EVERETT, Patrick Nixon, 1934-
TRANSITIONS OF THE $4T_2$ STATE IN PINK RUBY
AND DEVELOPMENT OF MEASURING TECHNIQUES FOR
SHORT LIFETIMES.

The University of Michigan, Ph.D., 1969
Physics, spectroscopy

University Microfilms, Inc., Ann Arbor, Michigan
TRANSITIONS FROM THE $^4T_2$ STATE IN PINK RUBY AND
DEVELOPMENT OF MEASURING TECHNIQUES FOR SHORT LIFETIMES

by

Patrick Nixon Everett

A dissertation submitted in partial fulfillment
of the requirements for the degree
of Doctor of Philosophy in
The University of Michigan
1969

Doctoral Committee:

Professor George I. Haddad, Chairman
Doctor Douglas E. Brown
Professor Thomas M. Dunn
Professor Emmett N. Leith
Doctor Paul D. Maker, Ford Motor Company
Professor Joseph E. Rowe
ABSTRACT
TRANSITIONS FROM THE $^4_{T_2}$ STATE IN PINK RUBY AND
DEVELOPMENT OF MEASURING TECHNIQUES FOR SHORT LIFETIMES
by
Patrick Nixon Everett
Chairman: George I. Haddad

At the time this investigation was undertaken the published experimental evidence indicated that the lifetime of the $^4_{T_2}$ state in pink ruby was approximately 50 ns. Observation of fluorescence from the $^4_{T_2}$ state had been reported but no details of the emission had been published.

In this investigation it was demonstrated by direct measurements that the $^4_{T_2}$ state lifetime is less than 2 ns at temperatures between 2° K and 300° K. No fluorescent emission from the $^4_{T_2}$ state was observed although extremely high excitation powers and sensitive detection equipment were used. It was demonstrated that the nonradiative transitions $^4_{T_2} \rightarrow {}^2E$ occur with a frequency which is greater by a factor of at least $3 \times 10^5$ than that of the fluorescent $^4_{T_2} \rightarrow {}^4A_2$ transitions. If the $^4_{T_2} \rightarrow {}^4A_2$ transitions are considered to be purely electronic, it is shown that the lifetime of the $^4_{T_2}$ state must be less than 45 ps. In the more likely event that the transitions are vibrationally assisted it is shown that the lifetime must be less than 3.5 ps.
A model of the transitions involving a Franck-Condon diagram, activation energies and frequency factors is discussed. It is shown that some of the previously proposed parameters are incompatible with the new experimental results. The activation energy for the $^4T_2 \rightarrow ^2E$ transition must be less than that which is equivalent to 2.5° K, and the corresponding frequency factor must lie between $2 \times 10^{10}$ and $10^{14}$/s.

Equipment with 1 ns resolution was developed to investigate the lifetime and emission spectrum at temperatures between 2° K and 300° K. The equipment has many novel features and is described. It includes a mode-locked Nd:glass laser whose output is frequency doubled and provides a train of subnanosecond pulses with a peak power of more than 1 GW. The laser resonator is stabilized by introduction of a converging lens. Pockels-cell switching is incorporated to allow extraction of just a few pulses for the output. High speed detection equipment was also developed and is described.
ACKNOWLEDGMENTS

The author is indebted to the members of his doctoral committee who have been extremely generous with their time and facilities. Without such generosity the project could never have been completed. Professor C. Kikuchi was co-chairman of the committee until he left on sabbatical and provided much help and encouragement in the early stages of the project. The author wishes to acknowledge many useful discussions with Dr. C. C. Aleksoff and Messrs. G. D. Currie and A. H. Francis, the careful editing by Miss Betty Cummings, and the competent typing by Miss Karen Young; and to express his gratitude to The Institute of Science and Technology for a $10,000 grant for the purchase of equipment, and to The Mitre Corporation for personal support in the form of a three-year fellowship.

Finally the author gratefully acknowledges his indebtedness to his wife for her time, patience and encouragement and for her efforts in keeping the contribution of our three sons reasonably constructive.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
</tr>
<tr>
<td>CHAPTER I. INTRODUCTION</td>
</tr>
<tr>
<td>1.1 Outline of the Study</td>
</tr>
<tr>
<td>1.2 Historical Note</td>
</tr>
<tr>
<td>1.3 Spectroscopy of Ruby</td>
</tr>
<tr>
<td>1.4 The Ruby Laser</td>
</tr>
<tr>
<td>1.5 The $^4T_2$ State</td>
</tr>
<tr>
<td>CHAPTER II. PRELIMINARY EXPERIMENT AND DISCUSSION OF FURTHER EXPERIMENTS</td>
</tr>
<tr>
<td>2.1 Initial Considerations</td>
</tr>
<tr>
<td>2.2 Maiman's Experiment</td>
</tr>
<tr>
<td>2.3 Preliminary Experiment</td>
</tr>
<tr>
<td>2.3.1 Discussion</td>
</tr>
<tr>
<td>2.3.2 Experiment</td>
</tr>
<tr>
<td>2.3.3 Results</td>
</tr>
<tr>
<td>2.4 Pollack's Experiment</td>
</tr>
<tr>
<td>2.5 Discussion of Further Experiments</td>
</tr>
<tr>
<td>2.6 Equipment Requirements</td>
</tr>
<tr>
<td>2.6.1 General</td>
</tr>
<tr>
<td>2.6.2 Excitation</td>
</tr>
<tr>
<td>2.6.3 Detection</td>
</tr>
<tr>
<td>2.7 Conclusions</td>
</tr>
<tr>
<td>CHAPTER III. DEVELOPMENT OF THE MODE-LOCKED LASER</td>
</tr>
<tr>
<td>3.1 Background</td>
</tr>
<tr>
<td>3.2 Initial Attempt at Mode-Locking</td>
</tr>
<tr>
<td>3.3 Achievement of Mode-Locking</td>
</tr>
<tr>
<td>3.4 Conclusions Drawn from the Initial Mode-Locking Experiments</td>
</tr>
</tbody>
</table>
3.5 Improvement on the State of the Art

3.5.1 Discussion
3.5.2 Results with the Modified Resonator
3.5.3 Choice of Dye
3.5.4 Reflecting Optics
3.5.5 Likelihood of Lasing
3.5.6 Conclusions on Reliability and Expected Output
3.5.7 Pulse Length
3.5.8 Improved Energy Output

3.6 Frequency Doubling

3.7 Form of Laser for Initial Lifetime Measurements

3.8 Laser Redesigned as a Result of Initial Experiments

3.8.1 Construction
3.8.2 Alignment
3.8.3 Monitoring of Output Energy
3.8.4 Resonator Configuration
3.8.5 Frequency Doubling and Pockels Cell Switching
3.8.6 Power Supply and Cooling

3.9 Summary

CHAPTER IV. DEVELOPMENT OF SUBSIDIARY EQUIPMENT AND TECHNIQUES

4.1 Introduction
4.2 Method of Aligning the Laser
4.3 Diode Calorimeter

4.3.1 Requirement
4.3.2 Construction of Diode Calorimeter
4.3.3 Calibration of Diode Calorimeter

4.4 Power and Energy Measurement of Individual Pulses

4.4.1 General Considerations
4.4.2 Direct Calibration of the UA 1240 Detector
4.4.3 Calibration of UA 1240 Detector with Diffuse Reflector

4.5 Solid-State Diode as a Mode-Locking Monitor
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6 Resolution of Pulses by Two-Photon Fluorescence</td>
<td>75</td>
</tr>
<tr>
<td>4.7 Photomultiplier and Its Circuitry</td>
<td>78</td>
</tr>
<tr>
<td>4.7.1 Choice of Photomultiplier</td>
<td>78</td>
</tr>
<tr>
<td>4.7.2 Development of Photomultiplier Circuitry</td>
<td>79</td>
</tr>
<tr>
<td>4.7.3 Impedance-Matching Cable</td>
<td>82</td>
</tr>
<tr>
<td>4.7.4 Dark Current Monitoring</td>
<td>83</td>
</tr>
<tr>
<td>4.7.5 Summary</td>
<td>84</td>
</tr>
<tr>
<td>4.8 Pockels Cell Switching</td>
<td>84</td>
</tr>
<tr>
<td>4.8.1 General</td>
<td>84</td>
</tr>
<tr>
<td>4.8.2 Construction</td>
<td>86</td>
</tr>
<tr>
<td>4.8.3 Operation</td>
<td>88</td>
</tr>
<tr>
<td>4.9 Transmission Monitoring of Saturable Dye</td>
<td>90</td>
</tr>
<tr>
<td>4.10 Dewar Equipment</td>
<td>90</td>
</tr>
<tr>
<td>4.11 Summary</td>
<td>92</td>
</tr>
<tr>
<td><strong>CHAPTER V. EXPERIMENTS</strong></td>
<td>93</td>
</tr>
<tr>
<td>5.1 Objectives</td>
<td>93</td>
</tr>
<tr>
<td>5.2 Lifetime Measurements</td>
<td>93</td>
</tr>
<tr>
<td>5.2.1 Measurements at 2° K and 77° K</td>
<td>93</td>
</tr>
<tr>
<td>5.2.2 Earlier Measurements at 77° K and 300° K</td>
<td>97</td>
</tr>
<tr>
<td>5.3 Radiative Emission from the $^4T_2$ State</td>
<td>98</td>
</tr>
<tr>
<td>5.3.1 Search with Spectrograph</td>
<td>98</td>
</tr>
<tr>
<td>5.3.2 Search with Monochromator and Fast Photomultiplier</td>
<td>102</td>
</tr>
<tr>
<td>5.4 Absorption Measurements at High Power</td>
<td>103</td>
</tr>
<tr>
<td>5.5 Two-Photon Luminescence</td>
<td>104</td>
</tr>
<tr>
<td>5.6 Summary</td>
<td>105</td>
</tr>
<tr>
<td><strong>CHAPTER VI. DISCUSSION AND CONCLUSIONS</strong></td>
<td>106</td>
</tr>
<tr>
<td>6.1 Direct Lifetime Measurement</td>
<td>106</td>
</tr>
<tr>
<td>6.1.1 Discussion</td>
<td>106</td>
</tr>
<tr>
<td>6.1.2 Analysis of Noise</td>
<td>108</td>
</tr>
<tr>
<td>6.1.3 Conclusion</td>
<td>109</td>
</tr>
<tr>
<td>6.2 Emission Spectrum of the $^4T_2$ State</td>
<td>109</td>
</tr>
<tr>
<td>6.2.1 Discussion of Models</td>
<td>109</td>
</tr>
<tr>
<td>6.2.2 Experimental Results</td>
<td>112</td>
</tr>
</tbody>
</table>
6.3 Indirect Estimates of Lifetime 112
   6.3.1 Simple Model 112
   6.3.2 Vibronic Model 115
6.4 Branching Ratio from the $^4T_2$ State 115
6.5 Discussion of Misu's Results 115
   6.5.1 Introduction 115
   6.5.2 Misu's Results 116
   6.5.3 Estimate of Lifetime of $^4T_2$ State Based on Misu's Results 119
   6.5.4 Discussion of Disagreement 121
   6.5.5 New Estimates for Activation Energies and Frequency Factors 121
   6.5.6 Conclusions 123
6.6 Summary 123
6.7 Suggestions for Further Work 124

APPENDIX A. EINSTEIN TRANSITION THEORY 126
   A.1 Introduction 126
   A.2 Summary of the Einstein Development 126
      A.2.1 Hypotheses 126
      A.2.2 Consider Thermal Equilibrium 127
      A.2.3 Results 128
   A.3 Modification of the Einstein Development for Solids 129
      A.3.1 Hypotheses 129
      A.3.2 Thermal Equilibrium 130
      A.3.3 Results 131
   A.4 Gain and Attenuation 131
      A.4.1 General Equation 131
      A.4.2 Transmission Measurements 132
      A.4.3 Optical Gain 133
   A.5 Summary 133

APPENDIX B. DISCUSSION OF MODE-LOCKING 134
   B.1 Introduction 134
   B.2 Cavities and Modes 135
      B.2.1 Stability 135
      B.2.2 Modes 136
### LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Electronic Energy Levels in Ruby, Indicating How They Arise from the Free</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Ion Terms Under the Influence of the Crystal Field. (Nelson and Sturge⁵)</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Transitions Relevant to Maiman's Experiment.</td>
<td>12</td>
</tr>
<tr>
<td>2.2</td>
<td>Experimental Arrangement for Lifetime Measurement.</td>
<td>16</td>
</tr>
<tr>
<td>2.3</td>
<td>Oscilloscope Traces of Photomultiplier Output.</td>
<td>17</td>
</tr>
<tr>
<td>3.1</td>
<td>Initial Geometries of the Laser.</td>
<td>28</td>
</tr>
<tr>
<td>3.2</td>
<td>Early Examples of Mode-Locked Output.</td>
<td>29</td>
</tr>
<tr>
<td>3.3</td>
<td>Mode-Locked Laser in an Early Form.</td>
<td>30</td>
</tr>
<tr>
<td>3.4</td>
<td>Variation of Beam Cross Section with Axial Distance in a Resonator with a</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Plane and a Spherical Mirror.</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>The Three Configurations of the Reflecting Optics.</td>
<td>37</td>
</tr>
<tr>
<td>3.6</td>
<td>Example of Ideal Q-Switched Mode-Locking and Typical Waveforms from the</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>Three Reflector Configurations.</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>Probability of Full Lasing as a Function of Cavity Length for Arrangements</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>&quot;S&quot; and &quot;L&quot;.</td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>Simultaneous Two-Photon Fluorescence Pictures and Oscillograms of Laser</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Output.</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>Efficiency of Frequency Doubling as a Function of Departure from Ideal</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Orientation.</td>
<td></td>
</tr>
<tr>
<td>3.10</td>
<td>The Portable Mode-locked Laser Assembly with Covers Removed.</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure | Description                                                                 | Page  
--- | --- | ---  
3.11 | The Nd:Glass Laser Section of the Assembly. | 51  
3.12 | Schematic of the Mode-Locked Laser Assembly. | 52  
3.13 | Excitation Pulses of 0.53 μm Wavelength. | 55  
4.1 | Photograph of the Diode Calorimeter. | 61  
4.2 | Solid-State Diode Calorimeter. | 62  
4.3 | Use of UA 1240 Detector with Diffuse Reflector. | 70  
4.4 | Solid-State Diode Assembly. | 73  
4.5 | Oscillograms of Laser Output Using the Solid-State Diode Assembly. | 74  
4.6 | Camera and Dye Cell for Two-Photon Fluorescence Pictures. | 77  
4.7 | Oscillograms Demonstrating Speed of Response of RCA C70045C Photomultiplier. | 80  
4.8 | Photomultiplier and Circuit Diagram Schematics. | 81  
4.9 | Photomultiplier Assembly and Impedance-Matching Cable. | 85  
4.10 | Pockels Cell Switching. | 87  
4.11 | Oscillograms Illustrating Pockels Cell Switching of Output. | 89  
4.12 | The Frequency Doubler, Spark Gap and Pockels Cell Section of Assembly. | 91  
5.1 | Experimental Arrangement for Lifetime Measurements. | 94  
5.2 | R-Line Luminescence at Low Temperatures as a Result of Three Excitation Pulses. | 96  
5.3 | R-Line Luminescence as a Result of the Full Train of Excitation Pulses. | 99  
5.4 | Experimental Arrangement with Spectrograph. | 100
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>Spectrograms of Ruby Emission.</td>
<td>101</td>
</tr>
<tr>
<td>6.1</td>
<td>Display Expected with Perfect Detection Equipment.</td>
<td>107</td>
</tr>
<tr>
<td>6.2</td>
<td>Structure of Green Absorption Band at 5° K. (McClure)</td>
<td>111</td>
</tr>
<tr>
<td>6.3</td>
<td>Configuration Coordinate Diagrams.</td>
<td>118</td>
</tr>
<tr>
<td>B.1</td>
<td>Plot of Laser Resonator Stability.</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>(Kogelnik)</td>
<td></td>
</tr>
<tr>
<td>B.2</td>
<td>Spatial Distribution of Laser Intensity Indicated by Burn Marks in Polaroid Film.</td>
<td>143</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Parameters of Saturable Dyes</td>
<td>35</td>
</tr>
<tr>
<td>3.2 Probability of Mode-Locking for Different Resonator Optics</td>
<td>38</td>
</tr>
<tr>
<td>3.3 Published Mode-Locking Results Compared with Those Obtained by the Author</td>
<td>48</td>
</tr>
<tr>
<td>4.1 Calibration of Diode Calorimeter</td>
<td>65</td>
</tr>
<tr>
<td>4.2 Power Calibration of UA 1240 for Slowly Varying Signals</td>
<td>68</td>
</tr>
<tr>
<td>4.3 Energy Calibration of UA 1240 for Short Pulses</td>
<td>68</td>
</tr>
<tr>
<td>4.4 Calibration of UA 1240 with Diffuse Reflector</td>
<td>69</td>
</tr>
<tr>
<td>5.1 Transmission Measurements at High Power</td>
<td>104</td>
</tr>
<tr>
<td>6.1 Misu's Estimates of Activation Energies and Frequency Factors</td>
<td>119</td>
</tr>
</tbody>
</table>
CHAPTER I. INTRODUCTION

1.1 Outline of the Study

Since the development of the ruby laser there has been considerable interest in the processes leading to R-line luminescence from the chromium ions in pink ruby. The laser output consists of stimulated emission in the R-lines. The emission is usually obtained by optically exciting the chromium ion upper electronic states $^4T_2$ and $^4T_1$. Subsequent nonradiative decay results in population of the $^2E$ state, which has a lifetime of approximately 5 ms. Decay from the $^2E$ state to the ground state $^4A_2$ is radiative, with a quantum efficiency greater than 50 percent. The emission is in the well-known R-lines.

The major topic of this thesis is an improved measurement of the lifetime of the $^4T_2$ state, and investigation of the emission spectrum of the $^4T_2 \rightarrow ^4A_2$ transition. To carry out the investigation, considerable equipment was developed featuring production of very short intense optical pulses and development of a high-speed detection system. Since much of the equipment is novel, and would be applicable to similar investigations in other materials and also in nonlinear optical applications, it is described in some detail.
Although ruby has been extensively investigated and exploited due to its many useful properties, some of its characteristics are not yet fully understood.

A preliminary experiment performed by the author cast doubt on a previous report\(^1\) concerning the \(^{4}T_2\) lifetime and the emission spectrum. The previous report had been cited as evidence for the "correctness" of some theoretical predictions\(^2,3\) of the lifetime. As ruby has considerable engineering importance and has in the past provided a good vehicle for testing and developing the theory relevant to ions in a strong crystal field, it was decided that the apparent discrepancies warranted further investigation.

The background for the study appears in the following sections of this introduction. In Chapter II, the preliminary experiment and conclusions are discussed leading to the design of further experiments and discussion of equipment requirements. A rather lengthy equipment-development phase followed the preliminary experiment. The equipment development is described in its historically correct position in the text. This is at the risk of some loss of continuity in the theoretical thread. It was considered important to emphasize the equipment aspects of this investigation since, although the equipment was "state of the art," it was the limiting factor in the experiments. Those less interested in equipment and techniques might skip Chapters III and IV, and proceed directly to the experiments and conclusions of
Chapters V and VI.

1.2 Historical Note

Interest in ruby has intensified since it has been shown to be useful as both a maser and a laser material. Pink ruby was first used in an experimental maser device in 1957. Maser is an acronym for microwave amplification by stimulated emission of radiation. The first maser was demonstrated in 1956 using gadolinium sulphate as the active material. Currently, when cooled with liquid helium, ruby is one of the most often used materials for the active part of the device. It is used in the construction of amplifiers which give high gain with low noise at frequencies in the region of $10^9$ Hz.

