TIME-RESOLVED LASER SPECTROSCOPY OF MERCURY MOLECULES.

RONALD J. NIEFER
University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
https://scholar.uwindsor.ca/etd/4394
NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur; SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.
TIME-RESOLVED LASER SPECTROSCOPY
OF Hg₂ MOLECULES

by

RONALD J. NIEFER

A Dissertation
Submitted to the Faculty of Graduate Studies through the
Department of Physics in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy
at the University of Windsor

Windsor, Ontario; Canada

1983.
ABSTRACT

Highly excited (Rydberg) states in Hg₂ molecules were populated by two successive laser pulses, a 'pump' and a 'probe' pulse, with several μs delay between them. The time-evolution of the band fluorescence emitted in the radiative decay of these states was analyzed with a transient digitizer and a spectrometer, yielding the average fluorescent decay times for the bands at 259 nm, 261.2 nm, 271.8 nm, 330 nm, 420 nm, 451.4 nm, 509.7 nm, and 632.6 nm, as well as the average lifetimes of the 6¹D₂ and 6¹D₂ atomic states which agree well with other recent determinations. Cross sections for the depopulation of several of the Rydberg molecular and atomic states induced by collisions with Hg atoms were also measured. The observed decay-times of the molecular bands and of the accompanying atomic fluorescence provide a basis for the assignment of the bands to specific molecular states and transitions. The structure of the molecular fluorescent bands near 420 nm, 509.7 nm, and 632.6 nm was analyzed and some molecular vibrational constants obtained. A quad-prism unidirectional achromatic beam-expander for use in the oscillator stage of a pulsed dye-laser was designed and tested.
ACKNOWLEDGEMENTS

I am most grateful to Dr. L. Krause for his supervision and sponsorship of this work, and for his critical reading of this dissertation in draft form. I am extremely grateful to Dr. J. B. Atkinson for his invaluable advice, suggestions, and contributions throughout the course of this work. I am very grateful to Dr. W. E. Baylis and to Dr. G. W. F. Drake for many useful discussions which helped in the interpretation of some of the experimental results. I am grateful to the faculty, staff, and graduate students of the Physics Department, with whom I have been associated over the years for many stimulating discussions.

Special thanks are due Mr. W. Brewe and the machine shop staff, Mr. B. Masse in the electronics shop, and Mr. R. Campbell and Mr. A. Ditchburn in the glass-working shop, for their assistance in the design and maintenance of much of the equipment used in this investigation, and to Mr. A. Buzdeo for his artistic skills in the preparation of many of the diagrams which appear in this dissertation.

I am very grateful to the Natural Sciences and Engineering Research Council Canada for financial assistance during part of my postgraduate studies.

Special thanks to my Parents, sister, Willy, Pat, and Red.
TABLE OF CONTENTS

PAGE

ABSTRACT iv

ACKNOWLEDGEMENTS v

LIST OF TABLES viii

LIST OF FIGURES ix

I. INTRODUCTION 1

II. THEORY 7

i) Population of the Hg$_2$O$^+$ Metastable Reservoir States

ii) The Rate Equations for the Population and Decay of Excited States

iii) Vibrational Band Structure of Hg$_2$

III. DESCRIPTION OF THE APPARATUS 18

i) General

ii) The Pump Laser

iii) The Probe Laser

iv) Continuous Excitation Sources

v) The Fluorescence Cell and Oven

vi) The Spectrometer and Data Acquisition System

IV. EXPERIMENTAL PROCEDURES 45

i) General

ii) Preparation of the Fluorescence Cell

iii) Preparation of Discharge Lamps

iv) Tests for Impurities in the Cell

v) Preliminary Search for cw-induced Fluorescence

vi) Pulsed Pump-and-Probe Experiments on Mercury Vapour
V. RESULTS AND DISCUSSION

i) Atomic Lifetimes
ii) Molecular Lifetimes and Vibrational Band Structures

VI. SUMMARY AND CONCLUSIONS

APPENDICES

I. Quad-Prism Unidirectional Achromatic Beam-Expander

II. Computer Simulation of the Decay of an Excited State Subjected to Pulsed Pumping

BIBLIOGRAPHY

VITA AUCTORIS
LIST OF TABLES

I. Probe dye-laser spectral output characteristics. 26
II. Argon-Ion Laser wavelengths and maximal powers. 32
III. Radiative lifetimes of the Hg $^1D_2$ and $^3D_2$ states. 64
IV. Vibrational analysis of the Hg$_2$ 420 nm band. 75
V. Vibrational analysis of the Hg$_2$ 509.7 nm band. 78
VI. Vibrational analysis of the Hg$_2$ 632.6 nm band. 82

AI-1. Angular relations in the beam expander for various magnifications. 124
LIST OF FIGURES.

1. Partial energy level diagram for the low-lying Hg and Hg₂ states. 6
2. Schematic diagram of the apparatus for 'pump-and-probe' measurements. 19
3. Side-view of the dye-laser arrangement. 22
4. Top-view of the dye-laser arrangement. 23
5. Ray-diagram of the spectral filter. 27
6. Schematic diagram of the apparatus for cw-induced fluorescence measurements. 31
7. Block diagram of the vacuum system. 35
8. Schematic diagram of the oven. 37
9. Schematic diagram of the apparatus for delayed coincidence measurements. 42
10. Schematic diagram of the distillation chain. 46
11. Spectrum of the Hg 335 nm and 485 nm molecular bands. 50
12. Time-decay spectra of the two-photon pumped Hg 61D₂ state. 62
13. Time-decay spectra of the two-photon pumped Hg 63D₂ state. 63
14. Direct and sensitized fluorescence produced by two-photon pumping the Hg 61D₂ and 63D₂ states. 66
15. Time-evolution of the 420 nm fluorescent band. 70
16. Variation of the fluorescent decay rates of the Hg₂ 420 nm, 509.7 nm, and 632.6 nm bands, with Hg vapour pressure. 72
17. Vibrational structure of the 420 nm band. 74
18. Vibrational separations between successive v'' levels in the 420 nm band. 75
19. Vibrational structure of the 509.7 nm band. 77
20. Vibrational separations between successive v'' levels in the 509.7 nm band. 78
21. Vibrational structure of the 632.6 nm band. 81

22. Vibrational separations between successive ν" levels in the 632.6 nm band. 82

23. Variation of the fluorescent decay rate of the Hg\(^2\) 451.4 nm band with Hg vapour pressure. 84

24. Time-evolution of the 435.8 nm atomic fluorescence and 262.2 nm molecular fluorescence following pulsed excitation. 89

25. Atomic fluorescence induced by pulsed 261.2 nm radiation. 95

26. Variation of the decay rate of 435.8 nm fluorescence with Hg vapour pressure. 96

27. Potential energy curves and molecular transitions for Hg\(^2\). 98

28. Time-evolution of the Hg\(^2\) 335 nm fluorescence, showing energy pooling effects. 100

AI-1. One-dimensional magnification at an air/glass interface. 109

AI-2. A prism-pair representing one-half of a quad-prism beam-expander. 112

AI-3. Layout of a quad-prism beam-expander. 115

AI-4. Variation of one-way transmission through a quad-prism beam-expander with prism apex angles. 116

AI-5. A plot of the variation of the exit angle from a quad-prism beam-expander with wavelength. 118

AI-6. Division of the wavefront at the entrance face of a prism covered with a single-layer anti-reflection coating. 119

AI-7. Interferograms of the narrowband and broadband outputs from a pulsed dye-laser employing a quad-prism beam-expander. 123

AII-1. Computer-simulated time-evolution of the decay of an excited state with pulsed pumping. 129
I. INTRODUCTION

The systematic study of excited dimers (excimers), diatomic molecules that have bound excited states but repulsive or weakly bound ground states, is of relatively recent date and has been spurred on by the invention of various excimer lasers. Until quite recently, very little was known about the low-lying energy states of the Hg$_2$ dimer, and almost nothing about the higher (Rydberg) states. Nevertheless, it was believed that the Hg$_2$ molecule might provide a vehicle for a powerful tunable visible and ultraviolet gas laser with a large energy storage capability and good resistance to damage at high power levels. Houtermans (1960) suggested the possibility of the Hg$_2$ system for such a laser, based on its then known properties. Various groups (Carbone and Lityak 1968; Hill et al 1973; Schlie et al 1974; Mosburg and Wilke 1977; Schlie et al 1980) investigated properties of Hg molecules to determine their potential as a viable laser medium. Most of the work was done with high energy discharge techniques and, consequently, differing values of gain and loss were obtained. Other results obtained by selective optical excitation of Hg$_2$ (Komine and Byer 1977; Drullinger et al 1977) indicated substantial loss in the ultraviolet, and a noticeably smaller but definite loss in some visible regions, attributable to Hg absorption. It became apparent that further theoretical and experimental investigation of
Hg$_2$ was required to understand the properties of the higher excited states, which might inhibit lasing action.

