Weak orange near 2 ev.</th>
<th>Weak blue-green near 2.5 ev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000-4000 A</td>
<td>KBrCl:Br, KBr:Cl, KI:Cl</td>
<td>NaCl:F, NaCl:Br, KCl:Br, KBr:I</td>
<td>NaCl:I</td>
<td>All the above.</td>
</tr>
<tr>
<td>2000-2900 A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rise and decay times were less than 50 milliseconds, the
flicker limit of the writer's eye.

Points to note are:

1) Emission width for RbCl:Br is considerably greater than
that for absorption, indicating a correspondingly smaller
curvature of excited states near their minima than that of
the ground state.

2) Line shape is accurately Gaussian. Assuming a parabolic
form of energy against co-ordinate, this implies that the
region of the ground state involved in emission transitions
may be regarded as straight. The Frank-Condon principle
gives this region as that corresponding to co-ordinates
near the excited state minimum.

3) The bulk of the emission lines occur in the region 2 -
2.5 ev while the bulk of the absorption lines occur in the
region 4.5 -5 ev.
FIG. 36
Intensity

EMISSION SPECTRA
3000-4000A Excitation.

Slits of 0.25mm

FIG. 37
Intensity

Cl⁻ in KBr.

Br⁻ in RbCl.

Energy

2.5

3

2

50

0
(6.5) ABSORPTION.

The measurements of Johnson F (66 and Figs 22 to 24) and Johnson D (51 and Figs. 16,19,20) have been shown to be reasonably correct. Some of their results create a false picture, and it is the writer's belief that this is largely due to lack of analysis of the experimental figures, rather than poor experimental accuracy. Measurements showing important differences and new results are shown in Figure 39 -43. Absorption coefficient in terms of density/cm is plotted against energy in electron volts. The original measurements have been graphed, a background fitted and difference taken. These differences multiplied by 1/sample thickness, are plotted as small circles. Most samples were approximately 1cm thick. The form of the original measurements can be reproduced by adding the differences to the background.

Since the impurity concentration in the samples is unknown, in absorption coefficients must be regarded as being/arbitrary units. Results are based on 6,3,4,6 and 3 samples respective-ly for Figs. 39 - 43 and two pure samples of each for all but Fig. 40. Each set of samples was taken from the same boule, grown by the Kyropoulos technique, except HbCl:Er.

These measurements were chosen to investigate line shape and search for possible phenomena characteristic of the doublet ground state of the halogens. This should provide further insight into the electronic mechanism and identify the absorption mechanism with transitions between levels associated with the halogen ion impurity. Data derived is
given in the Table. Energies are accurate to the nearest 0.01 ev and widths to the nearest 0.005.

Table 8.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl: I</td>
<td>3.45</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>0.125</td>
<td>0.255</td>
</tr>
<tr>
<td>KBr: I</td>
<td>3.26</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>0.305</td>
<td>0.485</td>
</tr>
<tr>
<td>KCl: Br</td>
<td>4.53</td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>KBrCl: Br</td>
<td>4.53</td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>0.365</td>
<td>0.355</td>
</tr>
<tr>
<td>NaCl: F</td>
<td>4.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>

There appears to be little difference to the final result whether the crystals have been grown by the Bridgman or the Kyropoulos method. For the latter, however, there appears to be a high rejection efficiency for impurities. The rejection factor is probably between 10 and 100, unless growth rates are small - a few mm/hour. The only boule of KBr: I grown contained a very small impurity concentration.

SHAPE: Any attempt to analysis the spectrum into components based on $1/(1 + x^2)$ fails, because this function is too broad in the tail. Above the region of the half width a Gauss curve fits extremely well. This was checked thoroughly for KClBr with an eye to the measurement of half width against temperature, and is clearly seen in Figs 39, 41, 43. Below the half width the curves are distinctly asymmetric, departure being greatest on the low energy side. Figs 39,
40, 41, 43 show this; it being especially clear for NaCl:P⁻, which has a single peak. This lack of symmetry in the tail complicates analysis into components. Gauss curves have been fitted to those experimental points above the half-width. Such an effect could not have been detected in the emission measurements since the tails were inaccessible in the stray background.