The laser arrived soon after the maser. It is an acronym for light amplification by stimulated emission of radiation. In 1960 the first laser was experimentally achieved\(^4\) (in the form of a regenerative oscillator). Ruby was the active material in the first experimental laser and still retains its importance as one of the most often used lasing materials. The reasons for its continued importance include the following: the output radiation is in the visible part of the spectrum, the crystal does not require cooling, high-energy output is obtained, and large crystals with high optical quality can be obtained.
1.3 Spectroscopy of Ruby

The rhombohedral crystalline form of aluminum oxide is called corundum when it occurs as a mineral, or sapphire when it is synthesized. The ionic crystal is very stable and hard. Each unit cell contains four aluminum and six oxygen atoms. A model of the crystal structure can be generated by placing $\text{Al}_2\text{O}_3$ molecules at the corners of a cube and then stretching the cube along one of the body diagonals. Another molecule rotated 180 degrees about its threefold axis is placed at the center of this distorted cube. The crystal has a threefold axis of symmetry along the stretched body diagonal. As might be expected from the rotational symmetry, the crystal is uniaxial with the threefold axis of symmetry being the optic axis.

Both the aluminum and oxygen ions have the electronic configuration of neon. The crystal is transparent to wavelengths between 0.3 and 5 $\mu$m. When chromium ions are substituted for some of the aluminum ions in the crystal, the material becomes ruby. The electronic configuration of the chromium ion in ruby is that of argon plus three "d" electrons. These extra electrons have a marked influence on the spectrum of the crystal.

For the free chromium ion, the terms which arise from the assumption of Russel-Saunders coupling suffice to approximately describe the possible electronic states. However in ruby the crystal field is sufficiently strong to require descriptions of the states in group theoretical terms. The
energy levels of the three "d" electrons as a function of a cubic electric field are illustrated in Fig. 1.1. However the crystal field is not exactly cubic but has a small trigonal component which is related to the above-mentioned stretching along the body diagonal of the unit cell. The effect of the trigonal field is to further split the energy levels as indicated in Fig. 1.1. The ground level is $^4\text{A}_2$, which is split into a pair of Kramer's doublets. For most laser purposes this splitting is unimportant, but in masers the two doublets are purposely split into a total of four levels by a magnetic field (Zeeman effect). The transitions at microwave frequencies between the resultant levels are used in the maser.

The metastable $^2\text{E}$ level is also split into a pair of Kramer's doublets (termed $^2\text{A}$ and $^2\text{E}$) by the trigonal field. The transitions from each of these doublets to the $^4\text{A}_2$ level are radiative and give the two R-lines. At room temperature, the thermal broadening of the R-lines is greater than the separation between the ground level doublets. However at approximately 80° K, the linewidths become sufficiently small that the splitting of the ground level can be resolved.

The energy levels as described apply for chromium concentrations of less than about 0.2 percent, i.e., for pink ruby. At higher concentrations the interaction of the chromium ions can no longer be neglected. These introduce extra lines which are weak to begin with but become stronger with increasing concentration. The ruby color then becomes
FIG. 1.1 ELECTRONIC ENERGY LEVELS IN RUBY, INDICATING HOW THEY ARISE FROM THE FREE ION TERMS UNDER THE INFLUENCE OF THE CRYSTAL FIELD. (Nelson and Sturge$^5$)
red. The discussion will be confined to pink ruby, as it is more useful for lasers and masers.

The spectroscopic data are discussed in further detail by McClure, Schawlow, and Maiman et al. The nomenclature of the states is discussed by Sugano. The theory of the Zeeman effect and the selection rules of the R-lines are discussed by Sugano et al. and Varsanyi et al.

1.4 The Ruby Laser

Laser outputs have been obtained from both the R-lines. However there is rapid relaxation between levels $2\tilde{A}$ and $\tilde{E}$ which in all practical cases leads to a Boltzmann distribution between them. The resultant higher population of the $^2E$ level together with a slightly higher transition probability for the lower energy $R_1$-line ensures that the laser output is always in this line unless special measures are taken.

The $^4A_2 + ^4T_2$ (green) and $^4A_2 + ^4T_1$ (blue) transitions are strongly light absorbing, and have broad linewidths so they are convenient for utilizing flash lamp energy to populate the upper levels. The upper-state population then decays rapidly through nonradiative transitions into the metastable $^2E$ level. When the optical excitation is sufficient, the population of the $^2E$ level becomes high enough, relative to that of the ground level, that stimulated emission in the R-lines predominates over the spontaneous emission. This results in lasing if the ruby is situated in a suitable optical resonator. Equations governing the optical gain of such a system are developed in Appendix A.
1.5 The $^4T_2$ State

The $^4T_2$ state forms the upper level for one of the two pumping transitions in the ruby laser. As nonradiative relaxation from $^4T_2 \rightarrow ^2E$ is so rapid ($> 10^9$ per second),\(^{12}\) the properties of the state are difficult to study experimentally. For this reason experimental data are scarce. One would expect a radiative $^4T_2 \rightarrow ^4A_2$ transition (as a complement to the absorption line) in addition to the non-radiative $^4T_2 \rightarrow ^2E$ transition. The major objective in this experimental program is to shed further light on the properties of the $^4T_2$ state and the relevant transitions, using equipment which is "state of the art" as regards resolution.

The history of the literature on transitions from the $^4T_2$ state in pink ruby is briefly as follows:

1960

Maiman\(^1\) reported that he had observed emission from the $^4T_2 \rightarrow ^4A_2$ transition in the green portion of the spectrum. From his measurements he concluded that the lifetime of the $^4T_2$ state is 50 ns. It should be mentioned that at that time he was mainly concerned with demonstrating that the lifetime of the $^4T_2$ state was short enough to make the ruby laser a practical device.

1962

Kiel\(^{13}\) estimated an upper limit for the lifetime of 1 μs from consideration of multiphonon processes and estimated it could even be less than 10 ns.
Malkin, from a harmonic approximation analysis of the interaction between an impurity ion and an ionic lattice, estimated the lifetime to be approximately 20 ns, an order of magnitude agreement with Maiman's measurement.

Misu identified emission from ruby near 16,100 cm⁻¹ (0.63 μm) at temperatures above 300° K as the \( ^4T_2 \rightarrow ^4A_2 \) emission. He explained the shift to a longer wavelength by means of a configuration diagram and the Franck-Condon principle.

Calviello et al., from an analysis of the variation of linewidths with temperature, concluded that the width of the \( ^4A_2 \rightarrow ^4T_2 \) absorption line is governed by the \( ^4T_2 \) lifetime, and hence the lifetime must be less than 0.1 ps.

Tsukerblat and Perlin, from a theory of many phonon, nonradiative transitions, estimated the lifetime to be approximately 20 ns, an order of magnitude agreement with Maiman's measurement.

Kisliuk and Moore identified radiation in the region of the R-lines (0.69 μm) as being the \( ^4T_2 \rightarrow ^4A_2 \) emission. Their measurements covered the range 300° K to 760° K. Like Misu, they used a configuration diagram and the Franck-Condon principle to explain the wavelength shift. They estimated
that the lifetime of the $^{4}T_{2}$ state may be as short as 1 ps.

The next entry was published during the preliminary experiment performed here which showed Maiman's figure was too high.

1967

Pollack$^{17}$ reported a direct measurement which showed that the rise time of the R-line emission is less than 5 ns after excitation into the $^{4}T_{1}$ level. On the assumption that the population decays through the $^{4}T_{2}$ level, he demonstrated that the lifetime of the $^{4}T_{2}$ state must be less than 5 ns at room temperature. This was the first published experimental measurement casting doubt on Maiman's result.

The next entry was published while the equipment was being developed for the major experiment.

1968

Pollack$^{12}$ having further refined his equipment, reported a direct measurement indicating the lifetime of the $^{4}T_{2}$ state to be less than 0.5 ns at 300° K. He was unable to make measurements at lower temperatures.
CHAPTER II. PRELIMINARY EXPERIMENT AND DISCUSSION OF FURTHER EXPERIMENTS

2.1 Initial Considerations

At the time the investigation was commenced (August 1967), the only experimental measurement of the lifetime of the \(^4\text{T}_2\) state was Maiman's,\(^1\) and was estimated to be approximately 50 ns. As was mentioned in the introduction, theoretical estimates have ranged from less than 10 ps to 1 \(\mu\)s. In addition, only Maiman\(^1\) and Misu\(^14\) have reported observation of the \(^4\text{T}_2 \rightarrow ^4\text{A}_2\) emission. Accordingly it was decided to attempt verification of their results.

2.2 Maiman's Experiment

Maiman irradiated a crystal of ruby with green light resulting in population of the \(^4\text{T}_2\) state. Two components of radiation reemitted from the crystal were observed in a direction perpendicular to the exciting beam: that which he believed to be due to spontaneous decay \(^4\text{T}_2 \rightarrow ^4\text{A}_2\), and that due to spontaneous decay \(^2\text{E} \rightarrow ^4\text{A}_2\). The energy levels involved are illustrated in Fig. 2.1. The lifetime of the \(^2\text{E}\) state is about 5 ms and is almost entirely due to radiative emission,\(^1\) hence the Einstein A coefficient \(A_{21}\) is approximately 200/s. He estimated \(A_{31}\) to be \(3 \times 10^5/s\) from measurements of the absorption coefficient and linewidth for the transition. The quanta per second from the two
FIG. 2.1 TRANSITIONS RELEVANT TO MAIMAN'S EXPERIMENT.
components of luminescence are given by $N_3 A_{31}$ and $N_2 A_{21}$, where $N_i$ is the population of state $i$. He measured the ratio of the two components and used an auxiliary condition applicable to steady-state conditions, $N_2 A_{21} = N_3 S_{32}$, where $S_{32}$ is the spontaneous transition probability for $^4T_2 \to ^2E$, and found $S_{32}$ to be about $2 \times 10^7/s$. As this is the fastest transition out of the state, he concluded that the lifetime of $^4T_2$ is approximately 50 ns. This is the figure widely quoted in texts on lasers.\textsuperscript{18-20}

2.3 Preliminary Experiment

2.3.1 Discussion. It was decided that, with the short pulses of high intensity now available from lasers, a more direct measurement could be attempted. It is interesting to note that Maiman's experiment was one of the key ones leading to the development of the first laser, and that now with the use of a laser the same measurement can be made with much greater accuracy.

The experiment duplicated Maiman's, except that the excitation was accomplished by a single pulse shorter than the expected lifetime of the $^4T_2$ state. After the impulse excitation, the depopulation rate of the state is given by

$$ \frac{dN_3}{dt} = -N_3 (S_{32} + A_{31}). \quad (2.1) $$

The last term is relatively small and can be neglected. Hence if the excitation is considered as an impulse causing $^4T_2$ to have an initial population $N_0$, the subsequent populatio
is

\[ N_3 = N_0 e^{-S_{32}t}. \]  \hspace{1cm} (2.2)

Virtually all the transitions from \(^4\text{T}_2\) are to the metastable \(^2\text{E}\) state. This empties relatively slowly \((A_{21} \ll S_{32})\), so initially the \(^2\text{E}\) population can be described by

\[ N_2 = N_0 (1 - e^{-S_{32}t}) \]  \hspace{1cm} (2.3)

and hence quanta radiate from the \(^2\text{E} \rightarrow ^4\text{A}_2\) transition at a rate

\[ Q = A_{21}N_0 (1 - e^{-S_{32}t}). \]  \hspace{1cm} (2.4)

The result is an exponentially damped rise in the R-line luminescence with a time constant of \(1/S_{32}\) which is the lifetime of the \(^4\text{T}_2\) state.

It follows that the lifetime of the \(^4\text{T}_2\) state is equal to the time constant associated with the exponentially damped rise of the R-line luminescence following an impulse of green excitation.

2.3.2 Experiment. The required intense pulse for optical excitation into \(^4\text{T}_2\) was obtained from a Q-switched Nd:glass laser. This laser emits a pulse lasting approximately 20 ns at a wavelength of 1.06 µm. The light was frequency-doubled using harmonic generation in a KDP crystal. The resultant pulse of green light, after filtering with a Fisch
Schurman BG-18 filter to reduce the intensity of the remaining 1.06 μm light, was used to excite the \(^4T_2\) state in the ruby sample. The sample was 1 inch long, 0.5 inch in diameter, Verneuil grown, with nominally 0.05 percent \(\text{Cr}_2\text{O}_3\) content by weight. The excitation light propagated in the axial direction. The resultant R-line emission \((^2E + ^4A_2)\) was observed in a direction perpendicular to the exciting beam with an RCA 7102 photomultiplier. A 5 nm bandpass filter centered at 694.3 nm and a Fisch-Schurman OG3 filter were placed in front of the photomultiplier to attenuate any scattered excitation light. The experimental arrangement is illustrated in Fig. 2.2.

The photomultiplier output was displayed on a Tektronix 585A oscilloscope. Sample traces appear in Fig. 2.3. Figure 2.3a was taken with the filters removed from the photomultiplier, and hence shows scattering from the excitation pulse swamping any luminescence. Figure 2.3b shows the rise of the R-line luminescence as a result of the excitation pulse. Figure 2.3c shows the subsequent decay of the R-line luminescence with approximately a 5 ms time constant.

2.3.3 Results. It is immediately apparent from Fig. 2.3b that the time constant for the rise in luminescence is considerably smaller than one would expect from Maiman's measurement. It is of the same order as the excitation pulse duration (i.e., about 20 ns) and hence the excitation pulse cannot be considered an impulse. It can be concluded that the lifetime of the \(^4T_2\) state is definitely less than 20 ns.
FIG. 2.2 EXPERIMENTAL ARRANGEMENT FOR LIFETIME MEASUREMENT.
FIG. 2.3 OSCILLOSCOPE TRACES OF PHOTOMULTIPLIER OUTPUT.
and probably even less than 10 ns. To obtain an exact upper bound for the lifetime would require comparison between a time integration of the excitation pulse shape function and the luminescence curve. In interpreting the results, some assumptions would have to be made concerning the time delays in the detection equipment. This exercise was not carried through as the author became aware of an investigation (at that time unpublished) which Pollack was conducting at TRW Systems.

2.4 Pollack's Experiment

Pollack was also measuring the lifetime of the $^4T_2$ state. He used a pulsed flash lamp which gave pulses of about 10 ns duration. As his lamp peaked in the blue, he was pumping into the $^4T_1$ state. He also observed the rise of the R-line luminescence subsequent to the excitation. On the assumption that the population decays to the $^2E$ state through the $^4T_2$ state, his experiment gave an upper bound for the lifetimes of both the $^4T_1$ and $^4T_2$ states. With his shorter pulses and faster detecting equipment, he found that the lifetime of each state is less than 5 ns. With the equipment then available, the author could not attain quite the same resolution.

2.5 Discussion of Further Experiments

The conclusion drawn from the preliminary experiment was that the lifetime of the $^4T_2$ state is much less than the value of 50 ns estimated by Maiman. Pollack's new
result indicated it to be less than 5 ns. Uncertainty also arose concerning the nature of the emission observed by Maiman and used as the basis for his $^4T_2$ lifetime estimate. The theoretical approaches used by Malkin, and by Tsukerblat and Perlin have also lost some validity, as their estimates gave agreement with Maiman's value.

It was decided that the topic deserved pursuing in three directions. These were: (1) possible improvement in time resolution, in the hope of actually measuring the lifetime; (2) finding whether the lifetime is lengthened at low temperatures and (3) investigating the emission spectrum, if any, from the $^4T_2$ state.

2.6 Equipment Requirements

2.6.1 General. The excitation pulse and the resolution of the detection equipment should be shorter than the expected lifetime in order to make a lifetime measurement. To investigate an emission spectrum, it is desirable to include a monochromator in the detection system. It is worth noting that Pollack was unable to incorporate a monochromator or do his measurement at temperatures lower than 300 °K because of a lack of sufficient excitation power.

The considerations pertaining to the various sub-systems of the equipment are discussed separately in the following sections.
2.6.2 Excitation. To improve materially upon Pollack's resolution of 5 ns, it is desirable to have excitation pulses lasting less than 1 ns. An important requirement also is that the excitation pulses must result in enough luminescence for the detector to follow faithfully; this is not a trivial requirement. The principal inherent noise contribution in a detection system with a resolution of approximately 0.5 ns is shot noise in the photocathode current. The current fluctuation due to shot noise can be expressed as

$$\Delta i_{\text{rms}} = \sqrt{2ie\Delta f}, \quad (2.5)$$

where $i$ is the current, $e$ is the electronic charge and $\Delta f$ is the bandwidth ($2 \times 10^9$ Hz). To obtain a signal-to-noise ratio of at least 10, then

$$i \geq 10\Delta i_{\text{rms}} \quad (2.6)$$

and so from Eq. 2.5

$$i \geq 200e\Delta f. \quad (2.7)$$

Hence

$$i \geq 6.5 \times 10^{-8} \text{ A} \quad \text{or} \quad 4 \times 10^{11} \text{ electrons/s.}$$

The most sensitive photocathode at a wavelength of 0.69 $\mu$m (S-20) has a quantum efficiency of 2.7 percent. Hence $1.5 \times 10^{13}$ photons/s are required at the cathode to ensure
sufficient signal-to-noise ratio. If an f/6 optical system with 25 percent transmission is used to collect the photons emitted from the ruby, it will have a collection efficiency of about $5 \times 10^{-4}$ (assuming isotropic radiation). Hence about $3 \times 10^{16}$ photons/s are required from the ruby. Since the radiative transition probability for the R-lines is $A_{21} = 200/s$, and the observation should start early in the buildup of the luminescence, certainly by the 10 percent point, and as photons/s are

$$Q = N_2 A_{21} \geq 3 \times 10^{16}, \quad (2.8)$$

where $N_2$ is the population in $^2E$, then we require that the total population $N_0$ initially in state $^4T_2$ as a result of the excitation pulse be

$$N_0 \geq \frac{3 \times 10^{16}}{200} \times 10 = 1.5 \times 10^{15}. \quad (2.9)$$

This means that, even with 100 percent utilization, at least $1.5 \times 10^{15}$ photons are needed in the excitation pulse, which corresponds to $6 \times 10^{-4}$ J at a wavelength of 0.53 mm. Hence, to be safe, there should be about 1 mJ in each excitation pulse. Since the excitation pulse should last less than 1 ns, if possible, this requires peak powers of more than 1 MW to be delivered within the absorption band of the ruby.

In the foregoing discussion an implicit assumption has been made that the information is to be obtained as the result of a single excitation pulse. If a long train of identical
pulses is used, a lower signal-to-noise ratio is acceptable as a sampling technique may be used which effectively averages over a large number of pulses. As the noise is random the averaging will attenuate it relative to the repetitive signal.

A study of available light sources indicated that the recently developed mode-locked lasers were the only sources which could give powers of the magnitude required in such short pulses; and further, the power and wavelength requirement limited the choice to lasers using the Nd ion. These lasers emit in the region of 1.06 μm and, as has already been demonstrated in the preliminary experiment, this wavelength, when frequency doubled, is suitable for the excitation.

Mode-locked lasers using the Nd ion have been reported in two forms, both producing subnanosecond pulses. The first\(^{22}\) is in glass in which the output consists of a Q-switched burst containing about thirty of the subnanosecond pulses at intervals of about 8 ns; the stronger pulses containing about 1 mJ of energy. The second form\(^{23}\) contains the ion in a crystal of yttrium aluminum garnet (YAG). This is operated to give a continuous train of subnanosecond pulses with pulse energies measured in microjoules.