Collisions of excited mercury atoms and molecules and the associated atomic and molecular fluorescence have been studied in this laboratory (Deech et al 1971; Pitre et al 1972; Phaneuf et al 1973; Skonieczny and Krause 1974; Siara and Krause 1975) and elsewhere (Drullinger et al 1977; Komine and Byer 1977; Stock et al 1978a, 1978b). Particular attention had been given to the well-known fluorescent band spectra which are observed when pure mercury at high density, or at low density in mixture with nitrogen, is irradiated with 253.7 nm resonance radiation. The molecular fluorescence consists of two principal bands centered at 335 nm and 485 nm, that are known to persist for milliseconds after the exciting light is extinguished. Phillips (1913) first observed the afterglow, and Rayleigh (1927, 1932) found that both bands decayed simultaneously and that the metastable $\delta^3P_0$ state, which is known to be populated by collisional transfer from the $\delta^3P_1$ state, was involved in their emission.

Franck and Grotrian (1921) were the first to associate the bands with electronically excited states of the Hg$_2$ molecule. Mrozowski (1937, 1944) suggested that radiative decay of the $A^3Q_u^-$ molecular state correlating with the $\delta^3P_0$ atomic state was responsible for the 485 nm band, and the $\delta^3P_1$ atomic state, was responsible for the 335 nm band, and constructed
potential energy curves based on this assignment. Experiments by McCoubrey (1954) cast some doubt on this interpretation; noting that the band intensity ratio \( I(485\, \text{nm})/I(335\, \text{nm}) \) was proportional to the square of the mercury density, he concluded that the 335 nm band was due to the radiative decay of the \( \Sigma^1_u \) state, and that the 485 nm band was due to collision-induced emission caused by a triple collision between two ground state mercury atoms and an \( \Sigma^1_u \) molecule.

It is well known that these bands appear in mercury at much lower pressure when nitrogen is present (Mrozowski 1937; Pringsheim 1949). This is thought to be due to the efficient collisional mixing of the \( 6^3P_1 \) and \( 6^3P_0 \) atomic states (Pitre et al 1972). Investigations of the band intensities in the presence of nitrogen and other gases (Fenzes et al 1967; McAlduff et al 1968) showed that the bands appeared only when absorption of the 404.7 nm line (\( 6^3P_1 \rightarrow 7^3S_1 \)) indicated the presence of metastable mercury atoms. Both authors were led to favour Mrozowski's original assignment.

More recent experiments (Drullinger et al 1977), coupled with the theoretical arguments of Smith et al (1977), provided conclusive evidence that the 335 nm band is due to the radiative decay of the \( 1_u \) state of Hg\(_2\) and the 485 nm band results from the radiative decay of a Hg\(_3\) state. The experiments also yielded fairly accurate energies of the electronic levels associated with the emission of the two
fluorescent bands, and of the primary molecular reservoir. Stock et al (1978) developed a kinetic model incorporating the lowest radiating \( \text{Hg}_1 \), \( \text{Hg}_2 \) and \( \text{Hg}_3 \) states, and the \( \text{Hg} \) and \( \text{Hg}_2 \) metastable 'reservoir' states. The model permits calculations of relative populations of these states and suggests a mechanism for the transfer of excitation energy among them.

Some spectroscopic work carried out on the higher molecular states (Takeyama 1952), indicated the existence of transitions between molecular Rydberg states, but very little quantitative information was available. Theoretical calculations (Hay and Dunning 1976; Mies et al 1978) predicted the locations of the low-lying \( \text{Hg}_2 \) states and indicated the possibility of absorption resulting in the population of more highly excited states. Subsequently, transitions between the low-lying metastable states and the radiating \( \text{Hg}_2 \) state were induced with a powerful infrared laser (Ehrlich and Osgood 1979b). Quite recently, Callear and Lai (1979, 1980, 1982) carried out extensive flash photolysis experiments and reported numerous visible and ultraviolet molecular absorption bands, many of which correlate with those seen by Takeyama (1952) in emission. However, the two investigations do not provide definite assignment of all the bands, even though many assignments were made to transitions between specific states.

In another series of experiments Ehrlich and Osgood (1978, 1979a) investigated the major \( \text{Hg}_2 \) ultraviolet band
located near 225 nm, which arises from transitions from the \( \Omega_u^+ \) state correlating with the \( ^1P_1 \) atomic state to the \( \Omega_g^+ \) ground state. The authors also reported very weak radiative transitions in the visible to some molecular states above the ground state. This large difference in intensity may well be due to the extremely large transition probability from this \( \Omega_u^+ \) state to the ground state (Mies et al 1978).

Figure 1 shows the approximate energies of the low-lying levels of \( \text{Hg}_2 \). The relative energies of these levels have been calculated by Mies et al (1978) by extension of their earlier calculations for \( \text{Mg}_2 \). The energy levels in Fig. 1 have been scaled to make them conform to the best available spectroscopic data (Callear and Lai 1962). For clarity, only the lowest \( \text{Hg}_2 \) levels are shown.

In this investigation, a 'pump-and-probe' time-resolved laser spectroscopic technique was used to populate some of the \( \text{Hg}_2 \) Rydberg states and to study the resulting molecular fluorescent bands and associated atomic fluorescence. The time-evolution of the molecular bands as well as some vibrational structures were studied, permitting conclusions concerning the assignment of several molecular transitions. Coupling between the molecular and atomic Rydberg states in mercury was also investigated.
Figure 1. Partial energy level diagram showing some low-lying Hg and Hg₂ states. The designations of the molecular states follow Callear and Lei (1982).
II. THEORY

i) Population of the $\text{Hg}_2 \; ^4\text{Og}^-$ Metastable 'Reservoir' States

Highly excited Rydberg states of $\text{Hg}_2$ can be populated by two main paths, by direct pumping from the ground state, or by excitation from some intermediate molecular state. Excitation from the ground state can make use of large ground state densities, but this advantage is offset by the complications of vacuum-ultraviolet techniques that are required, and by the restrictions on the number of accessible excited states, arising from selection rules for electronic transitions. Transitions from intermediate molecular states can be investigated in more accessible spectral regions, but it is necessary to produce a sufficiently high intermediate state population density. The $0^+$ and $8^-$ states, which correlate with the $\text{Hg} \; ^3\text{P}_1$ and $^3\text{P}_0$ atomic states, respectively, are the primary energy storage ('reservoir') states in $\text{Hg}_2$, since neither state can decay radiatively to the ground state. Consequently, if a large population density can be produced in these metastable states, subsequent transitions to higher states can then be investigated using spectroscopic techniques.

The van der Waals ground state of $\text{Hg}_2$ is essentially an unbound collision complex, with no appreciable population of stable bound molecules. Experimental values for the ground-state binding energy of about $460 \; \text{cm}^{-1}$ (Drullinger et al. 1977) agree quite well with theoretical calculations.
(Baylis 1977). Since a stable ground-state Hg₂ molecule is formed by a three-body collision, whereas it can be dissociated by a two-body collision, the Boltzmann distribution in the shallow ground-state potential well reduces the instantaneous population to a very small value; most of the population resides in ground-state atoms. Direct molecular excitation can still occur, but only by photoassociation of an atom pair (quasi-molecule), subject to the Franck-Condon principle as in the case of bound-bound transitions (Ehrlich and Osgood 1978). This photoassociation effect produces an absorption continuum extending approximately from 254 nm to 335 nm.