Following on the theoretical introduction to the results of half width against temperature, we consider the form of $P(E)$. The linearity of half-width against the square root of temperature at room temperature, allows discussion of the above results in terms of the classical formula for absorption.

$$P(E) = C \exp \left( -\frac{(E-E_0)}{kT} \right) \frac{d\sigma}{d\theta},$$

where

$C$ is a normalization constant, $E_0$ is the minimum energy in the ground state and $q$ is the configuration co-ordinate. Emission studies showed (qv.) that the curvature of the excited state was less than that of the ground state. Hence, assuming a parabolic form of $E$ against $q$, $E$ has the form:

$$E = -aq^2 + bq + c,$$

$a, b, c > 0$

Therefore $P(E)$ contains the factor $\frac{d\sigma}{d\theta} = \frac{1}{(b-2aq)}$, and this is just the form required to produce an asymmetric absorption curve with the most pronounced asymmetry in the low energy tail.

**DOUBLET STRUCTURE.**

For only one impurity ion, I⁻, has further analysis into
components been possible. From the existing data, NaCl:Br appeared a possibility, but not substructure was detected. To speculate a moment, one would consider the resolution of the 4.85 ev peak in NaCl:I⁻ and the 4.90 ev peak in NaCl:F⁻ a possibility. Both these peaks are much the broadest of those so far measured. Johnson F(96) from a consideration of isoelectronic series derives the absorption energies of free I⁻ as 2.94 and 3.15 ev. These values are sufficiently close to the values 3.45, 3.60 ev for NaCl:I and 3.26, 3.50 ev for KBr:I to add further weight to the suggestion that the absorption mechanism is localized in the negative ion impurity, and suggest further the possibility of all the peaks discovered by the Johnsons manifesting the doublet ground state structure.

IMPURITIES.

The distributors specifications for the samples of KCl and RbCl used here list the maximum limits of impurities as Cl⁻ 0.2%, I⁻ 0.05% and other less than 0.001%. The I⁻ manifests itself as a very small peak at 3.5 ev in Fig. 39 and 3.45 in Fig. 40.
FIG. 39
ABSORPTION SPECTRUM
OF Br\textsuperscript{-} in KCl.
Slits 0.25mm.

DENSITY

Energy

Background
FIG. 40

ABSORPTION SPECTRUM
OF Br⁻ in RbCl.
Slits 0.25mm
FIG. 41

ABSORPTION SPECTRUM
OF I⁻ in NaCl.

Slits 0.25mm
FIG. 42
ABSORPTION SPECTRUM
OF I\(^-\) in KBr.
Slits 0.25mm

FIG. 43
ABSORPTION SPECTRUM
OF F\(^-\) in NaCl.
Slits 0.25mm
CHAPTER VII

THEORY.

THE MODEL.

(7.1) THE FRANK-GONDON PRINCIPLE.

Lax (1952) has developed formal methods which support the configurational coordinate model and the application of the Frank-Gondon principle to crystals. Limitations are found in the application of the principle, both in the semiclassical, single, real coordinate treatment of William's type (1951a), and in the many coordinate, quantum mechanical method used for P-centres by Huang and Rhys (1950).

Lax gives the most frequently used approximations in order of validity as:

Table (9).

1) First order perturbation using Born - Oppenheimer wave functions.
2) (The Condon approximation). Same as (1) neglecting the nuclear position dependence of the electric dipole matrix elements on nuclear position. (Used by Huang and Rhys).
3) Semiclassical Frank-Gondon principle. No change of nuclei positions during transition. Given initial configuration probability based on quantum statistical mechanics.

Derived from (1), using a mean value approximation or by neglect of certain commutators. Gives the same integrated spectrum, mean absorption energy and half-width. Errors in higher moments small at high temperatures, unimportant even at 0°K if the electron - nuclear interaction is strong.
4) Classical Frank-Gondon principle. Same as (3) but using classical statistical mechanics.
5) Quasi-molecular viewpoint. Neglect of all but a small number of coordinates. This and (2), (3), (4) used in the Williams' papers. Coordinates not necessarily real. Need for a temperature dependent mass or stiffness.