It is conceivable that the use of a sampling technique in the detector system might allow the use of the continuously operating Nd:YAG laser in spite of the lower output. However the extra cost of that laser dictated against its use.
The Nd:glass mode-locked laser appeared suitable provided somewhat more than 1 mJ per pulse could be obtained and then the light frequency doubled with high efficiency. As frequency doubling efficiencies of better than 20 percent had been reported in the literature, it seemed that the approach would be practical; perhaps with a somewhat lower signal-to-noise ratio than actually desired.

2.6.3 Detection. The detection system requires some gain as the luminescent power is low. With the proposed excitation system, there is no long repetitive chain of identical pulses and hence a sampling system cannot be used. The problem then is to design a detector-amplifier-oscilloscope system with a resolution as close as possible to the estimated picosecond duration\(^{24,25}\) of the excitation pulses.

The fastest photodetectors have a resolution somewhat better than 1 ns. Oscilloscopes are available with similar resolution. The only suitable amplifiers with such resolution are the electron multipliers which are built into photomultipliers; so the problem simplifies to that of choosing a suitable photomultiplier-oscilloscope combination.

The fastest suitable oscilloscope commercially available is the Tektronix 519 traveling-wave oscilloscope with a resolution of 0.3 ns, and one was fortunately available for use. Its disadvantage is that 10 V input (into 125 Ω) is required to cause a deflection of 1 cm. Thus currents of about 100 mA are required from the photomultiplier. From
the earlier discussion the lowest useful cathode current would be about $10^{-8}$ A as anything less would be lost in the shot noise. Hence the requirements of the photomultiplier are that it must have a current gain capability of at least $10^6$, an S-20 response, deliver 100 mA output and have a resolution preferably better than 1 ns.

A survey of commercial photomultipliers showed that the choice was limited but that one could be obtained (developmental type RCA C70045C) which would just meet the requirements. It has a 0.5 ns rise time, and the fall time is not specified. The reason for the fall time not being specified is that photomultipliers are normally evaluated with electric sparks which have a sharp rise but a slow fall. The major problem with this photomultiplier would be that the 100 mA output will damage the dynodes if it lasts for more than 2 ps, whereas the lifetime of the R-line luminescence is 5 ms. This problem and its solution will be discussed in the chapter on equipment development.

### 2.7 Conclusions

It has been shown that Maiman's estimate of the $^4T_2$ lifetime was too high by at least an order of magnitude and that some theoretical estimates were also incorrect. In addition, the reported emission from the $^4T_2$ state needs further investigation.

The measurement of a subnanosecond lifetime requires detection equipment with a bandpass wider than 1 GHz. This results in a shot noise problem. The high power of the
mode-locked laser should result in a signal-to-noise ratio which is sufficient, by a small margin, to carry out the experiments provided care is exercised in optimizing the equipment.

The development and optimization of the equipment is described in Chapters III and IV.
CHAPTER III. DEVELOPMENT OF THE MODE-LOCKED LASER

3.1 Background

DeMaria, Stetser and Heynau\textsuperscript{22} first demonstrated mode-locked pulses from a Nd:glass laser in 1966. They used a passive mode-locking technique similar to that used by Mocker and Collins\textsuperscript{27} to obtain such pulses from a ruby laser in 1965. A saturable dye introduced into the cavity caused simultaneous Q-switching and mode-locking resulting in a train of very short pulses. The train had an envelope similar to that of a regular Q-switched output lasting about 200 ns. Within the envelope, the pulses were shorter than the resolution time of the detection system (0.5 ns) and were separated by twice the resonator transit time, about 9 ns for the resonators they used. The spectral content of the output indicated that the pulses could be as short as 0.1 ps. The individual pulses contained about 1 mJ.

DeMaria, Stetser and Glenn reviewed the properties of such lasers in some detail in a recent article.\textsuperscript{28}

By using two photon fluorescence in certain organic dyes, Giordmaine et al.,\textsuperscript{29} and Rentzepis and Duguay\textsuperscript{24} demonstrated in 1967 that such pulses were generally 10 ps in duration or less. More recently (1969), Shapiro and Duguay\textsuperscript{25} refined the measuring technique and demonstrated the pulses to be typically 0.25 ps long.
In Appendix B the theory and nomenclature applicable to mode-locked lasers is reviewed and discussed.

3.2 Initial Attempt at Mode-Locking

Attempts were initiated to duplicate DeMaria's sub-nanosecond pulses in November 1967. The development of the laser was started from a standard Optics Technology Model 130 laser which was available. The geometry of the laser is illustrated in Fig. 3.1a. There was room in the resonator to insert an Eastman dye cell No. 6088 which was filled with Eastman dye No. 9860 (proprietary) dissolved in dichloroethane.

The laser departed from DeMaria's in the following ways. The resonator was shorter, the laser rod ends were polished square rather than at Brewster's angle, one reflector was a TIR prism, and the other an etalon of flats rather than dielectric mirrors. Three months were spent in determining that this system would not mode-lock.

3.3 Achievement of Mode-Locking

A decision was made to duplicate DeMaria's laser more closely. The new geometry is illustrated in Fig. 3.1b. Evidence of mode-locking was immediately obtained but was somewhat inconsistent, as the pictures in Fig. 3.2 illustrate. The photograph in Fig. 3.3 shows the laser.

Considerable effort was expended on varying the parameters of the laser in efforts to improve the consistency of the output. The efforts were unsuccessful. The conclusion
FIG. 3.1 INITIAL GEOMETRIES OF THE LASER.
FIG. 3.2 EARLY EXAMPLES OF MODE-LOCKED OUTPUT.
FIG. 3.3 MODE-LOCKED LASER IN AN EARLY FORM.
was reached that, at the present state of the art, one can only hope to achieve a certain probability that full mode-locking will develop from the background noise. Because the noise itself is random, the extent of mode-locking will be somewhat random. As the mechanism is not fully understood, it is quite possible that apparently unimportant variations between different setups may affect the probability of attaining full mode-locking. This discussion is developed more fully in Appendix B.

A serious factor in the situation is that certain of the random waveforms obtained from this type of laser appear extremely destructive to the materials within the resonator. On several occasions, there was a noise sounding like a pistol shot from the laser during firing and subsequent examination showed damage to the dye cell windows or to the dielectric mirrors. It was the possibility of such damage which effectively limited the safe peak power output when using the DeMaria configuration. This limited the dye concentration which could be used, as higher dye concentrations increase the Q-switching and hence the energy stored in the amplifying medium.

3.4 Conclusions Drawn from the Initial Mode-Locking Experiments

The important features of passive mode-locking which have been established in the literature, and which were confirmed, are as follows.
1. Certain nonlinear absorbing dyes with a lifetime of approximately 10 ps do encourage the noise to develop into a fully mode-locked output.

2. Any partially reflecting elements within the resonator can degrade the extent of the mode-locking. For this reason, Brewster-angled laser rods should be used and dye cells or any other objects within the resonator should be designed such that any stray reflections promptly leave the resonator. Care must also be taken that no external equipment reflects light back into the resonator.

3. The saturable dye should be placed as close to one end of the resonator as possible to discourage multiple pulses within the basic period of the output. It was also found that care must be taken in specifying the mirrors, owing to the high-power densities. The high-damage threshold mirrors (500 MW/cm²) from Optics Technology Corp. are suitable, whereas the regular quality ones are not.

3.5 Improvement on the State of the Art

3.5.1 Discussion. With the above considerations in mind, it was decided that the mode-locking might be improved if the effective nonlinearity of the dye were increased. Optical reduction of the beam diameter in the dye seemed to be the simplest way of achieving this. The result would be an increase of the power density in the dye relative to that in the amplifying medium. As the increase in dye transmission is proportional to the power density (at low power), the
effective nonlinearity would be enhanced proportionately to the ratio of the beam cross section in the amplifying medium to that in the dye.

If the resonator includes a spherical mirror, the laser beam cross section becomes nonuniform with axial distance. The power density for a fundamental mode of such a resonator has a Gaussian variation with distance from the axis. If the radius of one-half maximum intensity is plotted against axial distance, it appears as shown in Fig. 3.4.

The desired effect is obtained by placing the dye near the flat mirror and the amplifying medium near the spherical mirror. The beam area in the dye is about half that in the amplifying medium with this arrangement. An additional feature is that the resonator is no longer on the border line of stability, as discussed in Appendix B.

3.5.2 Results with the Modified Resonator. As no spherical mirror was available, one was simulated with a spectacle lens (f.1. 2 m) and a plane mirror. The probability of obtaining full mode-locking was much improved by the modification. Due to this improvement, a spherical mirror was obtained (radius 2.15 m). On substituting the spherical mirror, with everything else the same, it was found that the spherical mirror also led to much more consistent mode-locking than the DeMaria configuration, as was expected. A surprising result though was that the spherical
FIG. 3.4 VARIATION OF BEAM CROSS SECTION WITH AXIAL DISTANCE IN A RESONATOR WITH A PLANE AND A SPHERICAL MIRROR.
mirror arrangement was not quite as consistent as the lens arrangement. The last effect has still to be explained. The losses from the system are greater with the lens and the optical quality of the resonator is also somewhat degraded, but it is not certain that either of these factors caused the effect.

In an effort to pin down the optimum parameters for the laser, a series of experiments was carried out to determine the effect of varying the parameters. The results follow.

3.5.3 Choice of Dye. Two dyes have been reported in the literature as suitable for mode-locking Nd:glass lasers. Both are proprietary Eastman products. The dyes are No. 9860 dissolved in dichloroethane and No. 9740 dissolved in chlorobenzene.

Curves of transmittance against steady-state power density have been published. Table 3.1 is constructed from these curves.

<table>
<thead>
<tr>
<th>Dye (Eastman)</th>
<th>Power density at which transmittance doubles from initial value of 0.25</th>
<th>( \frac{d(\text{transmittance})}{d(\text{MW per cm}^2)} ) at low power</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 9740</td>
<td>40 MW/cm(^2)</td>
<td>0.008 per MW/cm(^2)</td>
</tr>
<tr>
<td>No. 9860</td>
<td>55 MW/cm(^2)</td>
<td>0.006 per MW/cm(^2)</td>
</tr>
</tbody>
</table>
There has been no published comparison between the effectiveness of the two dyes for mode-locking. Accordingly, the two were compared in the DeMaria configuration (plane mirrors) and the No. 9740 was found to be slightly more consistent. It is assumed that this is due to the higher non-linearity at low power densities which should increase the likelihood of developing mode-locking from the original amplified noise.

3.5.4 Reflecting Optics. Three configurations of the reflecting optics were evaluated. The configurations are shown in Fig. 3.5. The cavity lengths were varied between 54 cm and 130 cm for all three configurations. The transmission of the dye cell was 81 percent at 1.06 µm wavelength. The laser did not always lase when fired. However each time it did an oscillogram was obtained. A total of 100 time-resolved oscillograms were taken using the United Aircraft 1240 detector and Tektronix 519 oscilloscope. The oscillograms were used to determine the number of pulses in the output per "round-trip" time of the cavity (≈ 7 ns). One such pulse was taken to indicate complete mode-locking. It was found that the form of the reflecting optics was highly significant whereas the cavity length was not. The results appear in Table 3.2
FIG. 3.5 THE THREE CONFIGURATIONS OF THE REFLECTING OPTICS.
Table 3.2
Probability of Mode-Locking for Different Resonator Optics

<table>
<thead>
<tr>
<th>Optics</th>
<th>Percentage of oscillograms showing complete mode-locking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane mirror</td>
<td>13</td>
</tr>
<tr>
<td>Spherical mirror</td>
<td>72</td>
</tr>
<tr>
<td>Plane mirror plus lens</td>
<td>90</td>
</tr>
</tbody>
</table>

When the mode-locking for the plane mirror arrangement was imperfect (most of the time), there were frequently as many as four pulses occurring in the cavity round-trip time. The spherical and lens mirror arrangements never showed more than two pulses in this time.

In Fig. 3.6a one of the better pulse trains obtained with the lens arrangement is displayed. Typical examples from all three arrangements are shown in Figs. 3.6a through d.

3.5.5 Likelihood of Lasing. The results of the preceding section indicated that when lasing was obtained, the plane mirror and lens arrangement was much more likely to give complete mode-locking. Another interesting result obtained was that the likelihood of lasing was dependent upon the optics and the cavity length. To further analyze the situation, another series of tests was carried out to observe the likelihood of lasing under different conditions.
FIG. 3.6 EXAMPLE OF IDEAL Q-SWITCHED MODE-LOCKING AND TYPICAL WAVEFORMS FROM THE THREE REFLECTOR CONFIGURATIONS.
The energy output of the laser was monitored using the diode calorimeter (to be described in Chapter IV).

The laser was always operated with an energy input approximately 5 percent above threshold. It was observed that the output was always either in the full output region of about 25 mJ total, or just observable, but less than 2 mJ. In the cases of full output, the waveforms would be as observed in Fig. 3.6; but in the case of the low-energy outputs a waveform could not be obtained because of triggering and timing problems. It is assumed that in the latter cases, the laser began to go into oscillation but the initial waveform was such that the losses in the dye were too great for oscillation to be sustained. This might be the case if the initial waveform were too uniform with time.* The results showed that the plane mirror arrangement always lased fully, whereas both of the other arrangements had a likelihood of full lasing which varied with cavity length in the manner shown in Fig. 3.7. The results of 282 firings are summarized in the curve. The results of the spherical mirror and lens mirror arrangements are combined as they were similar. To reduce the statistical variation, each point is the average of all readings taken with a cavity length within 10 cm of the indicated figure.

*The nonlinearity of the dye results in higher absorption from a signal with a uniform power level than from one with the same average power but fluctuating.
FIG. 3.7 PROBABILITY OF FULL LASING AS A FUNCTION OF CAVITY LENGTH FOR ARRANGEMENTS "S" AND "L."
3.5.6 Conclusions on Reliability and Expected Output. The conclusions were that sufficiently reliable mode-locking could be obtained if the lens mirror arrangement was used, with a cavity length less than 70 cm. The total energy output under these conditions was about 25 mJ, with about 1.2 mJ in each of the biggest pulses. Oscillograms such as those in Fig. 3.6 indicate that the individual pulses are no more than 0.5 ns long at half height. The shape of the pulse in the oscillograms is the characteristic response of the UA 1240 detector to a pulse shorter than its resolution time.

3.5.7 Pulse Length. The oscillograms showed that, when the laser was operating correctly, the output pulses lasted less than 0.5 ns. Pulse length measurements of better resolution were made using a modified form of the Giordmaine et al.\textsuperscript{29} two-photon fluorescence method. The method is outlined here and described in more detail in Chapter IV.

The laser output passes into a cell containing rhodamine 6G dissolved in ethanol and carbon tetrachloride. It strikes a mirror which reflects the beam almost back on itself. As the two-photon fluorescence is a quadratic effect, it is enhanced where a reflected pulse overlaps an incoming pulse. Hence a short pulse in the output produces a bright band at the mirror where it is reflecting back upon itself; and if there is more than one pulse, bright bands are produced where they cross in the dye. The fluorescence
track is photographed. The measurements were made with a resolution of approximately 5 ps. The results indicated that when the laser was carefully tuned, each pulse resolved in the oscillograms consisted of two or three narrower pulses, each of about 5 ps or less. The distance between these narrower pulses was dependent upon the distance between the laser mode-locking dye cell and the end mirror. These results are in agreement with those reported by previous investigators.\textsuperscript{24,28,29} Some photographs of the two-photon fluorescence appear in Fig. 3.8. The oscillograms appearing alongside were taken simultaneously with the UA 1240 detector and the Tektronix 519 oscilloscope using a beam divider.

3.5.8 Improved Energy Output. In the earlier experience with the plane mirror geometry, it was found that efforts to increase the energy output of the laser by increasing the dye concentration resulted in occasional damage to the laser components, particularly to the anti-reflection coating on the windows of the dye cell. With the lens mirror arrangement it was found possible to increase the concentration of the dye appreciably without the unfortunate results noted before. As the dye concentration was increased so as to obtain more output energy, it was observed that bleaching of the dye increased during operation. When the dye was sufficiently concentrated that the transmission at 1.06 μm was only about 50 percent, a milky brown deposit appeared in the dye in the area through which the laser beam passed.
FIG. 3.8 SIMULTANEOUS TWO-PHOTON FLUORESCENCE PICTURES AND OSCILLOGRAMS OF LASER OUTPUT.
A dye transmission of about 60 percent was found to provide a good compromise for obtaining higher energy without being troubled too much by bleaching or deposit formation. Under these conditions about 300 mJ was obtained in each pulse train (as measured by a TRG calorimeter). This corresponds to about 12 mJ in each of the bigger pulses.

3.6 Frequency Doubling

The laser output at 1.06 μm wavelength was frequency-doubled to 0.53 μm by passing through a crystal of KDP. The technique is described by Maker et al. \(^{33}\) It relies on the nonlinearity of the polarizability tensor. To obtain efficient frequency doubling the refractive indices for the two wavelengths must be matched. In KDP it is possible to choose a propagation direction such that the extraordinary index at 0.53 μm matches the ordinary index at 1.06 μm.

Two different KDP crystals were used in these experiments. Both were 5 mm square. One was 10 mm long in the propagation direction, and the other 20 mm. The shorter one gave about 18 percent energy conversion and the longer one, about 25 percent energy conversion. The crystals were oriented experimentally to maximize the energy output at 0.53 μm. A curve of energy output vs. orientation angle (in the plane including the c-axis) is shown in Fig. 3.9.
FIG. 3.9 EFFICIENCY OF FREQUENCY DOUBLING AS A FUNCTION OF DEPARTURE FROM IDEAL ORIENTATION.
3.7 Form of Laser for Initial Lifetime Measurements

For the initial lifetime measurements at 300° K and 77° K, the laser components were mounted on a granite block with top dimensions 4 feet by 10 feet. The laser cavity was 60 cm long and the configuration was as in Fig. 3.5c. The frequency doubling KDP crystal was located at approximately 90 cm from the laser output mirror. The Optics Technology Model 130 laser power supply was used, modified by disconnecting two of the three 220 μF storage capacitors. The 6 inches by 3/8-inch diameter Nd:glass rod was mounted in the Optics Technology Model 130 flash lamp housing.

The input to the flash lamps was about 500 J. When the laser was carefully tuned, it usually produced a train of pulses as illustrated in Fig. 3.6a. The oscillograms of the output were similar before and after frequency doubling. The total energy in the train at 1.06 μm was about 250 mJ, with about 10 mJ in each of the bigger pulses. After frequency doubling there was about 2 mJ in each of the bigger pulses.