The selection rules for allowed electric dipole transitions (Herzberg 1950), neglecting rotational effects, are: ΔL = 0, ± 1, g ↔ u, 0⁺ ↔ 0⁺, 0⁻ ↔ 0⁻, and 0⁺ ↔ 0⁻, assuming Hund's case (c) coupling, as well as standard notation.

According to Stock et al (1977), direct optical excitation from the X0 + ground state to the low-lying Hg₂ excimer levels may be accomplished by two distinct processes:

i) excitation to molecular vibrational levels extending from about kT below the 6⁢P⁰ atomic state to the dissociation limit of the 1u state;

ii) excitation to molecular vibrational levels lying more than about kT below the 6⁢P⁰ atomic state.

The first process is facilitated by a moderately high
absorption coefficient but, especially at high densities, the highly excited \( \text{Hg}_2 \) molecules undergo extensive rotational mixing with the \( \text{Hg}_2 \) state near the inner turning point of the repulsive part of the \( \text{Hg}_2 \) potential energy curve. This leads to the rapid dissociation of the excited molecules which are converted into \( \text{Hg} \, ^3\text{P}_0 \) atoms. The second process exhibits only a small amount of dissociation of the excimer, but has a substantially lower absorption coefficient since absorption occurs only from high up on the repulsive part of the ground-state potential energy curve. Both excitation schemes can be represented by the following equations:

\[
\begin{align*}
2\text{Hg}(^1\text{S}_0) + h\nu &\rightarrow \text{Hg}_2(^1\text{u}_v) \rightarrow \text{Hg}(^1\text{S}_0) + \text{Hg}(^3\text{P}_0) & (1) \\
\text{Hg}(^3\text{P}_0) + 2\text{Hg}(^1\text{S}_0) &\rightarrow (\text{Hg}_2)^* + \text{Hg}(^1\text{S}_0) & (2) \\
2\text{Hg}(^1\text{S}_0) + h\nu &\rightarrow \text{Hg}_2(^1\text{u}_v) \rightarrow (\text{Hg}_2)^* & (3)
\end{align*}
\]

Here, \( \text{Hg}_2(^1\text{u}_v) \) represents a vibrationally excited \( \text{Hg}_2 \) molecule, and \( (\text{Hg}_2)^* \) represents a molecule in any of the available molecular levels under thermal equilibrium conditions \( \text{O}_g^+, \text{O}_g^-, \text{O}_u^+, \text{O}_u^-, \text{O}_u \) and \( \text{1}_u \). Stock et al (1977) found that approximately 90% of the input energy corresponding to the first excitation scheme is channelled through the metastable \( \text{Hg}(^3\text{P}_0) \) state. A similar kinetic path is followed for molecules excited to within \( kT \) of the \( ^3\text{P}_1 \) atomic level, with subsequent collisional transfer to the \( ^3\text{P}_0 \) state. In the second scheme, two-body collisions are sufficient to thermalize the \( \text{Hg}_2 \) excimers to an equilibrium distribution consistent with the effective
temperature.

Under thermal equilibrium conditions the population of excimers is transferred into the lowest available states, consistent with the Boltzmann distribution. In \( \text{Hg}_2 \), the \( \text{O}_g^+ \) are the lowest excited dimer levels and, consequently, a large population of these levels is produced. The major loss channels from these metastable levels are two-body collisional transfer to the \( 1_u \) state which can radiate to the ground state (335 nm band), and three-body collisional formation of \( \text{Hg}_3 \) which can also radiate to the ground state (405 nm band). These can be represented by the following equations.

\[
\begin{align*}
\text{Hg}_2(\text{O}_g^+) + \text{Hg}(6\text{S}_0) & \rightarrow \text{Hg}_2(1_u) + \text{Hg}(6\text{S}_0) \quad (4) \\
\text{Hg}_2(1_u) & \rightarrow 2\text{Hg}(6\text{S}_0) + h\nu \quad (335 \text{ nm}) \quad (5) \\
\text{Hg}_2(\text{O}_g^-) + 2\text{Hg}(6\text{S}_0) & \rightarrow \text{Hg}_3 + \text{Hg}(6\text{S}_0) \quad (6) \\
\text{Hg}_3 & \rightarrow 3\text{Hg}(6\text{S}_0) + h\nu \quad (405 \text{ nm}) \quad (7)
\end{align*}
\]

As indicated in eqs. (1) - (7), the \( \text{O}_g^+ \) and \( 6^3\text{P}_0 \) metastable states are dominant in the long-time decay characteristics, forming the primary excitation energy storage for \( \text{Hg}_2 \) excimers. Consequently, spectroscopic investigations of highly excited states, utilizing stepwise excitation from intermediate states, would be facilitated by maximizing the \( \text{O}_g^+ \) and \( \text{O}_g^- \) populations; this can readily be done by producing a large population of \( \text{Hg}(6^3\text{P}_0) \) atoms.

Two-photon excitation of high-lying \( \text{Hg} \) atomic states can be used to bypass the intermediate molecular processes
and form a large population of excited \( \text{Hg}(6^3P_0) \) atoms according to the following scheme:

\[
\begin{align*}
\text{Hg}(6^1S_0) + 2h\nu & \rightarrow \text{Hg}(6^1D_2) \quad (8) \\
\text{Hg}(6^1D_2) & \rightarrow \text{Hg}(6s6p) + h\nu \quad (9) \\
\text{Hg}(6^1D_2) + \text{Hg}(6^1S_0) & \rightarrow \text{Hg}(6^3D_j, 6s7s) + \text{Hg}(6^1S_0) \quad (10)
\end{align*}
\]

where \( \text{Hg}(6s6p) \) are those states which are accessible by allowed electric dipole transitions; \( \text{Hg}(6^3D_j, 6s7s) \) are those states which are populated by collisions from the \( \text{Hg}(6^1D_2) \) state. The \( \text{Hg}(6^3P_2) \) state is metastable, and the \( \text{Hg}(6^1P_1, 6^3P_1) \) states are strongly radiation-trapped. Some energy deposited in the Hg vapour will be lost through the decay of the \( 6^1P_1 \) state, but it is expected that most of the energy (excluding that lost to cascade transitions) will be channelled into the \( \text{Hg}(6^3P_0) \) state and, consequently, into the \( \text{Hg}_2 \) \( 0^+ \) states. This excitation scheme produces a large population of \( \text{Hg}(6^3P_0) \) atoms and has the advantage of good penetration depth compared to resonance-line pumping.

\[\text{(ii) The Rate Equations for the Population and Decay of Excited States}\]

Highly excited molecular Rydberg states can decay radiatively or be collisionally transferred to other energy levels. They are particularly susceptible to collisional quenching because of the high density of molecular states at high energies. The population of a pulse-excited molecular state may be represented by the rate equation:
\[ \frac{\text{d}}{\text{dt}} [n_1(t)] = -\left( \Gamma_1 + Z_{12} \right) n_1(t) \] 

(11)

where \( n_1(t) \) is the instantaneous population in state 1, \( \Gamma_1 \) is the radiative decay constant \( (\Gamma_1 = 1/\tau_1) \), where \( \tau_1 \) is the corresponding lifetime, and \( Z_{12} \) represents the frequency of collisions per excited atom or molecule that result in the transfer from state 1 to state 2. In the absence of collisions, when the only decay path is spontaneous emission, \( Z_{12} = 0 \) and the solution of eq. (11) is:

\[ n_1(t) = n_1(t=0) \exp(-\Gamma_1 t) \] 

(12)

where \( n_1(t=0) \) is the initial population; it is assumed that there is no pumping of the excited state during its decay (for a discussion of the radiative decay of an excited state with pumping, see Appendix II). If the time-evolution of the radiation intensity emitted in the decay of the excited state is measured by monitoring the fluorescence with respect to the time when the excited state population was produced, and the measured fluorescent intensity plotted semilogarithmically, the plot should be a straight line with slope \(-\Gamma_1\). Equations (11) and (12) apply to both atomic and molecular states.