The feasibility of a single parameter-x- description rests on the possibility of evaluating the probability distribution \( P(q_1) \) for the initial state, an \( N \) dimensional integral, in the normal components \( q_1 \ldots q_N \) of the system. The integrand, being an exponential of a quadratic form, allows this evaluation if \( x \) is linear in the \( q_i \). But the transition energy \( E \) cannot always be expressed as a function of a single \( x \). For a trapped electron, however, \( E \) will usually depend strongly - i.e., nonlinearly - on a small number of nearest neighbour coordinates, and weakly - i.e., linearly - on many coordinates. In this case a suitable \( x \) can be found. Williams (1951a) uses the first and second nearest neighbour distances \( x, x' \). He derives \( P(x, x') \) by considering \( x, x' \) as real coordinates of a two particle physical system, using the classical distribution \( \exp \left(-V(x, x')/kT\right) \), where \( V(x, x') \) is evaluated by keeping all the other atoms fixed.

(7.2) WILLIAMS' CALCULATION (1951a) FOR AgCl:Ti

Free and ionic compounds of \( Ti^+ \) have a \( 6s^2 \quad 1S_0 \) ground state. The \( 6s6p \) lowest excited states of free \( Ti^+ \) are \( 3P_0, 1^2P, 1^4P \) in order of increasing energy. The
multiplicity selection rule $\Delta S = 0$ is not stringent, since
the coupling is not pure $LS$, but partly $J\bar{J}$. However,
$\Delta L = \pm 1$ and $\Delta S = 0, \pm 1$. Hence Seitz (1938) suggested
that the 6.3 and 5.0 absorption bands arise from $1S_0-1P_1$ and
$1S_0-3P_1$ transitions, while the 4.1 emission band is a
$3P_1-1S_0$ transition.

The only interaction energies strongly dependent on the
state of the $Tl^+$ are those between the $Tl^+$ and the six
nearest $Cl^-$ neighbours. Hence $x$ is the significant co-
ordinate. By imposing the restriction that under a change in
$x$ the remainder of the lattice moves to a position of minimum
energy, the energy of the system becomes a unique function
of $x$. This is approximated by only requiring the radial
displacement of the six second, $K$, neighbours to positions of
minimum energy.

The Madelung, exchange repulsion, ion - induced dipole
and van der Waals interactions are considered in detail. In
a subsequent paper Williams (1953), from consideration of the
poor experimental and theoretical agreement for $KCl:Sn^{++}$,
on the assumption of spherically symmetric excited states,
shows the need to allow for the angular dependence of the
excited wave functions. This modifies the exchange repulsion
energy and eliminates the coulomb overlap energy. Further,
to obtain better agreement with experiment it is found
necessary to allow for the perturbation of the atomic states
by the crystal field. Summation of these energy changes,
and correcting for the displacement of the remainder of the lattice to positions of minimum energy, gives the energy as a function of \( x \). A least square fit of these points yields,

1\( _{S_0} \), Energy = 8.43 \((\Delta x - 0.10)^2 + 0.16

3\( _{P_1} \), Energy = 4.42 \((\Delta x + 0.18)^2 + 4.65 \) ev.

Emission and absorption spectra are obtained by the methods outlined in section (6.2).

The details of contributions of the energy correction terms, for the evaluation of the absorption and emission peak energies, is shown in the following table in ev.

Including the effects of angular dependence and crystal field perturbation means that the table given in the original paper is incomplete. This has required interpolation for the excited state values of Table (10). The 3\( _{P_1} \) emission corrections are given for \( \Delta x = -0.16 \) instead of -0.18 involving an error of less than 0.5\%. The free ion transition energy is taken from Bacher and Goudsmit (1932).

**TABLE (10)**

<table>
<thead>
<tr>
<th></th>
<th>Absorption</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 1_{S_0} ), ( 3_{P_1} ), Change</td>
<td>( 1_{S_0} ), ( 3_{P_1} ), Change</td>
</tr>
<tr>
<td>Madelung</td>
<td>0.03 0.03 0</td>
<td>0.08 0.08 0</td>
</tr>
<tr>
<td>Replulsion</td>
<td>0.82 0.38 -0.44</td>
<td>1.68 0.58 -1.10</td>
</tr>
<tr>
<td>van der Waals</td>
<td>-0.64 -0.95 -0.31</td>
<td>-1.03 -1.53 -0.50</td>
</tr>
<tr>
<td>Dipole</td>
<td>-0.02 -0.02 0</td>
<td>-0.05 -0.03 -0.02</td>
</tr>
<tr>
<td>Perturbation</td>
<td>-0.91</td>
<td>-0.91</td>
</tr>
<tr>
<td>Total change</td>
<td>-1.66</td>
<td>-2.49</td>
</tr>
<tr>
<td>Ion level</td>
<td>6.49</td>
<td>6.49</td>
</tr>
<tr>
<td>Resultant</td>
<td>4.83</td>
<td>4.00</td>
</tr>
</tbody>
</table>
The Absorption, Emission values are low by 4, 2.5% respectively. At this level of approximation the Madelung and Dipole interactions may be neglected. Thus the angular dependence of the wave function of excited states of activator ions in ionic crystals and the perturbation of the free activator ion states by the crystal field are significant factors.