Table 3.3 compares the results from all the published reports, which could be found, with the results obtained here.
Table 3.3
Published Mode-Locking Results
Compared with Those Obtained by the Author

<table>
<thead>
<tr>
<th>Reported By</th>
<th>*Peak Power</th>
<th>Laser Rod Dimensions (cm x cm diameter)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>DeMaria et al.</td>
<td>3 MW</td>
<td>12.2 x 0.95</td>
<td></td>
</tr>
<tr>
<td>Stetser and DeMaria</td>
<td>200 MW</td>
<td>12.2 x 0.95</td>
<td></td>
</tr>
<tr>
<td>Penney and Heynau</td>
<td>250 MW</td>
<td>30.5 x 1.8</td>
<td>0.2 J/pulse, 0.8 ns</td>
</tr>
<tr>
<td>DeMaria et al.</td>
<td>600 MW</td>
<td>53.0 x 1.3</td>
<td>0.25 J/pulse, 0.4 ns, 2.8 kJ input</td>
</tr>
<tr>
<td>Basov et al.</td>
<td>800 MW</td>
<td>No details</td>
<td></td>
</tr>
<tr>
<td>DeMaria et al.</td>
<td>3.5 GW</td>
<td>76.0 x 1.8</td>
<td>7 J/pulse, 2 ns, 72 kJ input</td>
</tr>
<tr>
<td>Obtained Here</td>
<td>1 GW</td>
<td>16.0 x 0.95</td>
<td>Only 8 cm of rod is pumped</td>
</tr>
</tbody>
</table>

*These peak powers are based on an estimated pulse duration of 10 ps. A recent report by Shapiro and Duguay indicates the pulses were probably less than 1 ps long, hence
3.8 Laser Redesigned as a Result of Initial Experiments

3.8.1 Construction. The initial experiments showed the lifetime of the $^4T_2$ state to be still less than 2 ns at 77° K. It was decided that a measurement should also be made at liquid helium temperature. This required either that liquid helium equipment be set up in the Institute of Science and Technology or that the laser and existing equipment be moved to an existing helium facility.* It was decided that the latter would be the more practical approach.

The laser had not been designed to be portable so it had to be reengineered. As the initial experiments showed a shorter pulse train would be desirable, means were incorporated in the new version of the laser for extracting just a few pulses out of the train. A photograph of the new laser, without its covers, appears in Fig. 3.10. The details of the laser section appear more clearly in Fig. 3.11. A schematic of the whole assembly is shown in Fig. 3.12.

The bed consists of a box section 53 inches long, made by welding together two pieces of aluminum U channel 7 inches by 2.11 inches by 0.23 inch thick. The bulkheads are constructed from similar channel. The bed is supported by three leveling screws which sit on legs projecting upwards from a wooden base.

*Generously made available by Professor T. M. Dunn of the Department of Chemistry.
FIG. 3.10 THE PORTABLE MODE-LOCKED LASER ASSEMBLY WITH COVERS REMOVED.
FIG. 3.11 THE Nd:GLASS LASER SECTION OF THE ASSEMBLY.
FIG. 3.12 SCHEMATIC OF THE MODE-LOCKED LASER ASSEMBLY.
3.8.2 Alignment. A small He-Ne gas laser is used for alignment and is permanently attached underneath the main assembly bed. The gas laser beam passes through a folded optical path of about 200 cm before entering the Nd:glass laser through the 99.5 percent reflectance cavity mirror. The incorporation of the gas laser allows easy alignment of the laser by a technique previously described by the author. The gas laser beam also traces the Nd:glass laser output through the optics and into the experiment. This is an extremely useful feature allowing rapid alignment of all the components and correct aiming of the laser output on the sample. It should be noted that both of the cavity mirrors have reflectances of about 5 percent at the gas laser wavelength.

3.8.3 Monitoring of Output Energy. Underneath the bed there is a device for sliding a mirror into the folded optical path to reflect the small fraction of the Nd:glass laser energy which exits through the 99.5 percent cavity mirror. The slider reflects the energy into a diode calorimeter for monitoring the Nd:glass laser output. The slider has three positions. The first leaves the folded optical path open for alignment of the Nd:glass laser by the gas laser. The second introduces a plane glass slide at 45 degrees, so that a portion of the gas laser light returning from the Nd:glass laser is reflected into the calorimeter to check its correct position. The third introduces a mirror at 45 degrees so that all the Nd:glass laser light
exiting through the plane cavity mirror is reflected into the calorimeter. This also isolates the gas laser. The calorimeter appears in the foreground of Fig. 3.11.

3.8.4 Resonator Configuration. The configuration of the Nd:glass laser is as shown in Fig. 3.5c. The distance between cavity mirrors is 80 cm. The lens, with f.l. 2 m, is at 2 cm from the 99.5 percent mirror. The Optics Technology flash lamp and laser rod housing is centered at 17 cm from the 99.5 percent mirror.

3.8.5 Frequency Doubling and Pockels Cell Switching. The KDP frequency-doubling crystal (20 mm long) is in a gimbal mount to allow precise orientation. After traversing the KDP, the beam passes through a glass slide at 45 degrees and then through a Pockels cell and a polarizer. The glass slide diverts some energy to break down a spark gap which initiates the application of a pulse of 7000 V to the Pockels cell. The high-voltage pulse lasts for only 15 ns. When 7000 V is applied to the Pockels cell, the light at 0.53 μm wavelength has its polarization rotated through 90 degrees, while passing through the cell, into a plane which allows it to pass through the polarizer. The result is that only a few pulses of the frequency doubled laser beam pass through the output polarizer. A Fisch-Schurman BG-18 filter is used to absorb any remaining light at 1.06 μm wavelength. A typical oscillogram of the output appears in Fig. 3.13. The operation of the Pockels cell switching is described more fully in Chapter IV.
FIG. 3.13 EXCITATION PULSES OF 0.53 μm WAVELENGTH.
The incorporation of the spark gap, as well as providing the switching for the Pockels cell, solved a major experimental problem; that of reliably triggering the Tektronix 519 oscilloscope. For subsequent experiments, the oscilloscope was externally triggered by a pulse obtained from the spark gap circuit. Correct action of the spark gap was also monitored by recording a similar pulse on a storage oscilloscope. The output of the diode calorimeter (to be described in Chapter IV) was recorded on the second trace of the storage oscilloscope. Hence correct timing of the spark breakdown relative to the laser output was monitored.

3.8.6 Power Supply and Cooling. The laser is powered by a Variac-controlled 3000 V power supply which charges a bank of three 100 μF capacitors. An adjustable relay instrument controls the potential to which the capacitors are charged. A firing circuit delivers a 900-V pulse to the laser pulse transformer and a 15-V pulse to trigger the monitoring storage oscilloscope when the firing button is depressed. The 10 kV output of the pulse transformer ionizes the flash lamps and initiates the discharge of the capacitor bank. The capacitors discharge into the flash lamp circuit through a 100 μH inductor bank to give a pulse of light with about 0.3 ms halfwidth.

The power supply equipment was generously loaned by Dr. A. H. Francis of the Department of Chemistry.
The laser is cooled by a blower fan which draws air through an automobile air filter and delivers it through a flexible hose to the flash lamp housing. This can be seen in the foreground of Fig. 3.10.

3.9 Summary

A rugged and relatively compact laser assembly has been developed which is capable of delivering a train of three subnanosecond pulses of green light (0.53 \( \mu \)m wavelength). Each pulse has an energy of about 1 or 2 mJ, with a peak power of the order of 1 GW. The laser can be modified quickly for operation in other modes.

The incorporation of a gas laser allows rapid internal alignment and aiming of the output. Provision for energy monitoring is incorporated. An electrical pulse output from the Pockels cell switching circuit gives a timing base for experiments.
CHAPTER IV. DEVELOPMENT OF SUBSIDIARY EQUIPMENT AND TECHNIQUES

4.1 Introduction

The equipment requirements were set forth in Chapter II. The development of the intense laser light source was covered in the last chapter. The development of the necessary detection and monitoring equipment will be described here. This chapter will also include development of the Pockels cell switching of the light and some details of the laser alignment technique. The considerable equipment development was necessitated by the lack of an established technology in the control and measurement of subnanosecond optical signals.

4.2 Method of Aligning the Laser

The technique used was similar to that previously described\textsuperscript{39} by the author.

The laser mirrors were 99.5 percent and 55 percent reflective at 1.06 \textmu m wavelength. However, at the 0.633 \textmu m wavelength of the gas laser used for alignment, they were only about 5 percent reflective. It is interesting to note that some difficulty was found in distinguishing between the reflections from the back and front surfaces of the mirror. The back surfaces, which were wedged relative to the front surfaces, were antireflection coated for 1.06 \textmu m.
The differentiation between the reflections had to be on a trial and error basis.

The gas laser was placed at about 100 cm from the laser in such a way that its output beam passed along the intended axis of the laser. The components were aligned along the beam. A white plate with a 1 mm diameter hole was centered on the beam at the gas laser output. The mirrors were adjusted so that the reflections from their front surfaces passed back through the aperture. Generally an interference pattern was obtained on the white plate around the aperture. The pattern became a set of concentric rings when the mirrors were perfectly aligned. In the final portable version of the laser, the longer folded optical path incorporated four mirrors. As the mirrors were of rather poor quality, the reflected spots at the aperture plate did not produce a meaningful interference pattern. This reduced the accuracy of the alignment but after initial alignment with the gas laser one of the mirrors was finally adjusted to give maximum energy output from the laser. However very little final adjustment was required.

4.3 Diode Calorimeter

4.3.1 Requirement. This instrument was developed to indicate whether the laser was working correctly and to monitor the output energy. It has sufficient time resolution to indicate whether more than a single train of pulses is produced. This is rather important as a fairly small
increment of input energy above threshold can cause a double train output.

The output of the diode calorimeter is displayed on a Tektronix 564 storage oscilloscope. The display can be stored for more than thirty minutes, which is an experimental convenience. The alternative methods of monitoring the output require the experimenter's attention during firing of the laser, and so detract from his ability to experiment.

4.3.2 Construction of Diode Calorimeter. Without special precautions, there is a danger of "losing" such extremely short pulses when measuring energies with a diode detector. A biased Hewlett-Packard pin diode was used as the sensing element. The HP 4203 diode was selected for its high speed and nondirectional properties. In view of the high peak powers of about 1 GW, the diode was placed 5 cm from a diffuser. The diffuser consisted of two layers of opal glass to ensure that the response of the instrument would not be directional. Provision for attenuators was included between the diffuser and the diode. The details appear in the photograph in Fig. 4.1.

When light falls on the diode, the current which flows is used to charge a 0.001 μF capacitor, as indicated in the circuit diagram of Fig. 4.2a. The voltage across the capacitor gives a measure of the energy which has reached the diode, provided the time involved is considerably less than the decay time of the circuitry (about 1 ms).

A 0.01 μF capacitor provides the short-term energy store for the circuit. It can be seen that the only part of
FIG. 4.1 PHOTOGRAPH OF THE DIODE CALORIMETER.
FIG. 4.2 SOLID-STATE DIODE CALORIMETER.
the circuit which requires fast response is the ring consisting of the diode and two capacitors. As the pulses of light falling on the diode last about 1 ps, any stray inductance in the fast circuit could affect the response. To reduce that possibility, the diode and capacitors were built in a sandwich construction as shown in Fig. 4.2b. The copper plates, separated by Mylar, supply about 25 pF towards each of the capacitances and provide a low inductive circuit for the individual pulses.

The integrating capacitor voltage is monitored by a Tektronix storage oscilloscope, Model 564. The oscilloscope is triggered by the laser firing circuit. The stored sweep is at 0.1 ms/cm. The energy of the laser output train of pulses (lasting less than 0.5 μs) is registered as a vertical step in the stored sweep. A calibration was obtained relating the deflection volts with the energy entering the calorimeter.

In the portable version of the laser, this calorimeter received the light exiting through the 99.5 percent mirror and thus always monitored the laser output. For this purpose a neutral density one attenuator was incorporated. A typical voltage recorded on the oscilloscope was about 0.04 V. Calibration against a TRG Model 100 calorimeter indicated that the laser output was 3.2 J/V registered by the diode calorimeter.

4.3.3 Calibration of Diode Calorimeter. The calorimeter was calibrated with continuous power input from a
He-Ne laser. When power fluctuations are slow compared with the time constant of the instrument (about 1 ms), the current output is proportional to the incident light power. By comparing the calorimeter with a Coherent Radiation Model 200 power meter, it was found that the instrument gave 1.8 nA/mW of input, with no attenuators, at 0.633 μm wavelength. This is readily converted to an energy calibration for pulses lasting considerably less than the time constant of the instrument as follows

\[(\text{Current}) = K(\text{Power}) \]  \hspace{1cm} (4.1)

If both sides are integrated with respect to time, then

\[(\text{Charge}) = K(\text{Energy}) \]  \hspace{1cm} (4.2)

If the coulombs all go into the integrating capacitor, then the capacitor voltage "V" is given by

\[V = \frac{K}{C} (\text{Energy}) \]  \hspace{1cm} (4.3)

where "C" is the capacitance.

The requirement that virtually all the charge goes into the integrating capacitor is met if the measurement is completed in a time considerably less than the decay time constant of the instrument. The resultant energy calibration, using the spectral response characteristic of the diode, is given in Table 4.1.
Table 4.1
Calibration of Diode Calorimeter

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>J/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.53 μ</td>
<td>6.8 x 10^{-4}</td>
</tr>
<tr>
<td>0.633 μ</td>
<td>5.7 x 10^{-4}</td>
</tr>
<tr>
<td>1.06 μ</td>
<td>2.5 x 10^{-3}</td>
</tr>
</tbody>
</table>

4.4 Power and Energy Measurement of Individual Pulses

4.4.1 General Considerations. The United Aircraft Corp. detector UA 1240 was used with the Tektronix 519 oscilloscope for examining the details of the mode-locked train of pulses. Typical oscillograms appear in Figs. 3.6 and 3.13. The structure of the individual pulses in such oscillograms is a characteristic of the detecting system rather than the pulses. The detector is specified to produce electrical pulses of not more than 0.3 ns width at half maximum when following a light pulse lasting a shorter time. Since the plateau is just below the half-height and the response of the oscilloscope is 0.3 ns, the detector is within specifications. Until it was determined that the pulse shape was characteristic of the detector, there was some confusion as the pulse shape could have been the result of a double pulse from the laser.

Since the pulses are not resolved, their power cannot be measured by the detection system. However, their energy can be measured if two assumptions are made. The first assumption is that when an extremely short burst of photons
hits the cathode, the number of electrons arriving at the anode is the same as if the photons were spread over a longer period but the electrons are spread over about 0.3 ns (due to varying paths and electron-electron repulsion).

The second assumption is that the oscilloscope and cables will have approximately the same energy loss when following a signal lasting about 0.3 ns as when following a more slowly varying signal, although the pulse is lengthened to about 0.5 ns.

For slowly varying signals the oscilloscope current "i" is related to the received light power "W" by

\[ i = kW \quad , \quad \text{(4.4)} \]

and for short pulses, it follows from the preceding assumption that

\[ \int i \, dt = k \int W \, dt \quad , \quad \text{(4.5)} \]

If the impedance of the oscilloscope is "R," then the deflection plate voltage is given by

\[ V = Ri \quad . \quad \text{(4.6)} \]

Hence for short pulses,

\[ \int V \, dt = R \int i \, dt = Rk \int W \, dt \quad , \quad \text{(4.7)} \]

while for slowly varying signals
\[ V = R k W \]  \hspace{1cm} (4.8)

Thus the area under the pulse displayed on the oscilloscope is a measure of the actual light energy. Furthermore the factor

\[ K = R k \]  \hspace{1cm} (4.9)

can be obtained from a CW calibration.

4.4.2 Direct Calibration of the UA 1240 Detector. The detector was calibrated against a Coherent Radiation, Inc., Model 200 power meter, using a He-Ne gas laser as a source. The impedance of the 519 oscilloscope was simulated by a 125 \( \Omega \) resistor and the voltage developed across the resistor was measured with a microvoltmeter. The calibration at 0.633 \( \mu \)m wavelength was found to be

\[ K = 1.94 \mu V/mW \]  \hspace{1cm} (4.10)

As the detector has an S-1 response, this corresponds to \( K = 2.58 \mu V/mW \) at 0.694 \( \mu \)m. This compares with a tentative figure of \( K = 1.74 V/kW \) at 0.694 \( \mu \)m furnished by the manufacturer (revised from an earlier figure of 8.7). Differences between units could easily explain the discrepancies.

The measured calibration is translated to the wavelengths of the experiment in Table 4.2. As the average width of the characteristic display for a very short pulse is about 1 ns, then the area under such a pulse is given by

\[ \int V \, dt = V_p \times 10^{-9} \]  \hspace{1cm} (4.11)
where $V_p$ is the peak voltage.

Table 4.2

Power Calibration of UA 1240 for Slowly Varying Signals

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>W/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.06 $\mu$m</td>
<td>$2.2 \times 10^3$</td>
</tr>
<tr>
<td>0.53 $\mu$m</td>
<td>$1.2 \times 10^3$</td>
</tr>
</tbody>
</table>

Hence, from the foregoing, when a pulse characteristic of the detector is displayed, the energy incident on the detector can be obtained from the factors in Table 4.3.

Table 4.3

Energy Calibration of UA 1240 for Short Pulses

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>J/V peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.06 $\mu$m</td>
<td>$2.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>0.53 $\mu$m</td>
<td>$1.2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

As the mode-locked pulses contain 1 mJ or more, it can be seen that attenuation is desirable. The most practical way to attenuate a signal with extremely high power is to reflect it from a diffusing reflector. The attenuation is then adjusted by varying the distance between the detector and the diffusing reflector.

4.4.3 Calibration of UA 1240 Detector with Diffuse Reflector. A diffuse reflector was made by casting a plate
of plaster of paris which was then smoked with magnesium oxide from burning magnesium. The diffusing reflector was fastened to the end of a 50-cm long optical bench, perpendicular to the bench axis. The UA 1240 detector was supported on the bench. The distance of the detector cathode from the diffusing reflector could be varied and was indicated on the optical bench scale. The instrument was used as shown in Fig. 4.3. It was arranged so that the beam to be measured was always incident on the diffusing plate at 60 degrees, although tests showed that the measurement was unaltered even if the angle deviated by 15 degrees.

The calibration method of Section 4.4.2 was used. The inverse square law held over the adjustment range of 6 to 40 cm. The calibration factors which were obtained are listed in Table 4.4.

Table 4.4
Calibration of UA 1240 with Diffuse Reflector

<table>
<thead>
<tr>
<th>λ</th>
<th>W/V cm² (long pulses)</th>
<th>J/V cm² (pulses &lt; 1 ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.06 μ</td>
<td>1.5 x 10³</td>
<td>1.5 x 10⁻⁶</td>
</tr>
<tr>
<td>0.53 μ</td>
<td>7.8 x 10²</td>
<td>7.8 x 10⁻⁷</td>
</tr>
</tbody>
</table>

To obtain power or energy, the appropriate factor in Table 4.4 is multiplied by the peak voltage indicated on the oscilloscope and the square of the distance between the
FIG. 4.3 USE OF UA 1240 DETECTOR WITH DIFFUSE REFLECTOR.
reflector and cathode. Deflections of about 10 V (or 1 cm) on the oscilloscope are convenient so the instrument can measure pulse energies between 70 μJ and 30 mJ without any additional attenuators. This arrangement was used for all energy measurements of individual pulses. The measurements were compatible with energies of the full pulse train as measured by the diode calorimeter and the TRG Model 100 calorimeter. This implies that the necessary assumptions were valid.

The only problems with this detection system were that initially the characteristic pulse shape was confusing and the UA 1240 detector was prone to electric breakdown in its circuitry. The breakdowns caused considerable delays while the detector was being repaired. This problem was finally overcome by using only 1300 V for the high-voltage supply instead of the original 4000 V. There was no noticeable degradation in output.

Breakdown of the UA 1240 detector was troublesome as it was initially the only available instrument for checking whether the laser was mode-locking properly, i.e., producing subnanosecond pulses with the expected intervals. In the next section, the use of a solid-state diode for this purpose is discussed.

4.5 Solid-State Diode as A Mode-Locking Monitor

Delays caused by the breakdown of the UA 1240 detector indicated that a second detector capable of 0.5 ns resolution would be desirable. The characteristics of the
Hewlett-Packard HP 5082 series of pin photodiodes indicated that they would be fast enough if they could handle the 50 mA necessary to deflect the 519 oscilloscope trace by a reasonable amount.