In the presence of inelastic collisions, \( Z_{12} \neq 0 \) and the solution of eq. (11) is:

\[ n_1(t) = n_1(0) \exp\left(-\left(\Gamma_1 + Z_{12}\right)t\right) \] 

(13)

where
\[ Z_{12} = N \overline{v}_r Q_{12} \]  

(14).

\( N \) is the density of the collision partners (assumed to be ground-state Hg atoms), \( \overline{v}_r = (8kT/\pi \mu)^{\frac{1}{2}} \) is the mean relative speed of the colliding partners, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature of the vapour, and \( \mu \) the reduced mass. It is assumed in eq. (13) that there is no collisional back-transfer from state 2 to state 1.

The total cross section \( Q_{12} \) represents the average of the actual differential cross sections \( \sigma_{12}(\overline{v}_r) \), taken over the Maxwell-Boltzmann distribution \( P(v,T) \):

\[ Q_{12}(T) = \frac{\int_0^\infty \sigma_{12}(v)P(v,T)vdv}{\int_0^\infty P(v,T)vdv} \]  

(15)

Since at a fixed temperature \( \overline{v}_r \) and \( Q_{12} \) are constant, eq. (14) predicts a linear variation of \( Z_{12} \) with vapour density. Consequently, measurement of the effective decay rate of an excited state, extrapolated to zero vapour density, yields the radiative lifetime \( \tau_1 \). This value, when incorporated into eq. (13) permits the determination of \( Z_{12} \) and thus of \( Q_{12} \).

The assumptions made in this derivation are extremely simple and neglect other possible effects, such as collisional repopulation of the excited state and energy pooling effects resulting from collisions of two excited molecules; correction for these effects would require additional terms in eq. (11). However, this approach gives a
rough estimate of the total cross section for collisional quenching of excited atoms and molecules.

There are other effects which can influence the decay of excited molecules, such as Quantum Mechanical tunneling and predissociation. They can both lead to the transfer of excitation energy from an excited state to other molecular or atomic states. In the case of tunneling, which arises from an anti-crossing of two potential energy curves with the same $\Omega$ (projection of the total angular momentum along the internuclear axis) and the same symmetry properties, penetration of the wavefunction through the classically forbidden part of a potential barrier causes an effective leakage of the wavefunction through the barrier. Since vibrational frequencies are high, the probability of finding the atoms at an internuclear separation which corresponds to a dissociated molecule increases monotonically with time; the time required for tunneling to depopulate the molecular level is proportional to the area under the barrier. Higher vibrational levels tunnel out of the bound potential well more quickly than lower vibrational levels. In the case of predissociation, overlap of the wavefunction of a bound molecule with that of another configuration, which may correspond to an unbound molecule, can lead to similar transfer of the excited state population out of the bound state to a lower bound state or to a dissociative state. Both tunneling and predissociation can lead to extremely fast radiationless decay of molecular excited states.
iii) Vibrational Band Structure of Hg₂

The existence of vibrational states in diatomic molecules gives rise to band structure which corresponds to the various allowed vibrational transitions between a pair of electronic levels. Although there is no hard and fast selection rule for vibrational transitions between different electronic levels, the intensities of the transitions are governed by the appropriate Franck-Condon factors. Several useful molecular parameters can be obtained from the analysis of band spectra, based on the measured frequencies of the vibrational components.

The frequencies of the spectral lines (expressed in wavenumbers), corresponding to transitions between electronic states, either in absorption or in emission, (Herzberg 1950) may be represented by:

\[ \nu = \left( T'_{e} - T''_{e} \right) + \left( G'_{e} - G''_{e} \right) + \left( F'_{e} - F''_{e} \right) \]  

(16)

where the single-primed symbols refer to the upper state and the double-primed symbols to the lower state; the total energy is denoted by \( T \). The electronic energy is denoted by \( T_{e} \), the vibrational energy by \( G \), and the rotational energy by \( F \). If both upper and lower states are rotationless, the frequencies of the vibrational components are given by:

\[ \nu = G'_{e} - G''_{e} \]  

(17)
\[ \nu = \nu_e + \omega_e (v' + 1/2) - \omega_e x_e (v' + 1/2)^2 + \ldots \]

\[ - [\omega_{e}'' (v'' + 1/2) - \omega_{e}'' x_e (v'' + 1/2)^2 + \ldots] \]

(18)

where \( v' \) and \( v'' \) are the vibrational quantum numbers of the upper and lower states, respectively. \( \nu_e \) is the frequency corresponding to the electronic transition (neglecting vibration and rotation), \( \omega_e \) the vibrational frequency, and \( \omega_e x_e \) is the anharmonicity. The presence of anharmonicity in the oscillations leads to reduced vibrational spacing between successively higher vibrational levels and allows vibrational transitions with \( \Delta v \gg 1 \). Using eq. (18) for the analysis of the vibrational structure of an electronic band, it is possible to calculate the positions of the vibrational levels, the vibrational frequencies and the anharmonicities, as well as the force constants of the molecule in the two electronic states that are involved in the transition (Herzberg 1950).

The rotational structure of electronic transitions within a single vibrational band can be represented in a similar fashion. In this case, \( (T_e' - T_e'') + (B' - B'') = \nu_o \), and the frequencies of the rotational components (in wavenumbers) are expressed in terms of the rotational quantum number \( J \).

\[ \nu = \nu_o + F'(J') - F''(J'') \]

(19)

\[ \nu = \nu_o + B_v J'(J'+1) - D_v J'^2(J'+1)^2 + \ldots \]

\[- [B_v'' J''(J''+1) - D_v'' J''^2(J''+1)^2 + \ldots] \]

(20)

Equation (20) represents a band consisting of three
branches, \( Q, R \) and \( P \), corresponding to rotational transitions with \( \Delta J = 0, \pm 1 \). \( B_e = \hbar / (8\pi^2 c \mu_e^2) \) is the rotational constant (vibrationless); \( B_v = B_e - \alpha_e (v+1/2) \) is the vibration-dependent rotational constant where \( \alpha_e \) is a scaling factor to correct the rotational constant for different vibrational levels. \( \mu \) is the reduced mass of the molecule, \( r_e \) is the equilibrium internuclear distance and \( h \) is Planck's constant. \( D_v \) is the centrifugal stretching constant necessary to compensate for the increased nuclear separation due to rotational effects. In \( \text{Hg}_2 \), the situation is extremely complicated since there are approximately 20 relatively abundant isotopes, many of which have nuclei with non-zero nuclear spins; \( \text{Hg}_2 \) is also a very heavy molecule, which makes the rotational spacing very small. The resulting rotational spectrum is expected to be a virtually continuous distribution with the density of rotational lines typically \( 10^3 \) lines/cm\(^{-1}\) in the vicinity of each band head. To resolve rotational structure, high-resolution spectroscopic measurements would have to be performed using a single isotope of \( \text{Hg} \), preferably one with zero nuclear spin.
III. DESCRIPTION OF THE APPARATUS

i) General

The arrangement of the apparatus is illustrated schematically in Fig. 2. A YAG laser was used as the pump laser to produce a high transient population of excited metastable mercury molecules in a sealed-off quartz fluorescence cell containing Hg vapour. After a suitable delay, the excited vapour was probed with pulses from a nitrogen laser-pumped dye-laser. The resulting fluorescence was monitored at right angles to the laser beams and resolved with a photoelectric spectrometer. The output signals from the photomultiplier were recorded using gated detection techniques and a transient digitizer or a time to amplitude converter followed by a multichannel pulse height analyzer. The resulting time evolution spectra of the fluorescence were analyzed with a computer to yield decay times of the molecular and atomic fluorescence.

ii) The Pump Laser

The pump laser consisted of a Neodymium-3+:Yttrium Aluminum Garnet (YAG) pulsed laser/dye laser system. The YAG laser was a Quanta-Ray DCR-1A oscillator-amplifier unit. Specified maximal output energies were 650 mJ at 1064 nm, 200 mJ at 532 nm, and 30 mJ at 266 nm; pulse width and beam diameter were nominally 5-10 ns and 6.3 mm, respectively. The output at 1.064 μm was generated in a
Figure 2. Schematic diagram of the apparatus. Dye-Laser components: O-oscillator; A-amplifier; P-preamplifier. A-D, transient digitizer; D, photodiode; DP, dispersing prism; PB, Pellin-Broca prism; PM, photomultiplier; SA, signal amplifier; SF, spectral filter; X2, frequency-doubler. Components labeled in parentheses were used only in certain parts of the experiment.
Diffraction-Coupled Unstable Resonator which was fitted with the 'filled-in optics' mirrors. The output which was nearly diffraction limited, was amplified, when necessary, using a power amplifier stage. The YAG laser was always operated in the 'Q-switched' mode to generate short pulses of high-peak power.