To obtain a guide to the order of similar corrections for negative halides, assume that the only marked change in table (10) for such a case, would be the change in sign of the perturbation. Thus the corrections to the free ion levels would be +0.2 for absorption and -0.7 for emission. This indicates possible errors in the published data (Johnson P103,109), of electron affinities and free ion levels. For example: to reconcile the quoted value of 3.22 ev, the affinity of I_ with the peak at 4.82 ev and zero photoconductivity, requires a correction of greater than +1.6, whereas the above calculation indicates that the correction is small.

(7.3) CONCLUSION.

The investigation of any physical system falls naturally into two phases which may partially overlap. Firstly, there is the search for a mechanism or model, and secondly, the elaboration of the details of the model, usually in conjunction with a theoretical calculation. It cannot be too strongly pointed out that this work only
purports to provide a significant contribution for the first phase. That is, to justify the use of the configurational coordinate model and show that the electronic levels involved are associated with those of the activator ions. All other remarks are to be regarded as tentative, being merely a guide to orders of magnitude or possible details of the model, and so on.

The steps in establishing the mechanism are summarised below, from the results of Chapter VI.

1) Zero photoconduction shows that the band model is not applicable.

2) Transitions are within levels of the activator ion because of the barely significant change in peak position with temperature, and the close similarity in absorption for changes of the solvent anion, Table 11).

TABLE 11

<table>
<thead>
<tr>
<th>Emission energy</th>
<th></th>
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<tbody>
<tr>
<td>RbCl:Br</td>
<td>2.38</td>
</tr>
<tr>
<td>KBr:Cl</td>
<td>2.45</td>
</tr>
<tr>
<td>KI:Cl</td>
<td>2.30</td>
</tr>
<tr>
<td>NaCl:I</td>
<td>2.5, 2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Absorption energy</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl:F</td>
<td>4.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBr:Cl</td>
<td>4.82</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl:Br</td>
<td>4.87</td>
<td>4.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl:Br</td>
<td>4.83</td>
<td>4.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbCl:Br</td>
<td>4.83</td>
<td>4.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl:I</td>
<td>4.85</td>
<td></td>
<td>3.60</td>
<td>3.45</td>
</tr>
<tr>
<td>KBr:I</td>
<td>4.82</td>
<td></td>
<td>3.50</td>
<td>3.26</td>
</tr>
<tr>
<td>Mean</td>
<td>4.85</td>
<td>4.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rms dev.</td>
<td>0.03</td>
<td>0.03</td>
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<td></td>
</tr>
</tbody>
</table>
In fact for peaks A, B deviations from the mean are barely significant, except for NaCl:F.

3) The form of the half-width of an absorption peak against temperature and the line shape justify the configurational coordinate model.

The apparent independence of peaks A, B on anion, cation or impurity ion is surprising. Various models have been considered without success. For models based on motion of the electron in a well, attention is drawn to papers by Simpson (1949), and Krumhansl and Schwartz (1953). No general rule can be given for the ratio of absorption for A, B.

The elaboration of which levels of the activator impurities are involved and the lack of variation in energies A, B, remains. It is the writer's regret that his commitments have not allowed a detailed calculation, of the Williams type, for one of the above systems. Little further advance will be made in this problem until such a calculation is performed.
APPENDIX I
SLIT WIDTH FUNCTIONS FOR A GAUSS ABSORPTION CURVE.

\[
\begin{align*}
D_{\text{ideal}} &= (1 + e) D_{\text{obs}} \text{ at max.} \\
w(t) &= t \text{erf}(t) + N(t) \\
p(t) &= 2(2\pi)^{\frac{1}{2}} \frac{w(t) - w(0)}{t^2}
\end{align*}
\]