An HP 5082-4205 diode was chosen. Its pillbox-type package allowed it to be soldered directly into an assembly consisting of a copper-Mylar-copper sandwich capacitor fastened in the end of a sawed-off Tektronix-GR 125-Ω connector. The construction, illustrated in Fig. 4.4, results in the signal being launched into the 125-Ω coaxial cable with minimum inductance. This is important when considering such rapidly varying signals.

The sandwich capacitor, with about 25 pF, supplies the charge store for responding to the individual pulses. Between pulses it is replenished from the 0.01 μF ceramic capacitor and the bias power supply.

Attempts to calibrate the instrument indicated that it was in a nonlinear regime when detecting the mode-locked pulses and hence it was not suitable for measuring energy. However, the oscillograms of Fig. 4.5 show that it is suitable for monitoring whether such a laser is fully mode-locking. Its economy is worth noting in this rather expensive field.
(a) CIRCUIT.

(b) CONSTRUCTION.

(c) PHOTOGRAPH.

FIG. 4.4 SOLID-STATE DIODE ASSEMBLY.
FIG. 4.5 OSCILLOGRAMS OF LASER OUTPUT USING THE SOLID-STATE DIODE ASSEMBLY.
Resolution of Pulses by Two-Photon Fluorescence

Giordmaine et al. have reported that picosecond resolution of intense short pulses of light may be obtained from two-photon fluorescence in certain organic dyes. If the light passes through a cell containing the dye, its path is marked by a uniform track of two-photon fluorescence. If a mirror is placed in the dye to reflect the light back upon itself, the track of fluorescence is no longer uniform. Since the fluorescence is quadratic with the light intensity, areas where two pulses cross are brighter, and in the vicinity of the mirror a brighter area indicates where each pulse is being reflected back on itself.

DeMaria et al. have used rhodamine 6G dissolved in ethanol for analyzing pulse trains at 1.06 μm wavelength. Initially the same solution was used but problems arose from absorption in the solvent with long dye cells.

The transmissions of a few other solvents were measured at 1.06 μm wavelength. The results were that whereas ethanol has an absorption coefficient of 0.137, carbon tetrachloride is the best with an absorption coefficient of only 0.005. Rhodamine 6G is not soluble in carbon tetrachloride. However a saturated solution of the dye in ethanol is readily soluble in carbon tetrachloride.

For the two-photon fluorescence measurements a dye cell 10-cm long was used with a mirror at one end to reflect the laser beam back on itself within one degree. Care must be taken to avoid reflecting it exactly back upon itself, as
the resultant feedback into the laser upsets the mode-locking. The cell was constructed from glass slide plates cemented with epoxy. The dye solution consisted of a saturated solution of rhodamine 6G in ethanol, reduced with five parts of carbon tetrachloride. The calculated solvent absorption of 20 cm of this solution is 43 percent, whereas if ethanol alone were used it would be 93 percent.

The track of fluorescence was photographed with a Tektronix-Polaroid oscilloscope camera similar to that used for obtaining oscillograms from the 519 oscilloscope. A photograph of the camera and dye cell assembly appears in Fig. 4.6. It has an f/1.3 aperture and reduces by a factor of 0.5. Typical photographs of two-photon fluorescence appear in Fig. 3.8. Allowing for the refractive index, the folded path, and the photographic reduction, 1 cm on the picture corresponds to approximately 0.2 ns or 5.8 cm in air. Each of the fluorescent tracks covers about 0.85 ns, i.e., slightly more than the resolution of the oscillograms. The pictures indicate that the individual pulses lasted 10 ps or less.

The more recent work of Shapiro and Duguay\(^{25}\) indicate that such pulses are typically 0.25 ps long. This suggests that the pictures in Fig. 3.8 may not be fully resolving the pulses. Shapiro and Duguay used a much more elaborate technique with a dye path of only 28 μm. The two-photon fluorescence pattern was scanned by moving the dye cell for successive laser firings. The two-photon emission is
FIG. 4.6 CAMERA AND DYE CELL FOR TWO-PHOTON FLUORESCENCE PICTURES.
monitored with a photomultiplier. Their method gave a resolution equal to the dye cell length of 28 μm, equivalent to about 0.1 ps.

4.7 Photomultiplier and Its Circuitry

4.7.1 Choice of Photomultiplier. From the discussion of Chapter II, it is apparent that a photomultiplier with a resolution of less than 1 ns capable of driving the Tektronix 519 oscilloscope was required.

An RCA 4459 tube was evaluated experimentally, but its resolution could not be made better than 4 ns. An RCA C70045C tube was then obtained and experimentally demonstrated to have a resolution capability better than 1 ns by observing the very occasional dark current pulses which were large enough to trigger the Tektronix 519 oscilloscope (about 0.5 V).

At the time the photomultiplier was chosen, a survey of commercially available photomultipliers showed that the RCA C70045C was the only tube available with a rise time of 0.5 ns or less. The fall times of photomultipliers are not so closely specified, as the manufacturers normally evaluate them with spark illumination, and the sparks have slower fall times. The speed of this photomultiplier arises partly from a tapered matched strip line connecting the anode directly to the coaxial output, and partly from accelerating electrodes between adjacent dynodes.26

The speed of the photomultiplier was evaluated by two methods. In the first method, the dark current pulses which
occasionally could be observed on the Tektronix oscilloscope were photographed. In the second method, the output of the mode-locked laser, much attenuated, was detected by the photomultiplier and displayed on the 519 oscilloscope. Oscillograms obtained from both methods appear in Fig. 4.7.

4.7.2 Development of Photomultiplier Circuitry. For reasons discussed in Chapter III, the Tektronix 519 oscilloscope is the only one suitable for displaying the output of the photomultiplier. The oscilloscope requires about 50 mA input for a reasonable deflection. This is within the specification for the maximum current of 100 mA which the photomultiplier may deliver. A problem arises when the average current rating of the photomultiplier is considered. It is only permitted to deliver 1 mA averaged over any 10 μs interval, whereas the luminescence of the R-lines lasts for about 5 ms.

To overcome this problem a circuit was devised which automatically reduces the gain of the photomultiplier before it can be damaged by an excessive average current. With this circuit incorporated, the photomultiplier follows the rise of the R-line luminescence, but its output then falls to less than 1 mA within 1 μs.

The circuitry for supplying the correct voltages to the 14 dynodes and 14 accelerating electrodes, and for the automatic gain reduction, is shown in Fig. 4.8. The action of the gain reduction circuit is as follows: normally the six transistors pass no current, and so all the dynodes and
FIG. 4.7 OSCILLOGRAMS DEMONSTRATING SPEED OF RESPONSE OF RCA C70045C PHOTOMULTIPLIER.
FIG. 4.8 PHOTOMULTIPLIER AND CIRCUIT DIAGRAM SCHEMATICS.

\[ C_1 = 0.0033 \mu F \]
\[ C_2 = 100 \text{ pF} \]
\[ D = \text{IN}4154 \]
\[ T = 2N699 \]
\[ R = 40.2 \text{ k}\Omega \]
\[ \tau = 1 \text{ M}\Omega \]
anodes are kept at their design potentials by the resistor networks. When the photomultiplier is giving an output, most of the anode current is supplied through the last dynode which is DY 14. When this current is less than 0.25 mA the current flows through the 4K resistor. At more than 0.25 mA, the voltage drop across the 4K resistor exceeds 1 V, and then diode "D" is over the knee in its characteristic and it allows an appreciable current to flow from the base to the collector of the first transistor. This causes the emitter-collector impedance to drop, bypassing the first r/2 resistor through the base and collector of the second transistor. As a result of the collector current increasing in the same way in successive transistors, each of the r/2 resistors is bypassed. This results in accelerator electrodes A5 through A10 departing from their design potentials by as much as 500 V causing the gain to be reduced by a factor of more than $10^3$ when the anode current is 1 mA.

4.7.3 Impedance-Matching Cable. The characteristic impedance of the photomultiplier output is 50 Ω and that of oscilloscope is 125 Ω. An adaptor can be used with a resistive network to match the impedances but this produces an energy loss of about 50 percent. As the photomultiplier has to operate very near its limit to drive the 519 oscilloscope, energy losses are undesirable.

A piece of tapered coaxial cable was constructed which varied gradually from 50-Ω cable at one end to 125-Ω
cable at the other. The center conductors of the 50-Ω RG-58 A/U and the 125-Ω RG-63/U were already closely matched. The major difference lay in the dielectric section. Ten lengths of polyethylene tubing, each about six inches long, with sections varying in roughly equal increments between that of the 50-Ω cable and the 125-Ω cable were used to fabricate the dielectric of the tapered cable. They were carefully butted and taped together with 0.001-inch Mylar tape and then covered with flexible tinned copper braiding. The braiding was laid over the exposed shielding of the 50- and 125-Ω cables and taped down tight.

The impedance-matching adapting cable was checked for transmission against a resistively matched adapting connector and an unmatched one using the pulse generator in the 519 oscilloscope. The same step input with 0.3 ns rise time was used for all three adaptors. Relative to the resistively matched adaptor (T50/N125), the tapered matching cable gave a step output greater by a factor of 1.7. The factor for the unmatched adaptor (N50/N125) was 1.5, and the reflection was greater than with the matching cable.

4.7.4 Dark Current Monitoring. As the photomultiplier was operated so near its maximum ratings, it was considered advisable to monitor the dark current at all times.

Provision was made for extracting any steady anode current for monitoring purposes in the following manner. A 10 kΩ resistor with a 2 mm lead was soldered to the central
conductor of the impedance-matching cable, with minimum disturbance to the dielectric and shielding. The other end of the resistor was soldered to the central conductor of a length of RG-58A/U cable. The shielding of the two cables was soldered together and then securely taped. To allow use of this dc monitoring cable, the connection to the 519 oscilloscope was made through a Tektronix 0.01 μF coupling capacitor. Any dc (such as dark current, or background) was monitored with a picoammeter. This introduced no observable degradation of the detection system.

4.7.5 Summary. The resultant detection system has a resolution capability of less than 1 ns as evidenced by the oscillograms of Fig. 4.7. Although operating near the maximum ratings of the photomultiplier, the controlling and monitoring devices provide safety.

A photograph of the photomultiplier in its housing, with impedance-matching cable, is shown in Fig. 4.9. The size of the housing will be understood when it is mentioned that the photomultiplier outer case is operated at 5 kV.

4.8 Pockels Cell Switching

4.8.1 General. The Pockels cell was purchased from the Isomet Corp. (Model E0A-415-B). It consists of a crystal of deuterated KDP (potassium di-deuterium phosphate). There are ring electrodes on the entry and exit faces. In the absence of an electric field, the material is uniaxial. The orientation is such that the light travels along the axis of symmetry, thus the material does not change the polarization
FIG. 4.9 PHOTOMULTIPLIER ASSEMBLY AND IMPEDANCE-MATCHING CABLE.
properties of the light. When an electric field is applied, the crystal becomes birefringent. The orientation is such that the polarized laser light travels along the z-axis (axis of uniaxial symmetry, with no field), with the E vector initially bisecting the angle between the x- and y- principal axes. As the light propagates through the birefringent crystal, the components with E vectors along the x- and y- axes travel at different phase velocities. If the applied electric field is such that one of the components lags behind the other by one-half wavelength at the exit face, the light emerges with its resultant linear polarization rotated by 90 degrees. If the lag is not a multiple of one-half wavelength, the light emerges elliptically polarized.

The emerging light passes through an analyzing polarizer which passes light with an E vector at 90 degrees to the initial E vector direction. The result is that with zero potential on the Pockels cell electrodes, none of the light passes. When about 7000 V are applied to the electrodes, the half wave condition is met and most of the light is passed by the analyzer. Thus we have an optical switch which can be operated as fast as 7000 V can be switched.

DeMaria et al. have demonstrated that such voltages may be switched in nanoseconds by using the light from the laser to cause breakdown of a spark gap.

4.8.2 Construction. An adjustable spark gap was constructed and a rather simple circuit developed for the purpose. The circuit is illustrated in Fig. 4.10a. The
FIG. 4.10 POCKELS CELL SWITCHING.
500 pF capacitor is charged to a potential just below that sufficient to cause spontaneous breakdown of the spark gap. A few percent of the laser output, obtained from a beam splitter, is focused near the spark gap cathode with a lens. When the train of laser pulses is nearing maximum intensity, the spark gap breaks down, bringing point "a" to a potential of about 7000 V within a few nanoseconds. The arm of the circuit including the inductor, the 20-Ω resistor and the capacitative Pockels cell forms a damped resonant circuit. In the absence of the 40-Ω resistor, the potential at point "b" behaves as in Fig. 4.10b. The addition of the 40-Ω resistor causes the capacitance of the Pockels cell to discharge, resulting in the waveform oscillogram of Fig. 4.10c.

4.8.3 Operation. There are experimental problems in directly measuring these high potential transient signals without inadvertently modifying them. The oscillogram of Fig. 4.10c was actually from the output of an RCA 4459 photomultiplier observing polarized light at 0.53 μm wavelength passed by the Pockels cell analyzer combination. For this test the light was obtained from a conventional source and a monochromator. The switching was initiated by increasing the potential applied to the 500 pF capacitor until spontaneous spark gap breakdown was obtained.

When the system was used for switching the laser output, the oscillograms of Fig. 4.11 were obtained using the UA 1240 detector and the 519 oscilloscope. An enlarged
FIG. 4.11 OSCILLOGRAMS ILLUSTRATING POCKELS CELL SWITCHING OF OUTPUT.

(a) FREQUENCY DOUBLER OUTPUT.

(b) SWITCHED OUTPUT.

(c) SIGNAL REJECTED BY POLARIZER.
oscillogram of the output appears in Fig. 3.13. These show that the switching action under laser breakdown of the spark gap is similar to that caused by an over potential.

Deuterated KDP was chosen over the regular KDP for the Pockels cell because deuteration halves the switching voltage required. Even with deuterated KDP, the switching voltage is near the peak rated potential.

A photograph of the Pockels switch equipment appears in Fig. 4.12. The presence of two small antennae will be noted in the region of the inductor. One provides capacitive coupling for monitoring purposes (foreground of photograph) and the other is a single 2 mm diameter coil situated within the inductor. It provides inductive coupling for triggering the 519 oscilloscope during experiments.

4.9 Transmission Monitoring of Saturable Dye

It was found early that the transmission of the dye needs to be measured frequently as this is quite critical and the dye slowly bleaches. The bleaching is hastened by exposure to light from the laser flash lamps. A Beckman DU spectrophotometer was modified to accept the dye cell to allow convenient transmission measurement.

4.10 Dewar Equipment

For the early experiments at liquid nitrogen temperature, a conventionally designed glass dewar was used with four optical ports. The sample was mounted on a cold finger in the vacuum section. The copper cold finger formed the bottom of the liquid nitrogen chamber.
FIG. 4.12 THE FREQUENCY DOUBLER, SPARK GAP AND POCKELS CELL SECTION OF ASSEMBLY.
For the later experiments with both liquid nitrogen and liquid helium, a more advanced metal dewar system was used. This system featured a square section fuzed silica tube as the lower part of the chamber for the cryogenic fluid. The sample was lowered into the tube so that it was immersion cooled and light could pass in and out through the fuzed silica. The pressure could be reduced below the helium λ point to reach a temperature of 2° K.

4.11 Summary

The equipment and techniques which have been described in this and the preceding chapter, together with some commercially available equipment, were used to carry out the experiments to be described in the next chapter.

*Designed and generously made available by Dr. T. M. Dunn and Dr. A. H. Francis of the Department of Chemistry.
5.1 Objectives

The objectives of the experiments were (a) to measure the lifetime of the $^4T_2$ state in pink ruby and (b) to investigate the radiative emission spectrum of the $^4T_2$ state.

5.2 Lifetime Measurements

5.2.1 Measurements at 2° K and 77° K. The lifetime measurements at liquid helium temperature and the later ones at liquid nitrogen temperature were made with the equipment shown schematically in Fig. 5.1.

The laser was as described in Section 3.8. The output consisted of a few subnanosecond pulses of intense green light occurring at 5 ns intervals as illustrated in Fig. 3.13. These pulses entered the dewar, which is briefly described in Section 4.10, to excite the immersion-cooled ruby.

The ruby was a 1 cm cube, cut from a Verneuil grown boule and polished on four sides. It was nominally 0.05 percent Cr$_2$O$_3$ by weight. The excitation light traveled in the direction of the C-axis. Two lenses imaged the ruby onto the entrance slit of a 0.25 m Jarrell-Ash monochromator. Entrance and exit slits of 0.2 mm were used which gave a band pass of 13 nm. To remove the relatively intense scattered green light mixed with the red luminescence, a pair of Corning No. 2-58 glass filters were placed in front of the monochromator.
FIG. 5.1 EXPERIMENTAL ARRANGEMENT FOR LIFETIME MEASUREMENTS.
entrance slit. The light emerging from the exit slit was collected by the RCA C70045C photomultiplier. This had unconventional circuitry, as described in Section 4.7 to enable it to drive a Tektronix 519 oscilloscope for recording the fast rising waveform of the luminescence. Typical oscillograms appear in Fig. 5.2.

Scattering of the green excitation light was initially a problem. This was eliminated by including the two Corning No. 2-58 filters. Each of these has less than one percent transmission for the green light. Removal of one of them resulted in no observable change in waveform on the oscillograms, hence with both in position it is certain that no green light was recorded.

A more serious problem was that something else in the dewar system was converting green light into red light. The oscillogram in Fig. 5.2c was taken with the ruby sample and its holder removed. The signal disappeared when the light path from the dewar was blocked, eliminating the possibility of electromagnetic pickup. Tests on the filters and a piece of fused silica (similar to that used for dewar windows) eliminated them as the source of the red light. The fused silica showed some green to red conversion but not sufficient to explain the results. During the experiments, there was invariably a little "snow" in the cryogenic fluid and this was believed to be the source. This would explain the inconsistency of the effect. At times it was much more marked than the picture of Fig. 5.2c indicates. The "snow" is
FIG. 5.2 R-LINE LUMINESCENCE AT LOW TEMPERATURES AS A RESULT OF THREE EXCITATION PULSES.
believed to be composed principally of ice particles and the effect, a surface phenomenon. It should be remembered that the peak powers were of the order of 1 GW and that effects not normally observed might occur at these power levels. The effect was observed both with liquid nitrogen and with liquid helium in the dewar.

5.2.2 Earlier Measurements at 77° K and 300° K.
The measurements at 300° K and the earlier ones at 77° K were made with a similar setup.* For these experiments, a single pass 0.25 m Leiss monochromator was used. The liquid nitrogen dewar is briefly described in Section 4.10. The ruby had similar specifications to the one used for the later experiments but had unknown orientation and was only 5 mm in one of its dimensions. As the sample was situated in the vacuum section of the dewar, there were no problems with "snow" or bubbling of the coolant and the optical losses of the dewar were less than 20 percent. Various filter arrangements were used to (a) remove the infrared from the excitation pulses and (b) reduce the scattered green light mixed with the red luminescence. The latter is not a trivial problem as one can expect of the order of 1 kW of green to be scattered into the collecting optics during an excitation pulse, whereas there is only about 10 mW of luminescence following one pulse.

---

*The earlier measurements were made in the Radar and Optics Laboratory of the Institute of Science and Technology with much of the equipment generously made available by Dr. D. E. Brown.
For these earlier experiments, the Pockels cell switching arrangement was not used so that there were between twenty and thirty green pulses similar to those illustrated in Fig. 4.11a. These excited the ruby to produce the luminescence illustrated in Fig. 5.3.