The second harmonic at 532 nm was generated in a 50 mm-long Potassium-Dideuterium-Phosphate (KD*P) angle-tuned frequency-doubling crystal. When required, the fourth-harmonic at 266 nm was generated by frequency-doubling the 532 nm output in another KD*P angle-tuned crystal. Polarization orientation of the linearly-polarized output was achieved by rotating the plane of polarization of the 1.064 μm fundamental with a polarization rotator. The various outputs were spatially separated from each other with a Brewster-angle 90°-deviation Pellin-Broca prism made of Suprasil. The prism was oriented to minimize Fresnel reflection losses at the appropriate wavelength. Unused outputs were dissipated in a beam-dump to avoid spurious experimental effects and to reduce physical hazards from the laser.

When the fourth-harmonic was used to pump the Hg vapour, the beam was reduced to approximately 3 mm in diameter by two uncoated Suprasil lenses arranged as a Galilean telescope; this was done to increase the power density incident on the mercury vapour, and to produce a small excited volume for subsequent imaging onto the
detection system. Dielectrically coated high-power laser mirrors supplied by CVI Laser Corporation were used for beam handling. Beam quality of the second and fourth harmonics from the YAG laser was not particularly good; substantial irregularities in intensity existed across the laser beam, resulting from diffraction effects at the output coupler and from the sharp edge effects of the laser rods themselves. These irregularities presented some problems in efficient dye-laser pumping as well as in uniform excitation of the mercury vapour.

When exciting the mercury vapour by two-photon absorption, the 532 nm output from the YAG laser was used to pump a multi-stage dye-laser. The dye-laser was similar to the one shown in Figs. 3 and 4 except that three stages, instead of two, were used. Approximately 5% of the YAG output was used to pump a wavelength-defining oscillator, 25% of the residual energy was used to pump a high-gain preamplifier stage, and the rest was used to pump a low-gain power amplifier stage. The amplifier pump beams were appropriately delayed (Wallenstein and Hänsch 1975; Lawler et al 1976; Bos 1981; Mahon and Tomkins 1982), as shown in Fig. 4, to increase the overall efficiency of the system and to reduce amplification of spontaneous emission from the oscillator before it had reached threshold. The vertically polarized output from the dye laser consisted of a beam of cross-sectional area about 6 mm x 2.5 mm. The divergence of the output was minimized by a beam-expanding 3X Galilean
Figure 3. Side-view of dye-laser arrangement. The dye-cells are tilted approximately 3° to reduce spurious feedback and the output coupler is a 0.5° wedge. The etalon was not normally used.
Figure 4. Top-view of the dye-laser arrangement.
telescope between the preamplifier and power amplifier stages; the output was frequency-doubled in an Interactive Radiation model 532-120 angle-tuned 30 mm-long KDP crystal. The ultraviolet output at 280.293 nm was separated from the dye-laser output by a 60° Suprasil prism and directed into the fluorescence cell where it excited the $^1D_2$ atomic level by resonant two-photon absorption.

The in-house designed and built dye-laser was similar to the support-rod design used in the Molelectron DL-300 except for the oscillator which was of a design described in Appendix I; all stages of the dye laser were side-pumped. The YAG laser output was focussed into the dye-cell using anti-reflection coated BK-7 cylindrical lenses. The dye cells were Molelectron DL-051 magnetically-stirred cuvettes, holding approximately 2.5 cc of dye solution; the dye was stirred using external rotating magnets and teflon coated internal agitators. Three-dimensional adjustments on each stage permitted rapid and precise alignment for optimal efficiency. Rhodamine 6-G (R6G) supplied by Eastman Organic Chemicals, dissolved in A.C.S. grade Methanol was used as the lasing medium at concentrations of $5 \times 10^{-4}$ M in the oscillator, $2 \times 10^{-4}$ M in the preamplifier, and $5 \times 10^{-5}$ M in the power amplifier. The dye lasted a few days in the first two stages, and approximately one day in the power stage, depending on the incident power.

iii) The Probe Laser
The probe laser radiation was generated using a nitrogen laser-pumped 2-stage dye-laser consisting of an oscillator and an amplifier, as shown in Figs. 3 and 4. The nitrogen laser was similar to the Moletron model UV-22 and was also built in-house; it used a fast transverse discharge through pure $N_2$ at a pressure of 35–100 torr. The cavity was formed by a flat dielectrically coated total reflector supplied by Newport Research Corporation, and a flat uncoated Suprasil output window. The maximal output of the laser was measured to be approximately 2.5 mJ in a 10 ns FWHM pulse at 10 Hz; the output beam had a cross-section of about 6 mm x 32 mm and had moderately high divergence.

Approximately 25% of the nitrogen laser output was used to excite the dye-laser oscillator and the remainder was used to pump a single amplifier. The nitrogen laser output was focussed into the magnetically stirred, dye-cells with aspheric focussing lenses. An f=100 mm achromatic anti-reflection coated lens was used to focus the oscillator output into the amplifier dye cell. Various dyes were used both directly and with frequency doubling, as listed in Table I, depending on the desired spectral range.

When observing spectral features close to the exciting wavelength of the probe laser, a grating was placed in the output of the dye laser to act as a spectral filter. In such an arrangement, shown in Fig. 5, the collimated dye-laser output was made incident on a PTR 2400 1/mm holographic diffraction grating and the dispersed first-order spectrum
TABLE I

Nitrogen Laser-Pumped Dye-Laser Parameters. All pulse energies are for 2.5 mJ 337 nm pump and 10 Hz repetition rate; nominal pulse widths for dye laser outputs are < 8 ns. Solvents are: Eth = Ethanol; Meth = Methanol; p-diox = p-dioxane.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>Dye</th>
<th>Solv.</th>
<th>Conc. $(\times 10^{-3} \text{ M})$</th>
<th>$\Delta \nu$</th>
<th>Max. Energy $(\mu\text{J/pulse})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>420.0</td>
<td>S-420</td>
<td>Meth</td>
<td>1.0 0.8</td>
<td>0.3</td>
<td>200</td>
</tr>
<tr>
<td>451.4</td>
<td>7D4MC</td>
<td>Eth</td>
<td>10.0 8.0</td>
<td>0.2</td>
<td>350</td>
</tr>
<tr>
<td>488.0</td>
<td>7D4TMC</td>
<td>p-diox</td>
<td>10.0 8.0</td>
<td>0.2</td>
<td>400</td>
</tr>
<tr>
<td>518.0</td>
<td>C500</td>
<td>Eth</td>
<td>10.0 8.0</td>
<td>0.1</td>
<td>325*</td>
</tr>
<tr>
<td>522.4</td>
<td>C500</td>
<td>Eth</td>
<td>10.0 8.0</td>
<td>0.1</td>
<td>325*</td>
</tr>
<tr>
<td>543.6</td>
<td>C540A</td>
<td>Eth</td>
<td>10.0 8.0</td>
<td>0.3</td>
<td>250*</td>
</tr>
<tr>
<td>560.0</td>
<td>C540A</td>
<td>Eth</td>
<td>10.0 8.0</td>
<td>0.2</td>
<td>150*</td>
</tr>
<tr>
<td>660.0</td>
<td>R6G/CVP</td>
<td>Eth</td>
<td>2.5/3.3 2.5/3.3</td>
<td>0.3</td>
<td>75*</td>
</tr>
</tbody>
</table>