<table>
<thead>
<tr>
<th>(t)</th>
<th>(w(t))</th>
<th>(p(t))</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.398942</td>
<td>1.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.1</td>
<td>0.400936</td>
<td>0.9996</td>
<td>0.0004</td>
</tr>
<tr>
<td>0.2</td>
<td>0.406895</td>
<td>0.9968</td>
<td>0.0032</td>
</tr>
<tr>
<td>0.3</td>
<td>0.416762</td>
<td>0.9926</td>
<td>0.0075</td>
</tr>
<tr>
<td>0.4</td>
<td>0.430439</td>
<td>0.9869</td>
<td>0.0133</td>
</tr>
<tr>
<td>0.5</td>
<td>0.447797</td>
<td>0.9797</td>
<td>0.0207</td>
</tr>
<tr>
<td>0.6</td>
<td>0.468653</td>
<td>0.9708</td>
<td>0.0301</td>
</tr>
<tr>
<td>0.7</td>
<td>0.492880</td>
<td>0.9611</td>
<td>0.0405</td>
</tr>
<tr>
<td>0.8</td>
<td>0.520208</td>
<td>0.9499</td>
<td>0.0527</td>
</tr>
<tr>
<td>0.9</td>
<td>0.550431</td>
<td>0.9375</td>
<td>0.0667</td>
</tr>
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<td>1.0</td>
<td>0.583216</td>
<td>0.9243</td>
<td>0.0819</td>
</tr>
<tr>
<td>1.2</td>
<td>0.656103</td>
<td>0.8953</td>
<td>0.1117</td>
</tr>
<tr>
<td>1.4</td>
<td>0.736667</td>
<td>0.8638</td>
<td>0.1577</td>
</tr>
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<td>1.6</td>
<td>0.823242</td>
<td>0.8309</td>
<td>0.2035</td>
</tr>
<tr>
<td>1.8</td>
<td>0.914275</td>
<td>0.7974</td>
<td>0.2541</td>
</tr>
<tr>
<td>2.0</td>
<td>1.008791</td>
<td>0.7643</td>
<td>0.3084</td>
</tr>
</tbody>
</table>
APPENDIX 2.

Tables to convert Angstroms to Electron Volts.

To be able to convert a measurement in Angstroms rapidly into Electron Volts is a great convenience in both emission and absorption spectroscopy. No such table is in the literature.

Felt, Harris and DuMond give the factor for conversion from Kilo x-units to Electron Volts as 12370, and Wood gives a Kilo x-unit as 1.00202 Angstrom - whence

Energy in ev = \( \frac{hc}{\text{wavelength}} = 12370 \times 1.00202 / \text{wavelength in } \AA \)

\( = 12395 / \text{wavelength in } \AA \)

For UV or visible spectroscopy, measurements, in average work, are rarely better than ± 0.5Å; so values are calculated to four figures. Values in the body of the table have been calculated on a machine to 5 figures using reciprocals from Comrie's Tables, and rounded off. Use of the table of mean differences - which are SUBTRACTED - lead to errors not exceeding 2 milli ev in the early part of the table (3). There are two tables, (12) 4000-7000A, (13) 2000-5000A. The range may be extended by using a simple factor - e.g., in the region 20-70A values may be read as tenths of an ev.

Values are in milli-electron volts.
<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>3099</td>
<td>3060</td>
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<td>2987</td>
<td>2951</td>
<td>2916</td>
<td>7</td>
<td>15</td>
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<tr>
<td>250</td>
<td>2916</td>
<td>2883</td>
<td>2849</td>
<td>2817</td>
<td>2785</td>
<td>2754</td>
<td>6</td>
<td>13</td>
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<td>6</td>
<td>12</td>
</tr>
<tr>
<td>750</td>
<td>2609</td>
<td>2582</td>
<td>2556</td>
<td>2530</td>
<td>2504</td>
<td>2479</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>5000</td>
<td>2479</td>
<td>2453</td>
<td>2430</td>
<td>2406</td>
<td>2384</td>
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<td>2316</td>
<td>2295</td>
<td>2273</td>
<td>2254</td>
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<td>8</td>
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<td>500</td>
<td>2254</td>
<td>2232</td>
<td>2213</td>
<td>2193</td>
<td>2175</td>
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