5.3 Radiative Emission from the $^4T_2$ State

A search was made for radiative emission by two methods: first with the use of a spectrograph, which gave no time resolution; and second with the monochromator and fast photomultiplier arrangement.

5.3.1 Search with Spectrograph. The arrangement is shown in Fig. 5.4. Spectrograms were taken both with the laser and with a xenon lamp exciting the ruby. No difference was observed between the spectra. As more useful average excitation power was available from the xenon lamp, it was the preferred source. Spectrograms taken by both methods appear in Fig. 5.5. When the xenon lamp was used the following filters were included. Between the lamp and sample, Corning Nos. 1-69, 0-51 and 7-59 and 5 cm of 10 percent saturated solution of CuSO$_4$·5H$_2$O in water. Between the ruby and spectrograph, a Corning No. 3-68 filter.

No emission attributable to the $^4T_2 \rightarrow ^4A$ transition was observed, even when the exposure was 4000 times that necessary to record the R-lines. It should be noted that the film (AF 103) was also more sensitive in the region where any $^4T_2 \rightarrow ^4A_2$ emission would be expected. The emission in
FIG. 5.3  R-LINE LUMINESCENCE AS A RESULT OF THE FULL TRAIN OF EXCITATION PULSES.
FIG. 5.4 EXPERIMENTAL ARRANGEMENT WITH SPECTROGRAPH.
FIG. 5.5 SPECTROGRAMS OF RUBY EMISSION.
the vicinity of the R-lines was later demonstrated to decay at the same rate as the R-lines, i.e., with about 5 ms lifetime. This ruled out the possibility that it was associated with the faster transition.

At 77° K and above, both of the R-lines can be seen with the film overexposed in their vicinity in some of the pictures. At 77° K they are at shorter wavelengths than at 300° K. On reducing the temperature to 2° K, the position of the R$_1$-line is unchanged, but the R$_2$-line disappears. At such low temperatures there is negligible population of the upper state corresponding to the R$_2$-line.

The diffuse luminescence around the R-lines is normally assigned to vibronic bands$^{40}$ of the R-lines, while some of the sharper weak lines are assigned to transitions involving chromium ion pairs.$^{7,41}$

5.3.2 Search with Monochromator and Fast Photomultiplier. The arrangement shown in Fig. 5.1 was used. The slits of the monochromator were 5 mm wide, which gave a bandpass of 33 nm. Measurements were made with drum settings between 600 and 750 nm in steps of 10 nm wavelength. At no time was any short decay time light observed which could be attributed to the $^4T_2 \rightarrow ^4A_2$ transition. Except when the R-line luminescence was observed, no signal ever exceeded that obtained when the ruby was removed. The peak power of any such light was never more than that in the R-line luminescence.
The extremely short time resolution element of this experiment resulted in very high sensitivity for any signals of short duration. The sensitivity for signals lasting 1 ns or less was greater than that achieved with the spectrograph by a factor of about $10^8$. This includes a factor of 25 for the greater acceptance angle of the monochromator and associated optics.

The search for the $^4T_2 ightarrow ^4A_2$ emission covered the range 585 to 765 nm. At shorter wavelengths, filtering against scattered excitation light became difficult. The intense excitation light was in a band occupying 520 to 540 nm.

5.4 Absorption Measurements at High Power

The possibility should be considered that some higher-order absorption process was important at the power levels of the experiments. If this were happening, the interpretation of the experiments might be upset. To check this possibility, a transmission measurement was made at 300° K using the full train of mode-locked pulses.

The ruby, suitably apertured, was placed in the output of the frequency doubled laser. The transmitted energy was measured with the diode calorimeter. Measurements were normalized by repeating with (1) a similar sized piece of sapphire and (2) with no sample in the beam. The results are listed in Table 5.1.
Table 5.1
Transmission Measurements at High Power

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transmission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruby (E \perp C)</td>
<td>0.143</td>
</tr>
<tr>
<td>Sapphire</td>
<td>0.860</td>
</tr>
</tbody>
</table>

Since a reflection loss of 14 percent is expected with sapphire or ruby, the sapphire absorption was negligible and the corrected ruby transmission was 0.167.

Earlier experiments* indicated that the absorption cross section (E \perp C) at 530 nm has 0.97 of its value at the peak wavelength of 550 nm. Dodd et al.*2 have published transmission measurements on rubies of known concentration which show that pink ruby obeys Beer's law. Using their results, the measured transmission indicated a Cr$_2$O$_3$ content of 0.04 percent by weight. Since this was very close to the nominal value of 0.05 percent, it was concluded that higher-order effects were not important in this experiment.

5.5 Two-Photon Luminescence

It was thought that, with peak powers in the GW range, two-photon absorption might occur in the ruby if it were irradiated with light at 1.06 \mu m wavelength.

When the ruby was irradiated with the output of the

*Carried out at Mitre Corporation, unpublished.
mode-locked laser at 1.06 \( \mu m \), R-line luminescence was observed. The maximum efficiency of converting infrared photons into red ones was of the order of \( 10^{-7} \). If the efficiency had been higher, it would have been an interesting way of exciting the \( ^4T_2 \) state for the major experiment as the green scattering problem would have been much reduced. With the low efficiency achieved, the luminescent power was not high enough to be observed with the high-speed detection equipment. It could only be observed on an oscilloscope by using a high impedance circuit which destroyed the speed. The speed of the circuitry was sufficient however to show that the luminescence decayed with a 5 ms time constant indicating that it was the R-line luminescence.

5.6 Summary

Experiments have been carried out to investigate the lifetime and emission spectrum at various temperatures. The results and their implications will be discussed further in Chapter VI.

The possibility of nonlinear absorption was investigated but found to be not important in these experiments.

R-line luminescence was observed as a result of irradiation with light of wavelength 1.06 \( \mu m \). As the conversion efficiency was only of the order of \( 10^{-7} \), it was not pursued.
6.1 Direct Lifetime Measurement

6.1.1 Discussion. It was shown in Section 2.3.1, that if an impulse of excitation results in a population $N_0$ of state $^4T_2$, then the ensuing population of state $^2E$ is given by

$$N = N_0(1 - e^{-S_{32} t}).$$

The rate of emission of photons into the luminescence from the $^2E \rightarrow ^4A_2$ transition is proportional to $N$. Hence if the receiving equipment were perfect, we would expect an oscilloscope taken with one excitation pulse to have a waveform

$$V = V_0(1 - e^{-S_{32} t}),$$

where $V$ is the oscilloscope voltage, and $V_0$ depends on the strength of the impulse excitation. Figure 6.1 illustrates the waveform to be expected if there are a few excitation impulses separated by a time much greater than $1/S_{32}$. As the equipment is not perfect, a degraded version is seen in the oscillograms of Fig. 5.2. The principal causes of degradation are as follows.

1. Shot noise. From the discussion in Chapter III, a signal-to-noise ratio in the vicinity of 10:1 is expected.

2. Delay. The photomultiplier is the slowest responding
FIG. 6.1 DISPLAY EXPECTED WITH PERFECT DETECTION EQUIPMENT.

(a) EXCITATION PULSES.

(b) RESULTING LUMINESCENCE.
unit in the detection equipment. It has a time resolution of about 1 ns and hence will cause smearing of rapidly changing signals. Its "smearing function" is an unknown quantity. However its effect can only result in an oscilloscope with a waveform that rises more slowly than is the case with ideal equipment. Hence if the waveform has an approximately exponential delay, the apparent time constant will give an upper bound to the value of $1/S_{32}$.

3. Saturation of photomultiplier. The photomultiplier becomes nonlinear in this range. Examination of the oscillograms indicates that the gain drops as a function of time when the output exceeds 20 mA (2 V). In view of the saturation, the emphasis in the interpretation of the results is placed on the luminescence that follows the first reasonable sized pulse.

4. Green to red conversion in the absence of the ruby. This unanticipated problem is the most difficult one. Its magnitude was variable and so it is difficult to allow for it in the interpretation.

6.1.2 Analysis of Noise. From Eq. 2.5, the signal-to-noise ratio S/N is given by

$$\frac{S}{N} = \frac{\Delta i_{\text{rms}}}{i} = \sqrt{\frac{2e\Delta f}{1}},$$  \hspace{1cm} (6.2)

where $i$ is the photocathode current. For the oscillograms of Fig. 5.2, the photomultiplier had 5 kV applied which should have ensured a current gain of $10^7$. The deflection of about 2 V with such a gain indicates a cathode current of
about $2 \times 10^{-9}$ A. From Eq. 6.2, this cathode current should lead to a signal-to-noise ratio of 0.5. As the ratio is nearer 0.2, this suggests that the photomultiplier is exhibiting less than the expected gain. The result indicates that when the deflection reaches 2 V, the gain has dropped by a factor of about six from its value for small signals.

6.1.3 Conclusion. The degradation of the signal prevents interpretation of the oscillograms with the expected 1 ns resolution. However the pictures in Figs. 5.2 and 5.3 do indicate the time constant $1/S_{32}$ is certainly less than 2 ns. Since $S_{32}$ is the dominant transition probability from the state, it follows that the lifetime of the $^4T_2$ state is less than 2 ns in the temperature range 2° K to 300° K. The same result would also be expected at higher temperatures.

6.2 Emission Spectrum of the $^4T_2$ State

6.2.1 Discussion of Models. Apart from reports by Maiman\textsuperscript{1} and Misu,\textsuperscript{14} which have been interpreted as erroneous, emission from the $^4T_2 + ^4A_2$ transition has never been definitely observed. It was hoped that with the extremely high sensitivity of this experiment, the emission would be observable. Knowledge of the spectrum would have cleared up some uncertainties concerning the $^4T_2$ state.

The simplest model on which to base the discussion has the broad green absorption band, centered at 550 nm, assigned to the purely electronic $^4T_2 + ^4A_2$ transition. The 70 nm half width of the absorption band is considered to be
due to the broad energy spread of the \(^4\text{T}_2\) state. From Einstein transition theory, discussed in Appendix A, radiative \(^4\text{T}_2 + ^4\text{A}_2\) transitions are expected to complement the absorbing \(^4\text{T}_2 + ^4\text{A}_2\) transitions. The emission spectrum is expected to be the same as the absorption spectrum. From the strength of the absorption, the Einstein radiative-transition probability can be calculated.

At temperatures below 200° K, structure can be seen in the absorption spectrum which is reproduced in Fig. 6.2. McClure\(^6\) attributed the structure to vibrational activity. He tentatively assigned the first peak at about 597 nm as the electronic origin and the peaks at shorter wavelengths as due to vibronic transitions. Thus the major portion of the absorption curve represents transitions to excited phonon levels of the \(^4\text{T}_2\) state. It follows from the Einstein transition theory that the major portion of the emission spectrum would represent transitions to excited phonon levels of the ground state, and hence would be shifted to longer wavelength.

If the vibrational modes associated with the \(^4\text{T}_2\) state are similar to those associated with the \(^4\text{A}_2\) state (which is reasonable as it is the same lattice), then on the basis of McClure's assignment, the emission would have its peak at about 650 nm.

It is possible that the electronic origin is at an even longer wavelength than that suggested by McClure. If so, the emission would peak at a wavelength longer than
FIG. 6.2 STRUCTURE OF GREEN ABSORPTION BAND AT 5° K.
(McClure[^])
650 nm. Kisliuk and Moore\textsuperscript{16} have concluded, from variation of the \(^2\!E\) lifetime with temperature, that the peak emission might be at a wavelength nearer 700 nm. This would place the electronic origin at about 600 nm.

6.2.2 Experimental Results. In spite of the high excitation power and sensitivity of the detection equipment, no emission was observed which could be attributed to the \(\text{^4}T_2 \rightarrow \text{^4}A_2\) emission. The search covered the range where emission might be expected from the models just discussed.

The lack of emission did allow some conclusions to be drawn regarding the lifetime. They will be discussed in the next section.

6.3 Indirect Estimates of Lifetime

6.3.1 Simple Model. The \(\text{^4}A_2 \rightarrow \text{^4}T_2\) transition is assumed to be purely electronic. As discussed in Section 6.2.1, the radiative transition probability \(A_{\text{31}}\) for the transition \(\text{^4}T_2 \rightarrow \text{^4}A_2\) can be estimated from absorption measurements. Maiman\textsuperscript{1} has estimated a value of \(3 \times 10^5/\text{s}\); Kisliuk and Moore\textsuperscript{16} a value of \(3 \times 10^4/\text{s}\). In view of the disagreement, the estimate is detailed in Appendix C leading to a value of \(6.4 \times 10^4/\text{s}\) for the spontaneous transition probability. This estimate can be used, in conjunction with the experimental observation of the weakness of such emission, to investigate further the lifetime of the \(^4T_2\) state. The transitions involved in the following discussion are indicated schematically in Fig. 2.1. The relations used are derived in Section 2.3.1.
As the result of an excitation pulse, the $^4T_2$ state will have a population of

$$N_3 = N_0 e^{-S_{32}t}.$$  

Hence green photons will be emitted from the $^4T_2 + ^4A_2$ transition at the rate $A_{31}N_0 e^{-S_{32}t}$. We will take 1 ns as a resolution element of the detection equipment. During the first resolution element, the number $n_g$ of green photons emitted is given by

$$n_g = \int_0^{10^{-9}} A_{31}N_0 e^{-S_{32}t} dt$$

$$= \frac{A_{31}N_0}{S_{32}} \left[ 1 - e^{-S_{32} \times 10^{-9}} \right]. \quad (6.3)$$

The contribution of the radiative population decay is neglected, as it has already been shown that $S_{32} > 5 \times 10^9/s$, and $A_{31}$ is only $6.4 \times 10^4/s$. After about 4 ns, the population of the $^4T_2$ state will have dropped to practically zero and that of the $^2E$ state will have risen to practically $N_0$. The number of red photons $n_r$ emitted in one resolution element from the $^2E + ^4A_2$ transition is

$$n_r = A_{21}N_0 \times 10^{-9}. \quad (6.4)$$

The value of $A_{21}$ is only $2 \times 10^2/s$, and so the decay of the $^2E$ population in such times need not be considered. When the value of $A_{21}$ is substituted in the above, then
From Eqs. 6.3 and 6.5, the ratio between the maximum number of green photons emitted in a resolution element and the maximum number of red photons emitted in a resolution element as a result of one excitation pulse is given by

\[
\frac{n_g}{n_r} = \frac{A_{31}[1 - e^{-S_{32}x10^{-9}}]}{S_{32} \times 2 \times 10^{-7}}. \tag{6.6}
\]

Examination of the absorption curve for ruby shows that in the experiment where the monochromator was set at 600 nm, with a passband of 33 nm, the assumptions lead us to expect about 7 percent of the emitted green photons to fall within the monochromator passband. In the experiment fewer green photons were detected than red ones in any time resolution element, i.e., experimentally the ratio of emitted photons satisfies

\[
\frac{n_g}{n_r} < \frac{100}{7}. \tag{6.7}
\]

By using the estimate \(A_{31} \sim 6.4 \times 10^4/s\) Eqs. 6.6 and 6.7 give

\[
\left(\frac{S_{32}}{1 - e^{-S_{32}x10^{-9}}}\right) > \left(\frac{6.4 \times 10^4}{2 \times 10^{-7}}\right) \times \frac{7}{100}, \tag{6.8}
\]

which has a solution

\[
\text{...}
\]
As the nonradiative transition $^4T_2 \rightarrow ^2E$ governs the lifetime of the $^4T_2$ state, then the lifetime $\tau$ satisfies

$$\tau = \frac{1}{S_{32}} < 45 \text{ ps.} \quad (6.10)$$

### 6.3.2 Vibronic Model

On the basis of the vibronic model, at low temperatures one would expect the $^4T_2 \rightarrow ^4A_2$ emission due to purely electronic transitions to fall within the range 595 to 610 nm. Emission at longer wavelengths would result from transitions to excited phonon levels of the $^4A_2$ state. The unsuccessful search for emission with the monochromator and fast photomultiplier covered the range 585 to 765 nm so that any such emission is extremely weak. The observations showed that there were never more green photons emitted than red ones in any period of 1 ns. Hence Eq. 6.7 becomes

$$\frac{n_g}{n_r} < 1. \quad (6.11)$$

If the phonon modes associated with the $^4T_2$ state are at all similar to those associated with the ground $^4A_2$ state (which is a reasonable assumption, as they are likely to be lattice modes), the estimate of $A_{31} \sim 6.4 \times 10^4$/s still holds. Equations 6.6 and 6.11 then give

---

*Described in Section 6.2.1.*
\[ S_{32} > 3.1 \times 10^{11}/s. \quad (6.12) \]

Hence the lifetime of the \( ^4T_2 \) state satisfies
\[ \tau < 3.2 \text{ ps.} \quad (6.13) \]

### 6.4 Branching Ratio from the \( ^4T_2 \) State

The ratio between transitions ending in the metastable \( ^2E \) state and those ending in the ground \( ^4A_2 \) state is given by
\[ R \sim \frac{S_{32}}{A_{31}}. \quad (6.14) \]

By using the estimated value of \( A_{31} \) and Eqs. 6.9 and 6.12, the following results are obtained.

1. For the simple model, \( R > 3.4 \times 10^5 \).
2. For the vibronic model, \( R > 4.8 \times 10^6 \).

It can be concluded that any radiative emission from the \( ^4T_2 \rightarrow ^4A_2 \) can be ignored as a laser loss mechanism.

### 6.5 Discussion of Misu's Results

#### 6.5.1 Introduction
Misu\(^1\) investigated emissions from optically excited ruby at temperatures between 300\( ^\circ \) K and 650\( ^\circ \) K. He reported feeble emission in the region of 620 nm and assigned it to the \( ^4T_2 \rightarrow ^4A_2 \) transition. He used a configuration coordinate diagram in the interpretation of his results. From the relative strengths of the various emissions at different temperatures, he estimated activation energies and frequency factors for the nonradiative transitions.
The model he used can be described in the following manner in terms of potential energy curves. Figure 6.3a shows schematic curves of potential energy vs. a generalized coordinate. To obey the Franck-Condon principle, radiative transitions between electronic states must follow vertical lines on such a diagram. If the possibility of tunneling is precluded, nonradiative transitions can take place only where energy curves cross.

For a typical crossover point, there is an activation energy $E$ and a frequency factor $C$. Consider such a point in Fig. 6.3b, where the curve corresponding to state "1" crosses that of state "2." Transitions will occur at a net rate

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = C(2:1) \left( N_2 e^{-E/kT} - N_1 e^{-E_1/kT} \right)$$

$$= C(2:1) e^{-E/kT} \left( N_2 - N_1 e^{-\Delta/kT} \right), \quad (6.15)$$

where $N_1$ and $N_2$ are the population densities of the electronic states. The populations at the crossover points are considered to arise from excited phonon levels of the electronic states. They are assumed to be close enough to thermal equilibrium within any one electronic state for the Boltzmann ratio to apply. The possibility of degeneracies is not considered.

6.5.2 Misu's Results. From his observations of the relative strengths of the emissions at various temperatures,
(a) SCHEMATIC CURVES FOR RUBY.

(b) TYPICAL CROSSING POINT.

FIG. 6.3 CONFIGURATION COORDINATE DIAGRAMS.
Misu estimated the activation and frequency factors for the three nonradiative transitions corresponding to the crossover points in Fig. 6.3a. His results are summarized in Table 6.1.