Frequency-Doubled Dye-Laser Output Characteristics, corresponding to maximal input at the fundamental wavelength (*). Pulse widths are nominally < 8 ns.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>Production (nm-Crystal)</th>
<th>Energy (\muJ-max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>* 259.0</td>
<td>518.0 - KDP</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>* 261.2</td>
<td>522.4 - KDP</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>* 271.8</td>
<td>543.6 - KDP</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>* 290.0</td>
<td>560.0 - KDP</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>* 330.0</td>
<td>660.0 - KDP</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

(* Energies are as quoted above.)
Figure 5. Ray-diagram for the spectral filter used to reduce stray dye-laser light.
was selectively transmitted by a 4 mm aperture located about 8 m away. In this way it was possible to observe parts of the fluorescent spectrum close to the exciting wavelength, without interference from the broad-band superradiance which normally accompanies pulsed dye-laser light. The fluorescence cell and detection electronics were located about 15 m from the probe dye-laser to reduce electrical interference caused by the pulsed discharge; consequently, the direction of the dye-laser output, after passing through the grating filter, depended on the wavelength. Since the fluorescing volume of mercury vapour was defined by the output direction of the pump laser and location of the fluorescence cell, only small wavelength changes of the probe laser could be accommodated before the two beams no longer overlapped in the same region of mercury vapour. Major wavelength changes (more than 0.1–0.2 nm) required a substantial readjustment of the beam-handling optics to maintain correct overlap of the pump and probe beams in the fluorescence cell. Beam steering from the probe laser to the fluorescence cell was accomplished with silicon monoxide-coated aluminized mirrors.

The probe laser system was triggered after a suitable delay using an in-house built delay generator which produced a fixed delay of 650 ns or a continuously variable delay from 2 µs to 500 µs. The delay jitter between the trigger pulse and the optical output was found to be approximately 10 ns. Trigger pulses generated by sampling the output from
the pump-laser with an E.G.&G. SGD 100-A photodiode were used when highly accurate timing was required; the 'sync' output from the YAG laser was used when less stringent pulse-timing was acceptable.

The temporal characteristics of the pulsed lasers were measured using a Lasermetrics model 3117 high-speed photo detector; specified rise and fall times were 150 ps and 250 ps, respectively, into a 50 ohm resistive load. The output from the detector was applied to a Tektronix model 7844 dual beam oscilloscope containing a 7A19 plug-in amplifier, which had a specified 3-dB bandwidth of 500 MHz. Pulse shapes were recorded photographically or measured electrically with the TAC/MCA arrangement described later.

Spectral profiles were recorded photographically using dielectrically coated etalons. Dye-laser bandwidths in the blue-green spectral range were measured with a Molelectron DL 026-A etalon which had a specified free spectral range of 1.123 cm\(^{-1}\) and a Finesse of approximately 10. Bandwidths in the yellow-red spectral range were measured photographically using a Quanta-Ray FPA-1 etalon with a specified free spectral range of 1 cm\(^{-1}\) and Finesse of approximately 15.

Output pulse energies were measured using a Scientech model 362 power meter equipped with a surface-absorbing calorimeter detector. YAG and YAG-pumped dye-laser output energies were measured by means of partial reflections of the laser beam; this was necessary to avoid damage to the surface of the sensing element. Corrections were calculated
using appropriate Fresnel equations corresponding to the polarization of the incident laser light.

iv) Continuous Excitation Sources

Two alternative excitation sources were used: a cw laser and a spectral lamp; the arrangement of the apparatus for cw laser-pumping is shown in Fig. 6. The laser was a Spectra-Physics model 170-00 Argon-ion laser, with up to .8 watts TEM-00 output at 514.5 nm. This output was optimally focused (Boyd and Kleinman 1968) by a f=210 mm coated achromatic lens into an Interactive Radiation model 520-004 temperature-tuned 50 mm-long Ammonium-Dihydrogen-Phosphate (ADP) crystal. The ultraviolet output at 257.2 nm was separated from the fundamental wavelength component with a 60° Suprasil prism and the remaining 514.5 nm laser radiation was used to pump a Spectra-Physics model 375 dye-laser.

The various laser wavelengths available from the Ar+ laser are listed in Table II; the powers available are specified both for the laser operating at a single wavelength (not single mode) and for the laser operating in the 'all-lines' mode. The different wavelengths had to be separated from each other externally when the laser was operated in the all-lines configuration. As indicated in Table II, certain spectral lines were not available when the laser was used in other than the single wavelength mode. The cw dye laser was operated with R6G dissolved in an ethylene
Figure 6. Schematic diagram of the apparatus used to search for cw-induced fluorescence. ADP, frequency-doubling crystal; P, 60° prisms; PM, photomultiplier tube.
**TABLE II**

Argon-Ion Laser Wavelengths and Maximal Powers.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Power Single-Line Operation (Watts)</th>
<th>Power All-Lines Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>514.5</td>
<td>8.0</td>
<td>6.0</td>
</tr>
<tr>
<td>501.7</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>496.5</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>498.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>476.5</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>472.7</td>
<td>0.3</td>
<td>N/A</td>
</tr>
<tr>
<td>465.8</td>
<td>0.2</td>
<td>N/A</td>
</tr>
<tr>
<td>457.9</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>454.5</td>
<td>0.2</td>
<td>N/A</td>
</tr>
<tr>
<td>363.8</td>
<td>N/A</td>
<td>0.3</td>
</tr>
<tr>
<td>351.1</td>
<td>N/A</td>
<td>0.3</td>
</tr>
</tbody>
</table>
glycol solution and generated up to 1.0 W of laser radiation in the spectral range from 565 nm to 655 nm when pumped by 6 W of 514.5 nm light, with a typical spectral bandwidth of 0.25 nm at 590 nm.

The mercury spectral lamp consisted of a cylindrical Suprasil bulb approximately 15 mm in diameter and 70 mm-long, a side arm about 10 mm in diameter and 25 mm-long, fused coaxially onto the main body of the lamp, served as a mercury reservoir. After high-temperature bakeout, a drop of natural mercury was distilled into the lamp. Argon (Union Carbide 99.9995%) at a pressure of about 0.75 torr was used as the carrier gas. The side-arm permitted regulation of the vapour pressure, independently of the temperature of the lamp body which was placed in the tank-coil of a high-power RF oscillator. The narrow-line output from the lamp was used for resonance-line pumping at 253.7 nm, and for spectrometer calibration.

v) The Fluorescence Cell and Oven

The sealed-off cylindrical fluorescence cell, approximately 7 cm-long and 4 cm in diameter, was constructed of non-fluorescing Suprasil quartz and was fitted with two parallel 1.5 mm-thick Suprasil end windows which were fused to the cell body. A side-arm approximately 15 cm-long and 1.5 cm in outside diameter made from ordinary quartz was fused to the cell and served as a reservoir for the liquid mercury. With such an arrangement there were no
pressure gradients between the cell and side-arm. The side-arm was filled with approximately 5 g of natural triple-distilled mercury supplied by Englehard Industries.

The cell was connected by means of graded seals to a glass vacuum system shown schematically in Fig. 7. High vacuum was achieved using an Edwards E02 diffusion pump filled with Edwards Santovac 5 fluid and backed by an Edwards ED 100 two-stage rotary pump. A water-cooled 'chevron' baffle prevented backstreaming of pump fluids. A liquid-nitrogen trap was used to further reduce contamination of the cell by pump fluids. An Edwards QSB2 butterfly valve, located directly above the diffusion pump, permitted isolation of the pump from the vacuum system for outgassing and leakage tests.