### Table 6.1

Misu's Estimates of Activation Energies and Frequency Factors

<table>
<thead>
<tr>
<th>Point</th>
<th>Parameter</th>
<th>Experimental Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$C(\text{^4T}_2 : \text{^2T}_1) = C_a$</td>
<td>$(2.7 \pm 1.0) \times 10^8 \text{ s}^{-1}$ $2300 \pm 230 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$(\text{^4T}_2 : \text{^2T}_1) = \varepsilon_a$</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>$C(\text{^4T}_2 : \text{^2E}) = C_b$</td>
<td>$(4.4 \pm 1.1) \times 10^8 \text{ s}^{-1}$ $2700 \pm 230 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$(\text{^4T}_2 : \text{^2E}) = \varepsilon_b$</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>$C(\text{^4T}_2 : \text{^4A}_2) = C_c$</td>
<td>$(5 \pm 3) \times 10^{11} \text{ s}^{-1}$ $4000 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$(\text{^4T}_2 : \text{^4A}_2) = \varepsilon_c$</td>
<td></td>
</tr>
</tbody>
</table>

### 6.5.3 Estimate of Lifetime of $\text{^4T}_2$ State Based on Misu's Results

The values of the frequency factors and activation energies given in Table 6.1 can be used to estimate the nonradiative lifetime of the $\text{^4T}_2$ state at any temperature of interest, as follows.

Consider state $\text{^4T}_2$ populated as a result of an impulse of green excitation light. Thereafter the population density $N(\text{^4T}_2) = N_3$ is given by (neglecting the slower radiative transitions)
\[
\frac{dN_3}{dt} = -C_\alpha e^{-\xi_{i}\phi/kT} \left[ N_3 - N(2T_1)e^{-3900/kT} \right] \\
- C_\beta e^{-\xi_{b}\phi/kT} \left[ N_3 - N(2E)e^{-3000/kT} \right] \\
- C_\gamma e^{-\xi_{c}\phi/kT} \left[ N_3 - N(4A_2)e^{-17000/kT} \right].
\] (6.16)

At temperatures below 400° K, the last term of each expression can be ignored (these correspond to upward transitions). So

\[
\frac{dN_3}{dt} = -N_3 \left( C_\alpha e^{-\xi_{i}\phi/kT} + C_\beta e^{-\xi_{b}\phi/kT} + C_\gamma e^{-\xi_{c}\phi/kT} \right).
\] (6.17)

At 300° K, \(kT = 210 \text{ cm}^{-1}\). Using Misu's experimental values

\[
\frac{dN_3}{dt} = -N_3 \left( 2.7 \times 10^8 e^{-2300/210} + 4.4 \times 10^8 e^{-2700/210} \\
+ 5 \times 10^{11} e^{-4000/210} \right)
\]

\[
= -N_3 \left( 9.2 \times 10^3 + 1.2 \times 10^3 + 2 \times 10^3 \right) \\
= -10^4 N_3.
\] (6.18)

Hence the population of state \(^4T_2\) should decay according to the equation

\[
N_3 = N_0 e^{-10^4 t}.
\] (6.19)

It follows that the nonradiative lifetime of \(^4T_2\) at 300° K should be approximately 100 μs. If the analysis is performed for lower temperatures, the expected nonradiative lifetime becomes longer (10^{10} s at 77° K).
As the observed lifetime is less than 0.5 ns at 300° K, and has been shown here to be less than 2 ns at 77° K and 2° K, either the model or the parameter values are faulty.

6.5.4 Discussion of Disagreement. The principal assumptions in the model are that a Boltzmann distribution of population among the phonon levels of any electronic state is achieved before many transitions are made to another electronic state and that degeneracies can be ignored.

The numbers are more open to criticism. They are based on the observation of emission in the green which this author was unable to duplicate. The only other experimenter who has reported the green emission is Maiman. Other observers have reported that they, like the author, were unable to duplicate Maiman's observation.

If the model is valid, the activation energy must be much lower than Misu's value of 2700 cm\(^{-1}\) in view of the lifetime measurement at 2° K. Also, as the radiative emission is predominantly from the \(^2E\) level at all temperatures, \(C(\,^{4}T_{2};\,^{2}T_{1}) \ll C(\,^{4}T_{2};\,^{2}E)\).

6.5.5 New Estimates for Activation Energies and Frequency Factors. The width of the \(^4T_2 + ^4A_2\) absorption band is 3000 cm\(^{-1}\) or less at temperatures between 2° K and 300° K. To satisfy the Heisenberg uncertainty principle, a lower limit of 0.01 ps must be put on the lifetime of the \(^4T_2\) state. It has already been shown experimentally that the lifetime is less than 2 ns at 2° K, and Pollack\(^{12}\) has shown that it is less than 0.5 ns at 300° K. From these
facts, the following relations hold. At 300° K

\[ C_{be} \left( \frac{-\xi_b}{300} \right) < 10^{14}/s \]  
(6.20)

and

\[ C_{be} \left( \frac{-\xi_b}{300} \right) > 2 \times 10^9/s. \]  
(6.21)

At 2° K

\[ C_{be} \left( \frac{-\xi_b}{2} \right) < 10^{14}/s \]  
(6.22)

and

\[ C_{be} \left( \frac{-\xi_b}{2} \right) > 5 \times 10^8/s, \]  
(6.23)

where \( \xi_b \) is measured in degrees Kelvin. The model requires that

\[ \xi_b \geq 0. \]  
(6.24)

Equations 6.20 and 6.24 give

\[ \xi_b < 25° K. \]  
(6.25)

Equations 6.20 and 6.21 then give

\[ 2 \times 10^9 < C_b < 10^{14}/s. \]  
(6.26)

The limiting values of the activation energy and frequency factor given by Eqs. 6.25 and 6.26 follow from the direct measurements of the \( ^4T_2 \) lifetime.
If the estimated lifetimes from the indirect analysis of Section 6.3 are used, the limits can be brought closer together. If the "simple" model of Section 6.3.1 is used, then the results become

$$\varepsilon_b < 2.5^\circ K$$

$$2 \times 10^{10} < C_b < 10^{14}/s. \quad (6.27)$$

If the "vibronic" model of Section 6.3.2 is used, then the results become

$$\varepsilon_b < 1.25^\circ K$$

$$3 \times 10^{11} < C_b < 10^{14}/s. \quad (6.28)$$

6.5.6 Conclusions. The emission which Misu reported in the region of 620 nm could not be observed although the equipment of this experiment was much more sensitive. It is concluded that the values of activation energies and frequency factors estimated from his observations are inaccurate. The lack of $^4T_2 \rightarrow ^4A_2$ emission observed in these experiments allows limits to be placed on the activation energy and frequency factor associated with the $^4T_2 \rightarrow ^2E$ transition. These are detailed in Section 6.5.5.

6.6 Summary

Instead of obtaining an accurate value of the $^4T_2$ lifetime and the emission spectrum from the $^4T_2$ state, as was originally intended, the conclusions of previous reporters have been upset. The most noteworthy conclusion may be that
in such a well-studied material as ruby, only the ground and metastable states are well understood.

The direct measurement showed that the $^4T_2$ lifetime is less than 2 ns at all temperatures investigated. From the failure to observe any radiative emission from the $^4T_2 \rightarrow ^4A_2$ transition, it was shown that the lifetime is certainly less than 45 ps. With the vibronic model, the lifetime must be less than 3.2 ps.

Misu's results are discussed in the light of these experiments and it is shown that his estimated activation energies and frequency factors should be modified.

6.7 Suggestions for Further Work

As the properties of the $^4T_2$ state are so different from that expected from previous reports, the equipment developed was only able to establish upper bounds on some of the parameters. To investigate the lifetime further by a direct measurement, a shorter time resolution would be required. In this experiment, shot noise limitations were approached so even higher excitation powers would be required owing to the increased bandwidth of the detection system. The higher excitation power could be obtained by using a laser amplifier after the mode-locked laser. The higher power might allow observation of the emission spectrum. The spectrum would be very valuable as it would aid in determining the electronic origin of the $^4T_2$ state, and improve the indirect lifetime measurement. However with the higher powers, great care would
have to be taken to filter out scattered excitation and light from frequency conversion as a result of other mechanisms.
APPENDIX A. EINSTEIN TRANSITION THEORY

A.1 Introduction

In the form originally developed by Einstein the transition theory was particularly applicable to gases. The medium was assumed isotropic and the details of line shape were not discussed. As a result, the treatment was very simple and elegant. In the following sections Einstein's treatment is summarized and then the modifications for dealing with line shape and anisotropy are introduced.

A.2 Summary of the Einstein Development

A.2.1 Hypotheses. Suppose \( Z_m \) and \( Z_n \) are two possible quantum states of a gas molecule with energies \( E_m \) and \( E_n \) such that \( E_m > E_n \). Einstein made the following postulates concerning transitions between the two states.

1. Spontaneous transitions. A molecule is able to pass spontaneously from state \( Z_m \) to \( Z_n \) with the emission of radiative energy \( (E_m - E_n) \) at a frequency \( \nu \). The probability of such a transition is \( A_{mn} \) per second, where \( A_{mn} \) is a constant.

2. Absorbing transitions. Suppose there is a radiation field present with density \( \rho \) defined such that the energy in a volume \( V \) and a frequency interval \( d\nu \) is \( \rho V d\nu \). Under the action of the radiation a molecule in state \( Z_n \)
can make a transition to state $Z_m$ while absorbing energy $(E_m - E_n)$. The probability of this transition is $B_{nm} \rho$ per second, where $B_{nm}$ is a constant.

3. Induced emission. In the same way, a molecule in state $Z_m$ can be induced to make a transition to $Z_n$ while emitting energy $(E_n - E_m)$. The probability is $B_{mn} \rho$ per second where $B_{mn}$ is a constant.

A.2.2 Consider Thermal Equilibrium. If there is a large number of such gas molecules in thermal equilibrium with their surroundings the transitions sum to zero. If there are $N_i$ molecules per unit volume in state $Z_i$, it follows that

$$N_m (A_{mn} + B_{mn} \rho) = N_n B_{nm} \rho. \quad (A.1)$$

But from statistical mechanics, in thermal equilibrium

$$N_m = N_n \frac{g_m}{g_n} \exp \left( \frac{E_n - E_m}{kT} \right), \quad (A.2)$$

where $g_i$ is the multiplicity of state $Z_i$. The last two equations give

$$g_n B_{nm} \rho \exp \left( \frac{E_m}{kT} \right) = g_m (B_{mn} \rho + A_{mn}) \exp \left( \frac{E_n}{kT} \right). \quad (A.3)$$

In thermal equilibrium, if $T$ becomes infinite so does $\rho$, hence the following relation must hold

$$g_n B_{nm} = g_m B_{mn}. \quad (A.4)$$
If Eq. A.4 is substituted into Eq. A.3, the following is obtained

\[ \rho = \frac{A_{mn}}{B_{mn}} \frac{1}{\exp\left(\frac{E_m - E_n}{kT}\right) - 1} . \]  

(A.5)

Compare this with Planck's radiation law

\[ \rho = \frac{8\pi\hbar\nu^3}{c^3} \frac{1}{\exp\left(\frac{E_m - E_n}{kT}\right) - 1} , \]  

(A.6)

where \( c \) is the velocity of light in the medium. It follows that

\[ \frac{A_{mn}}{B_{mn}} = \frac{8\pi\hbar\nu^3}{c^3} \]  

(A.7)

and

\[ E_m - E_n = \hbar\nu. \]  

(A.8)

\section*{A.2.3 Results}

The hypotheses are plausible and the conclusions are consistent with quantum theory. The Einstein coefficients are clearly related to the matrix element and the oscillator strength of the transition. The hypotheses are plausible and the conclusions are consistent with quantum theory. The Einstein coefficients are clearly related to the matrix element and the oscillator strength of the transition. The hypotheses are plausible and the conclusions are consistent with quantum theory. The Einstein coefficients are clearly related to the matrix element and the oscillator strength of the transition.

For a dipole transition, the relations are as follows:

\[ A_{mn} = \frac{64\pi^2}{3} \frac{e^2}{\hbar c^3} \nu_{nm}^3 |\tilde{x}_{mn}|^2 , \]  

(A.9)

\[ B_{mn} = \frac{8\pi^3}{3} \frac{g_m e^2}{g_n \hbar^2} |\tilde{x}_{mn}|^2 \]  

(A.10)
where $X_{mn}$ is the matrix element, $v_{nm}$ is the frequency of interaction given by Eq. A.8, $e$ is the electronic charge, $f_{mn}$ is the oscillator strength, and $m$ is the electron mass.

The Einstein hypotheses give a good physical insight. However they take no account of transition linewidths or anisotropy of the medium. Both of these factors become important when the reasoning is applied to solids.

A.3 Modification of the Einstein Development for Solids

A.3.1 Hypotheses. Einstein's three hypotheses can be modified to take into account the line shape and anisotropy as follows:

1. Spontaneous emission. A molecule is able to pass spontaneously from state $Z_m$ to $Z_n$. The probability of a transition is $A_{mn}$ per second. The probability of a transition such that the emission is into a frequency interval $dv$ at $v$ and into a solid angle $d\Omega$ in direction $\Omega$, with polarization $i$, is

$$P = A'_{mnij}(\Omega) g(v) \ dv \ d\Omega \ per \ second, \quad (A.12)$$

where $A'_{mnij}(\Omega)$ is the anisotropic A coefficient. $g(v)$ is the line shape function, defined such that

$$\int_0^\infty g(v) \ dv = 1. \quad (A.13)$$
The two $A$ coefficients are related by

$$A_{mn} = \int_0^{4\pi} \sum_\text{pol.} A'_{mn i}(\Omega) \, d\Omega,$$

(A.14)

where the summation is over the two possible polarizations for any direction $\Omega$. In the isotropic case Eq. A.14 becomes

$$A_{mn} = 8\pi A'_{mni}. \quad \text{(A.15)}$$

2. Absorbing transitions. Suppose the radiation density is $\rho(v)$ at frequency $v$. Then the probability that the energy in a frequency interval $dv$, with polarization $i$, traveling in a solid angle $d\Omega$ will cause an absorbing transition is given by

$$P = B'_{nmi}(\Omega) \rho_i^i(v) g(v) \, dv \, d\Omega,$$

(A.16)

where $B'_{nmi}(\Omega)$ is the anisotropic $B$ coefficient for absorption and $\rho_i^i(v)$ is the density of the energy traveling in direction $\Omega$ with polarization $i$. Note that the energy density is "per unit solid angle," as well as "per unit volume" and "per unit frequency interval," when dealing with the anisotropic case.

3. Induced emission. The probability of induced emission into a frequency interval $dv$ is similarly given by

$$P = B'_{nmi}(\Omega) \rho_i^i(v) g(v) \, dv \, d\Omega \text{ per second.} \quad \text{(A.17)}$$

A.3.2 Thermal Equilibrium. When the system is in thermal equilibrium, for any polarization, direction, and
frequency element, the transitions of the three types must sum to zero. It follows from Eqs. A.12, A.16 and A.17 that

\[ N_m (A'_{mni} + B'_{mni} \rho^i) = N_n B'_{mni} \rho^i. \]  

(A.18)

It can be seen that this is very similar to Eq. A.1 obtained for the simpler situation. Exactly the same reasoning as before results in the following relations

\[ g_n B'_{nmi} = g_m B'_{mni}. \]  

(A.19)

and

\[ \frac{A'_{mni}}{B'_{mni}} = \frac{\hbar v^3}{c^3}. \]  

(A.20)

A.3.3 Results. The hypotheses are just as plausible as the original Einstein ones and the results are still consistent with quantum theory. Similar relations are found between the coefficients. The development allows correlation between absorption and emission measurements on anisotropic materials.

A.4 Gain and Attenuation

A.4.1 General Equation. Let us consider the interaction between polarized radiant energy traversing a medium, and two electronic states of molecules in the medium. Suppose the traveling radiation field has energy density \( \rho^i(\nu) \), defined such that \( \rho^i(\nu) \, d\nu \, d\Omega \) is the energy per unit volume in \( d\nu \) and \( d\Omega \). The rate at which \( \rho^i \) changes as the wave
passes through the medium can be obtained from Eqs. A.12, A.16 and A.18. As each transition results in the gain or loss of energy $h\nu$, then (using a frame of reference which moves with the radiation)

$$\frac{d\rho_i}{dt} = h\nu (N_{m' mni} + N_{n' i} B_{nmi} - N_{n' i} B_{i nmi}) g(\nu).$$ \hspace{1cm} (A.21)

If we now change to a stationary frame of reference and consider a slab of the medium with a steady energy input through one surface, the growth (or decay) of the radiation as it passes through the medium is given by

$$\frac{d\rho_i}{d\lambda} = \frac{h\nu}{c} (N_{m' mni} + N_{n' i} B_{nmi} - N_{n' i} B_{i nmi}) g(\nu),$$ \hspace{1cm} (A.22)

where $c$ is the speed of the radiation through the medium and $\lambda$ is the distance traversed.

A.4.2 Transmission Measurements. For a typical transmission measurement the spontaneous transitions can be ignored so that Eq. (A.22) becomes

$$\frac{d\rho_i}{d\lambda} = -\rho_i \frac{h\nu}{c} g(\nu) (N_{n' nmi} - N_{m' mni}).$$ \hspace{1cm} (A.23)

It follows that the absorption coefficient $\alpha$ (anisotropic) is given by

$$\alpha = \frac{h\nu}{c} g(\nu) (N_{n' nmi} - N_{m' mni}).$$ \hspace{1cm} (A.24)

and the transmission $T$ is given by
For most transmission measurements, the upper state population is negligible and so the last term of Eq. A.24 disappears.

A.4.3 Optical Gain. If the population can be inverted such that $N_m B'_m > N_n B'_n$ then the absorption coefficient given by Eq. A.24 becomes negative giving rise to optical gain.

A.5 Summary

The Einstein transition theory has been developed for application to solids. Equations have been obtained relating the attenuation or gain of a medium to the anisotropic transition coefficients. The relations are used in Appendix C for estimating the ruby $^4T_2 + ^4A_2$ radiative-transition probability from absorption measurements.
B.1 Introduction

Laser resonators generally have dimensions which are extremely large compared with optical wavelengths. As a consequence they have many resonances closely spaced in frequency. Each possible resonance is termed a "mode." Typically the axial modes of a resonator may be separated by about $10^9$ Hz. This is equivalent to a wavelength separation of about 10 pm in the optical region. As these modes are so closely spaced, a number of them are normally excited in a laser oscillator as the linewidth of the active material usually spans at least several of the resonator axial modes. Unless special precautions are taken in the design of a laser, the amplitudes of the individual modes vary rapidly in an apparently random manner. The resultant intensity of the output of such a "free-running" laser has apparently random fluctuations.

Interesting results can be obtained when a device is incorporated into the laser to allow controlled flow of energy between the modes. Energy may be spread fairly evenly over a large number of modes, or it may be funneled into one mode depending on the control device. In the case where the energy is divided uniformly over a large number of modes, it is possible to obtain a definite phase relationship between the modes in addition to a uniform amplitude. In the special
case where the phase relation is such that the modes all go through an instantaneous maximum at some instant of time, the laser is said to be "mode-locked," as the modes are then locked in amplitude and phase. The output of the laser in the time domain is then a train of very short pulses with the pulse separation determined by the resonator length. It is easily verified that when such an output is expanded in a Fourier series the components correspond to the mode situation described.

There is a slight problem in terminology as it is possible for the modes to be locked in amplitude without the special phase relation described. In a sense "mode-locking" then exists and indeed a periodic output is expected. However, as the aim of mode-locking is generally to produce a train of very short pulses, this should be considered only partial mode-locking. The term "mode-locking" should be reserved to describe the situation when the special phase relationship is achieved, evidenced by the train of very short pulses.

B.2 Cavities and Modes

B.2.1 Stability. Any laser oscillator consists of a resonator containing an amplifying material. The resonator usually consists of two mirrors which trap radiation. The mirrors can be either flat or spherical.

The basic requirement of a resonator is that it be capable of trapping radiation (i.e., stable). This can be
checked on purely geometric grounds. In Fig. B.1 the plot shows the stability of different resonators, where $d$ is the cavity length and $R_1$ and $R_2$ are the radii of curvature of the mirrors.

**B.2.2 Modes.** If the wave equation is solved, putting in the resonator boundary conditions, only certain solutions are found consistent with a standing wave in the resonator. It is found that the eigenvalues of frequency are given by

$$\nu = \nu_0(q + 1 + \alpha), \quad \text{(B.1)}$$

where

$$\nu_0 = \frac{c}{2d} \quad \text{(B.2)}$$

and

$$\alpha = \frac{(2p + \ell + 1)}{\pi} \arccos \left[ \left(1 - \frac{d}{R_1} \right) \left(1 - \frac{d}{R_2} \right) \right]^{1/2}, \quad \text{(B.3)}$$

where $q$, $p$ and $\ell$ are integers describing the "mode numbers." The "fundamental" or "axial" modes are with $p = \ell = 0$. The others are "higher-order" modes. Attempts are usually made to suppress the higher-order modes as they degrade collimation of the output beam.

It follows from Eq. B.1 that the frequency interval between modes with the same $p$ and $\ell$, but successive values of $q$ (the longitudinal mode number), is given by
FIG. B.1 PLOT OF LASER RESONATOR STABILITY.
(Kogelnik\textsuperscript{30})
\[ \Delta \nu = \nu_0 (1 + \alpha) = \frac{c}{2d} (1 + \alpha). \] 

(B.4)

### B.3 Laser Output

#### B.3.1 Free-Running Laser

In most lasers at least a few modes oscillate simultaneously. There is very little energy transfer between these modes and they fluctuate in amplitude and possibly phase in a random manner. Such a laser has no periodicity in output.

#### B.3.2 Partial Mode-Locking

Let us now consider what happens to the output of a laser if it is postulated only that the individual modes have amplitudes and phases which are constant with time. We will however allow the individual amplitudes and phases to be arbitrary. The discussion will be confined to modes having the same values of \( p \) and \( l \).

At a considerable distance from the laser the output, in the direction of maximum intensity, can be considered a plane wave even if the mirrors are spherical. A mode \( q \) will contribute an electric field given by

\[ E_q(x, t) = A_q R e^{i \left[ 2\pi \nu_0 (t-x/c) + \phi_q \right]} \] 

If we sum the electric fields of all the modes, and use Eq. B.1, then

\[ E(x, t) = \sum E_q \]

\[ = R e^{i \left[ 2\pi \nu_0 (1 + \alpha)(t-x/c) + \phi \right]} \sum A_q e^{i \left[ 2\pi \nu_0 q(t-x/c) + \phi_q \right]} \] 

(B.6)
Now we ask what the situation is two cavity lengths further away, i.e., let \( x \rightarrow x + 2d = x + \frac{c}{\nu_o} \) (from Eq. B.2), then

\[
E(x+2d,t) = R e e^{-i \left[ 2\pi \nu_o (1+\alpha)(t-\frac{x}{c}) - 2\pi (1+\alpha) \right]}
\]

\[
\sum_q A_q e^{-i \left[ 2\pi \nu_o q(t-\frac{x}{c}) + \phi_q - 2\pi q \right]}
\]. \hspace{1cm} (B.7)

As \( q \) is an integer, then it follows that

\[
E(x+2d,t) = R e e^{-i \left[ 2\pi \nu_o (1+\alpha)(t-\frac{x}{c}) - 2\pi \alpha \right]}
\]

\[
\sum_q A_q e^{-i \left[ 2\pi \nu_o q(t-\frac{x}{c}) + \phi_q \right]}
\]. \hspace{1cm} (B.8)

Compare this with Eq. B.6. It can be seen that

\[
E(x+2d,t) = E(x,t)
\] \hspace{1cm} (B.9)

except for a phase factor of \( 2\pi \alpha \). As a conventional detector only records intensity, the output will appear to be periodic with a period of \( 2d \). Hence it will also be periodic in time with period \( 1/\nu_o \). Note that for plane mirrors \( \alpha = 0 \) hence even the phase factor disappears.

This hypothetical case has been presented in the above detail because the result is closely related to the waveforms observed when the laser was used in the "DeMaria" configuration, i.e., with plane parallel mirrors. In this configuration, the output intensity was always periodic with a period of twice the cavity length (neglecting the
relatively slow rise and fall of the envelope). It seems that the degree of mode-locking postulated at the beginning of this section was always present. However it was only in about 13 percent of the laser firings that much stronger mode-locking was demonstrated, of the type to be described in the next section.

**B.3.3 Full Mode-Locking.** We will define "full mode-locking" in the following manner. (1) Adjacent cavity modes with the same values of \( p \) and \( l \) are oscillating with equal amplitude and no other modes are oscillating and (2) the phases are such that at some instant in space and time all the modes are simultaneously going through a maximum. Choosing that instant as zero, we can write

\[
A_q = A \quad \text{for } q = m+1, m+2, \ldots m+n
\]

\[
A_q = 0 \quad \text{for all other } q
\]

\[
\phi_q = 0. \quad (B.10)
\]

Equation B.6 then becomes

\[
E(x,t) = R e^{i \left[ 2 \pi v_0 (1+\alpha)(t-x/c) \right]}
\]

\[
\cdot \sum_{q=m+1}^{m+n} e^{-i2\pi v_o q(t-x/c)} A
\]

\[
(B.11)
\]

Summing the geometric series gives

\[
E(x,t) = R e^{-i2\pi v_o \left( \frac{2m+n+1}{2} + 1+\alpha \right)(t-x/c)}
\]

\[
\cdot \sin n\pi v_o (t-x/c) \frac{\sin \pi v_o (t-x/c)}{\sin \pi v_o (t-x/c)} \quad (B.12)
\]
Noting that the mean value of $q$ is $\bar{q} = \frac{2m+n+1}{2}$ and using Eq. B.1, then

$$\bar{v}_q = v_0 (\bar{q} + 1 + \alpha) = v_0 \left(\frac{2m+n+1}{2} + 1 + \alpha\right) \quad (B.13)$$

and Eq. B.12 becomes

$$E(x,t) = \Re \left[ A e^{i2\pi \bar{v}_q (t-x)} \sin \frac{n\pi v_0 (t-x)}{c} \right] \frac{\sin \pi v_0 (t-x)}{\sin \pi v_0 (t-x)} \quad (B.14)$$

A conventional detector will only register intensity given by

$$I = A^2 \frac{\sin^2 n\pi v_0 (t-x)}{\sin^2 \pi v_0 (t-x)} \quad (B.15)$$

For large $n$ this approaches a $\delta$-type function with height $n^2A^2$ and half width \(\frac{2d}{n} \left(\frac{1}{v_0}\right)\) in time. It is repeated at intervals of $2d \left(\frac{1}{v_0}\right)$ in time. Of course the phase difference $2\pi\alpha$ will still be there but not observed.

Equation B.15 describes the form of the output intensity obtained in about 13 percent of the cases with the "DeMaria" configuration, 72 percent of the cases when one of the flat mirrors was replaced by a spherical mirror, and 90 percent of the cases when a converging lens was added to "DeMaria's" configuration.

B.4 Mode Structure of Laser Output

In the foregoing analysis, the possibility of finite values for the "off axis" mode numbers $p$ and $l$ was included
although it complicated the equations slightly. The motivation was provided by the photographs in Fig. B.2. These are photographs of burn marks in exposed Polaroid film made by the laser output. Suitable attenuation was used so that the spatial distribution of the intensity would be indicated. If \( p \) and \( \lambda \) were zero, the output would have had a Gaussian intensity distribution. The observed distribution is indicative of nonzero values for \( p \) and \( \lambda \).

### B.5 The Saturable Dye

In these lasers mode-locking is encouraged with the use of a saturable dye. The nonlinearity of the dye results in energy transfer between the modes as discussed by DeMaria. 28

Using the dye absorption cross section given by Mauer, 32 and assuming that the pulse length is less than the dye upper level lifetime, it is possible to estimate how much energy can be absorbed by the dye before it becomes transparent. If the dye initially has a transmittance of 60 percent then approximately 10 \( \mu \text{J/cm}^2 \) in a short pulse will render it transparent to any further energy in that pulse. Measurements indicate that half the energy output is through about 0.1 \( \text{cm}^2 \), hence the dye cannot extract more than about 1 \( \mu \text{J} \) from a pulse in any one passage. As about 10 mJ were obtained in individual pulses, the effect of the dye as an attenuator can be practically ignored in the final stages of the lasing.
FIG. B.2 SPATIAL DISTRIBUTION OF LASER INTENSITY
INDICATED BY BURN MARKS IN POLAROID FILM.
Fleck has simulated the passively mode-locked laser on a computer. He demonstrated that an initially random signal, after repeated amplification and passage through a saturable dye in a laser resonator, can be expected to develop into the pulsed output associated with full mode-locking. For the simulation, Fleck assumed an initial dye transmittance of 76 percent. DeMaria also discusses a computer simulation with assumed dye transmittance of 80 percent but points out that such simulations are unrealistic as the dye concentration is much weaker in practice. This point is emphasized as DeMaria's comment is the only reference the author has found on the actual concentrations used by previous investigators. It does indicate that the dye concentration found optimum in these experiments (transmission = 60 percent) is much higher than normally used.

There has been no really satisfactory published explanation of how mode-locking actually develops from the noise background in such a laser. There have been qualitative discussions but no theory against which numbers can be checked except by modeling on a computer and seeing whether the model mode-locks. In these circumstances, the science involved in improving mode-locking must of necessity be rather empirical.

B.6 Summary

After spending many months attempting to duplicate DeMaria's results, the conclusion has been reached that full mode-locking is not assured with his configuration. The
conclusion is that in duplicating the present published state of the art one can only hope to achieve a certain probability that full mode-locking will develop from the background noise. Because the noise is random, the extent of mode-locking also will be somewhat random. This work has demonstrated that the probability of achieving full mode-locking is considerably enhanced by including converging optics in the cavity. A lens appears to be more effective than a spherical mirror with similar converging power. The greater consistency of output obtained allows higher output energies without the risk of damage to the optical components.
APPENDIX C. ESTIMATE OF RADIATIVE TRANSITION PROBABILITY
FOR TRANSITION $^4T_2 + ^4A_2$

C.1 Introduction

The radiative transition probability $A_{31}$ for the transition $^4T_2 + ^4A_2$ may be estimated from information regarding the $^4T_2 + ^4A_2$ absorption. To make an accurate estimate, the anisotropic nature of the radiative process should be taken into account. The Einstein transition theory is used to make the estimate. However the theory is usually developed only for the isotropic case. In Appendix A, a development for the anisotropic case is given. The results are used in the following analysis.

Let the population density of the $^4A_2$ state be $N_1$. For a typical absorption measurement the population of the $^4T_2$ state can be ignored. If Eq. A.24 is integrated across the linewidth, then

$$\int \alpha \, dv = \frac{\hbar}{c} N_1 B_{13i} \int \nu \, g(\nu) \, dv,$$  \hspace{1cm} (C.1)

where $\alpha$ is the absorption coefficient and $B_{13i}(\Omega)$ is the anisotropic B coefficient for the $^4T_2 + ^4A_2$ transition corresponding to direction $\Omega$ and polarization $i$. Since $g(\nu)$ has a finite value over only a small range of $\nu$ and noting $\int g(\nu) \, dv = 1$, very little accuracy is lost if Eq. C.1 is rewritten as
\[ \int \alpha \, dv = \frac{\hbar \nu}{c} N_1 B_{13i}. \quad (C.2) \]

The atomic absorption cross section \( \sigma \) (anisotropic) is related to \( \alpha \) by

\[ N_1 \sigma = \alpha. \quad (C.3) \]

Also from Eq. A.19

\[ B'_{13i} = \frac{g_3}{g_1} B'_{3li}, \quad (C.4) \]

where \( g_3 \) and \( g_1 \) are the multiplicities of the states \( ^4T_2 \) and \( ^4A_2 \), respectively. Equations C.2 through C.4 give

\[ \int \alpha \, dv = \frac{\hbar \nu}{c} \frac{g_3}{g_1} B'_{3li}. \quad (C.5) \]

Equation A.20, which relates the \( A' \) and \( B' \) coefficients, then gives the following

\[ A'_{3li} = \frac{g_1}{g_3} \left( \frac{\nu}{c} \right)^2 \int \sigma \, dv. \quad (C.6) \]

### C.2 Estimate of Transition Probability

To a reasonable degree of accuracy, Eq. C.6 may be rewritten as follows

\[ A'_{3li} = \frac{g_1}{g_3} \left( \frac{\nu}{c} \right)^2 \sigma_m w, \quad (C.7) \]

where \( \sigma_m \) is the peak absorption cross section, \( w \) is the line half width of \( 6.5 \times 10^{-13} \) Hz (70 nm), \( \nu \) is the center frequency
of the line which is $5.5 \times 10^{14}$ Hz (550 nm), $c$ is the velocity of light in ruby which is $1.70 \times 10^{10}$ cm/s. The degeneracies of the $^4T_2$ and $^4A_2$ states are $g_3 = 12$ and $g_1 = 4$, respectively.

Using the above values we arrive at

$$A'_{31i} = 2.27 \times 10^{22} \sigma_m.$$  \hspace{1cm} (C.8)

Dodd et al.\textsuperscript{44} have published measurements which allow calculation of the principal values of $\sigma_m$. They are as follows

\begin{align*}
\alpha \text{ spectrum (E} \perp \text{ C,B} \perp \text{ C)}, & \quad \sigma_m = 14.2 \times 10^{-20} \text{ cm}^2 \\
\sigma \text{ spectrum (E} \perp \text{ C,B} \parallel \text{ C}), & \quad \sigma_m = 14.2 \times 10^{-20} \text{ cm}^2 \\
\pi \text{ spectrum (E} \parallel \text{ C,B} \perp \text{ C}), & \quad \sigma_m = 5.22 \times 10^{-20} \text{ cm}^2. \hspace{1cm} (C.9)
\end{align*}

Hence the values of $A'_{31i}$ for the three principal spectra are

$$\begin{align*}
A'_{31\alpha} &= 3.2 \times 10^3 \\
A'_{31\sigma} &= 3.2 \times 10^3 \\
A'_{31\pi} &= 1.2 \times 10^3 \\
\end{align*} \text{ per second, per steradian} \hspace{1cm} (C.10)$$

To obtain the total transition probability $A_{31}$, $A'_{31i}$ is integrated over all possible directions and polarizations. It is intuitively reasonable to suppose that

$$A_{31} = \int \sum_i A'_{31i} \, d\Omega = 2 \times 4\pi \left( \frac{A'_{31\alpha} + A'_{31\sigma} + A'_{31\pi}}{3} \right),$$  \hspace{1cm} (C.11)

where the factor two accounts for the two polarizations, $4\pi$ is from integrating over all solid angles, and the term in parentheses is the appropriate mean of $A'_{31i}$. It is certainly
correct in the isotropic case. Cantor* has verified it for the uniaxial case which applies here. Substituting Eq. C.10 into C.11, the following result is obtained

\[
A_{31} = 6.4 \times 10^{10}/s. \quad (C.12)
\]

This is the estimated radiative transition probability for transition \( ^4T_2 \rightarrow ^4A_2 \).

---

LIST OF REFERENCES


42. Einstein, A., Physikalische Zeitschrift 18, 121 (1917).


<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Einstein A coefficient, and amplitude of electric field</td>
</tr>
<tr>
<td>A'</td>
<td>anisotropic A coefficient</td>
</tr>
<tr>
<td>4A2</td>
<td>ground state of chromium ion in ruby</td>
</tr>
<tr>
<td>B</td>
<td>Einstein B coefficient</td>
</tr>
<tr>
<td>B'</td>
<td>anisotropic B coefficient</td>
</tr>
<tr>
<td>C</td>
<td>capacitance, and frequency factor</td>
</tr>
<tr>
<td>c</td>
<td>velocity of light in medium</td>
</tr>
<tr>
<td>d</td>
<td>length of resonator</td>
</tr>
<tr>
<td>E</td>
<td>energy, and electric field</td>
</tr>
<tr>
<td>E'</td>
<td>metastable state of chromium ion in ruby</td>
</tr>
<tr>
<td>e</td>
<td>electronic charge</td>
</tr>
<tr>
<td>f</td>
<td>oscillator strength</td>
</tr>
<tr>
<td>Δf</td>
<td>bandwidth of detector system</td>
</tr>
<tr>
<td>g</td>
<td>degeneracy of state</td>
</tr>
<tr>
<td>g(v)</td>
<td>line shape function</td>
</tr>
<tr>
<td>h</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>I</td>
<td>intensity</td>
</tr>
<tr>
<td>i</td>
<td>current, and polarization</td>
</tr>
<tr>
<td>ΔIrms</td>
<td>current fluctuation at photocathode</td>
</tr>
<tr>
<td>J</td>
<td>energy in joules</td>
</tr>
<tr>
<td>K</td>
<td>calibration constant</td>
</tr>
<tr>
<td>k</td>
<td>calibration constant, and Boltzmann constant</td>
</tr>
<tr>
<td>l</td>
<td>distance, and mode number</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>m</td>
<td>electronic mass, and an arbitrary integer</td>
</tr>
<tr>
<td>N</td>
<td>population, and detector noise current</td>
</tr>
<tr>
<td>η</td>
<td>number of photons emitted, and an arbitrary integer</td>
</tr>
<tr>
<td>P</td>
<td>probability</td>
</tr>
<tr>
<td>p</td>
<td>mode number</td>
</tr>
<tr>
<td>Q</td>
<td>number of photons per second emitted</td>
</tr>
<tr>
<td>q</td>
<td>longitudinal mode number</td>
</tr>
<tr>
<td>R</td>
<td>impedance, branching ratio, and mirror radius</td>
</tr>
<tr>
<td>S</td>
<td>nonradiative transition probability, and detector signal current</td>
</tr>
<tr>
<td>T</td>
<td>temperature in degrees kelvin, and transmission</td>
</tr>
<tr>
<td>( ^{4}<em>{2}T</em>{1} )</td>
<td>an excited state of the chromium ion in ruby</td>
</tr>
<tr>
<td>( ^{4}<em>{2}T</em>{2} )</td>
<td>an excited state of the chromium ion in ruby</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>V</td>
<td>potential in volts, and volume</td>
</tr>
<tr>
<td>W</td>
<td>pumping rate, and power in watts</td>
</tr>
<tr>
<td>w</td>
<td>line half width</td>
</tr>
<tr>
<td>( \hat{X} )</td>
<td>matrix element</td>
</tr>
<tr>
<td>x</td>
<td>distance</td>
</tr>
<tr>
<td>Z</td>
<td>quantum state</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>absorption coefficient, and a constant related to resonator parameters</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>energy difference</td>
</tr>
<tr>
<td>( \mathcal{E} )</td>
<td>activation energy</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>wavelength</td>
</tr>
<tr>
<td>( \nu )</td>
<td>frequency</td>
</tr>
<tr>
<td>( \rho )</td>
<td>energy density</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>absorption cross section</td>
</tr>
<tr>
<td>( \tau )</td>
<td>lifetime of state ( ^4T_2 )</td>
</tr>
<tr>
<td>( \phi )</td>
<td>phase angle</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>direction</td>
</tr>
<tr>
<td>( \Delta\Omega )</td>
<td>element of solid angle</td>
</tr>
</tbody>
</table>