The main pumping stage was isolated from the rest of the system by a glass stopcock lubricated with Apiezon-L grease. A titanium getter-pump and a 'U'-tube' cold trap, which could be cooled with either liquid-nitrogen or dry ice, completed the vacuum system. Pressure in the roughing line was measured with a CVC GTC-004 thermocouple gauge and high vacuum in the glass section of the system was measured with a CVC GIC-028-2 ionization gauge; both gauges were connected to a Bendix GIC-300 control unit. The quartz sections of the vacuum system were baked as necessary using an oven fitted with chromel-A resistance wire elements. Temperatures of the order of 900 K were used to bake the cell and reduce subsequent outgassing of absorbed and
Figure 7. Block diagram of the vacuum system. RP, rotary pump; G1, thermocouple gauge-head; DP, diffusion pump; BV, chevron baffle; V, butterfly valve; CT1, liq. N$_2$ cold-trap; SC, glass stopcock; TP, titanium getter-pump; G2, ionization gauge-head; CT2, 'U-tube' cold-trap; C, quartz cell; DC, distillation chain; R, Hg reservoir; X, detachment point; S, graded seals.
adsorbed contaminants.

During the experiments, the sealed-off cell with the side-arm was mounted in a two-compartment double-walled oven depicted in Fig. B. The compartment which enclosed the side-arm, contained a thermally isolated 50-watt tubular power resistor which was fitted over the lower side-arm section of the cell, thermal contact being provided by thin copper foil wrapped around the side-arm inside the heater. The inside of the heating element was sealed off at one end with a castable ceramic cement in which two chromel-alumel thermocouples were embedded in close proximity to the copper foil, permitting determinations of temperature and thus Hg vapour pressure. The main oven which contained the body of the cell was approximately cubical in shape, about 15 cm in height. The sides and top of the inner box were made of 1 mm stainless steel sheet attached to a 6.3 mm-thick stainless steel base. The oven had heating elements which consisted of helically wound sections of chromel-A 1.0 mm-thick resistance wire connected in a series/parallel arrangement to permit operation at a high temperature with reasonable voltages and currents. Both sections of the oven were powered by separate Variac autotransformers connected to 120 VAC wall outlets. Two chromel-alumel thermocouples were mounted adjacent to but not touching the cell for measurement of the main oven temperature. Thermal as well as electrical insulation for the heater elements was provided by a 6 mm-thick asbestos layer on the inside of the oven. A
Figure 8. Schematic diagram of the oven. TC<sub>1-4</sub>, chromel-alumel thermocouples; W<sub>1</sub>-W<sub>2</sub>, suprasil windows.
layer of copper foil was wrapped around the side-arm section and extended from the main oven down to but not into the side-arm heater; this layer of copper produced a moderately uniform thermal gradient between the two oven compartments.

The inner box of the main oven was separated from the outer housing by three ceramic spacers to reduce heat conduction losses. The outer jacket of the oven assembly was made of 6.3 mm aluminum plate, clad with thin sheets of copper to which were soldered 6.3 mm-OD lengths of copper tubing for cooling water. This provided thermal safety, as well as a moderately stable external ambient temperature which was fairly constant over periods of several weeks and showed only slight long-term variation. The space between the inner and outer parts of the oven compartments was filled with mica chips (vermiculite) insulation to further reduce thermal losses. Access for light into and out of the cell was provided by quartz sleeves installed between the inner and outer boxes. These access ports were closed off on the outside by 1.5 mm-thick Suprasil windows to reduce heat loss by convection and to eliminate thermal Schlieren effects.

Temperatures were measured with thermocouples connected to separate digital voltmeters for the main and the side ovens; thermoelectrically induced voltages were converted to temperatures using Leeds and Northrup thermocouple conversion tables. The provision of several thermocouples at various locations in the main and side ovens permitted
monitoring of the temperature in each compartment and the detection of thermal gradients, and also provided insurance in case one of the junctions should fail (the inside of the oven was not readily accessible for minor repairs). The thermocouples were room temperature-referenced by comparison with a mercury thermometer, and periodic adjustments in the offset were made to maintain the room temperature reference point on the voltmeters.

vi) The Spectrometer and Data Acquisition Equipment

Fluorescence emitted by the Hg vapour in the cell was observed at right-angles to the laser beams and was focussed at the entrance slit of a SPEX model 1402 double spectrometer. The 0.85 m focal length spectrometer was equipped with two 1800 line/mm holographic gratings blazed at 500 nm in the first order and arranged in a Czerny–Turner mounting. The instrument had an effective speed of f/7.8 and a reciprocal linear dispersion of 0.304 nm/mm at 514.5 nm in the first order. The efficiency of the spectrometer was specified to be approximately 60% at 514.5 nm when used in the first order, but was found to drop off substantially in the ultraviolet. Suprasil lenses were used between the cell and the spectrometer to increase collection efficiency and to maximize resolution by illuminating the entire grating.

The spectrometer was equipped with a RCA C31034 photomultiplier whose GaAs photocathode had a virtually flat
spectral response extending from 200 nm to 900 nm, with a specified peak quantum efficiency of about 35% at 300 nm. The 11-stage electron multiplier was of a linear focused type with passive biasing achieved by means of a resistive voltage divider chain; capacitors were used between the last few dynodes to increase linearity when dealing with short duration high-amplitude pulses without sacrificing cw performance. The photomultiplier tube had a measured current gain of about $10^6$ at -1800 V and a specified single-pulse rise-time not exceeding 2.5 ns. It was mounted in a Products For Research model TE-104 thermoelectrically cooled and electromagnetically shielded housing, which was capable of maintaining the tube at approximately \(-50^\circ\) C. Such refrigeration of the photomultiplier reduced the dark-current by a factor of about 1000. The exit slit of the spectrometer was imaged on the photocathode using Suprasil lenses.

Negative high voltage for the photomultiplier tube was provided by an Ortec model 456 power supply. When monitoring continuous photon fluxes, signals from the photomultiplier’s anode were amplified by a Keithley model 417 picocammeter and recorded on a Heath-Schlumberger strip-chart recorder. Phase-sensitive detection of signals was accomplished by means of a Princeton Applied Research model 124 lock-in amplifier and model 222 variable speed chopper. With pulsed excitation and fluorescence, the output pulses from the photomultiplier were directed to pulse-amplifying circuits.
When dealing with individual photons, the output from the photomultiplier was amplified with an Ortec model 9301 preamplifier which had a measured gain of 8 and a specified rise-time of less than 1.5 ns.

When experimental data were analyzed using multichannel analysis techniques as shown schematically in Fig. 9, the preamplifier output was sent to an Ortec model 9302 amplifier-discriminator whose output was applied to the stop input channel of an Ortec model 467 Time-to-Amplitude Converter (TAC); the start pulses were obtained by sampling the pulsed light source with an E.G.&G. SGD 100A fast photodiode. Saturation of the diode was prevented by using neutral density filters between a ground-glass diffuser and the photocathode of the diode. An Ortec model DB 463 delay-box was used on the start input to position the stop pulses within the acceptance time-window of the TAC, whose output pulses were accumulated in a 512 channel Northern Scientific model NS-900 pulse height analyzer (MCA). The resulting time-decay spectrum was recorded on a Teletype printer. All signal lines were made from RG-58A/U coaxial cable; the preamplifier output was routed through doubly-shielded cable to reduce noise pickup.

In most of the experiments, the preamplifier output was analyzed with a Biomation model 6500 waveform recorder which acted as a transient digitizer. It had 1024 sequential channels for accumulating and storing data in the form of 6-bit binary words. The fastest time-resolution of the
Figure 9. Schematic diagram of the apparatus for the delayed-coincidence measurements. X2, frequency-doubling crystal; D, photodiode; PM, photomultiplier tube; HV, high voltage power supply; AMP, signal pulse-amplifier; DISC, discriminator; DP, dispersing prism.
instrument was 2.0 ns per channel, and on this setting a
2.048 µs segment of the incoming signal could be digitized
and stored internally; the longer time-settings were used
when recording slowly varying signals. Temporal accuracy of
the digitizer was checked using a Fluke model 1953-A
frequency counter. The crystal-controlled time-base of the
waveform recorder was found to be extremely accurate.

Digitized outputs from the waveform recorder were
transferred, under computer control, to a Commodore PET
model 2001 microcomputer; subsequent signal segments were
recorded, transferred, and added to the computer’s memory. A
periodically updated histiographic representation of the
microcomputer memory contents was displayed on the
computer’s video monitor. The data stored in the memory were
printed and/or plotted, as required, on an EPSON model MX-80
dot-matrix printer. The experimental data were stored on
5-1/4 inch magnetic diskettes using a Commodore model 4040
dual floppy-disk drive; this permitted subsequent retrieval
for analysis and visual inspection. The PET computer was
also connected to the SPEX compudrive controller on the
spectrometer and, in this way, the resident control program
(Atkinson 1982) in the microcomputer also served as a master
control for the spectrometer, enabling the computer to
increment the wavelength setting of the spectrometer and
scan the fluorescence spectrum. The data were analyzed using
an IBM 370-3031 computer and a modified version of the
FRANTIC program (Rogers 1962) to extract relevant parameters
from the accumulated signals. The data could also be directly transferred to the IBM computer from the microcomputer memory under interactive control of the microcomputer.
IV. Experimental Procedures

i) General

A population of metastable $\text{Hg}_2$ molecules was produced in a sealed-off quartz fluorescence cell using pulsed laser light. The metastable molecules were probed with radiation from a second laser to induce fluorescence from higher excited (Rydberg) states. The fluorescence was resolved with a spectrometer and detected with a photomultiplier; the resulting signal was registered using gated detection techniques and recorded to detect spectral features induced by the probe laser. The analysis of the data yielded information on the time-evolution and band-structure of the molecular fluorescence.

ii) Preparation of the Fluorescence Cell

Before the experiments, the cell was cleaned with a dilute solution of HF, rinsed several times with distilled water and attached to the vacuum system. A distillation chain shown in Fig. 10, which contained an evacuated and sealed ampoule of redistilled mercury, was also attached to the vacuum system. The entire assembly was evacuated to $1 \times 10^{-7}$ torr and baked out, the pyrex sections at about 250°C with heating tapes, and the quartz sections at about 625°C with an electrically heated oven. After approximately two days of baking under vacuum, the diffusion pump was isolated from the system and outgassing rates were measured to check.
Figure 10. Schematic diagram of the distillation chain. Only two of the four distillation bulbs are shown. S, quartz-to-pyrex graded seals.
for small leaks, none of which were found. The ampoule containing mercury was opened by means of a magnetic breaker and mercury was slowly distilled into the first bulb of the distillation chain with heating tapes; a small amount of mercury was left in the initial reservoir to avoid the transfer of slightly less volatile components. The ampoule section was then detached and processed to recover the useful components and materials. Since a sealed-off cell was planned, special attention was given to the sealing points. A torch was used to heat the slightly preconstricted areas until some softening of the quartz was evident; this procedure was repeated several times at both seal-off points to reduce to a minimum the outgassing of potential contaminants. The "U-tube" cold-trap was filled with liquid-nitrogen and the titanium getter was turned on. When the diffusion pump was isolated from the vacuum system, no significant pressure rise was found; the pressure remained at approximately $1 \times 10^{-8}$ torr. The diffusion pump was reconnected to the system and the mercury was distilled into the next reservoir bulb. During all the distillations, the adjacent bulb was maintained at room-temperature to condense the vapour, and the balance of the system was baked as above. During the last distillation, the entire baking system was turned off. The mercury fluorescence cell was then sealed off from the vacuum system; the "U-tube" cold-trap was also detached from the system since it contained a coating of mercury condensed from the vapour.
present in the system during distillation. The vacuum system was then available for the fabrication of Hg lamps with little contamination from mercury vapour.

iii) Preparation of Discharge Lamps

Quartz electrodeless discharge lamps were used in certain cw fluorescence experiments. The shells were filled as follows: A manifold containing several lamp bodies and another Hg-ampoule were attached to the vacuum system and subjected to the evacuation and baking procedures described above. A 1-liter flask of argon (Union Carbide - 99.999% pure) was also attached to the system to provide the buffer gas used in the lamps. The argon was purged of any residual reactive contaminants with a heated cesium getter for approximately 16 hours. A drop of natural mercury was distilled into each lamp and argon was admitted to the system through a dry-ice cold-trap. Based on past experience in this laboratory, two lamps each with argon pressures of 0.75, 0.90, and 1.05 torr were made; the argon pressure was determined with an oil manometer separated from the rest of the system by a dry-ice cold-trap.

iv) Tests for Impurities in the Cell

The cell was installed in the oven, and the following two tests for the presence of impurities were carried out (Drullinger et al 1977).

a) With approximately 1 atm of mercury vapour in the
cell, a 6 Watt beam of 488 nm light from an Ar+ laser was focused into the cell. Since no fluorescence was detected, the cell was deemed uncontaminated.

b) The mercury vapour was illuminated with 257.2 nm radiation from the frequency-doubled Ar+ laser and the resulting fluorescence was recorded using a picoammeter. The fluorescence spectrum, as shown in Fig. 11, was compared to known spectral emission characteristics of Hg vapour under similar conditions. Since no spurious spectral features were detected, the cell was considered acceptable.

v) Preliminary Search for cw-induced Fluorescence

An initial investigation into cw-induced fluorescence changes in Hg vapour was carried out by means of both continuous laser excitation and resonance line pumping with a spectral lamp. A sealed-off quartz fluorescence cell containing Hg vapour and approximately 75 torr of purified nitrogen was constructed as outlined previously; the N₂ molecules assist molecular formation at low Hg densities (Pitre et al 1972). As shown in Fig. 6 the frequency-doubled output from the Ar+ laser (estimated power of 10 mW) of wavelength 257.2 nm was directed into the fluorescence cell and the undoubled visible output was recovered and used to pump the cw dye-laser. The dye-laser output was chopped at 300 Hz and mixed colinearly with the ultraviolet beam as shown in Fig. 12. The fluorescence was dispersed by means of the spectrometer and the fluorescent signal was monitored.
Figure 11. Spectrum of the 335 nm and 485 nm band fluorescence produced by 257.2 nm laser radiation. The Hg density was $3 \times 10^{18}$ cm$^{-3}$ and the temperature 725 K. The spectral components at 257.2 nm and 514.5 nm are due to scattered radiation. The atomic lines result from indirect excitation of the Hg $7^3S_1$ state.
using the lock-in amplifier. The region 200 nm - 900 nm was sampled every 0.5 nm with the spectrometer to look for changes in the fluorescent signal as the dye-laser was slowly scanned from 565 nm to 655 nm. Since no induced changes were detected, this approach was abandoned.

The Ar+ laser was operated in the 'all-lines' mode, and the 514.5 nm radiation was separated from the output and frequency doubled to generate the 257.2 nm pump beam which was then directed through the cell. The 488 nm line was chopped at 300 Hz and mixed colinearly with the ultraviolet pump beam; the molecular fluorescence was scanned and monitored for changes in the spectrum (Drullinger et al 1977) using the spectrometer and lock-in amplifier. The other laser lines (indicated in Table II) were then mixed with the ultraviolet pump beam and the fluorescence was again monitored with the spectrometer and lock-in amplifier. The 257.2 nm output intensity was found to be substantially less than when the ion laser was operated on a single line, but no induced changes in the fluorescent signal were detected.

The ion laser was subsequently mode-locked by means of a quartz cube and ultrasonic piezoelectric transducer in an attempt to increase the ultraviolet output from the frequency-doubling crystal. The power in the visible region, emitted by the laser, was found to be reduced by approximately 65% but the induced fluorescent intensity was essentially unchanged. Since no substantial increase in pump
power was realized, the mode-locked operation, which was relatively unstable, was abandoned.

A $\text{N}_2$ laser-pumped dye-laser operating in the range 475 nm - 510 nm was used in conjunction with the 257.2 nm pump beam to excite the ultraviolet $\text{Hg}_2$ fluorescence reported by Drullinger et al. (1977); gated detection of the fluorescence was used to monitor the region 200 nm - 245 nm, while the pulsed dye-laser was tuned across its output range. This was done in order to increase any instantaneous induced fluorescence that might be present, in keeping with the much higher peak power available near 488 nm.

In yet another attempt to excite molecular fluorescence with cw sources, the 253.7 nm output from a high-power RF mercury lamp was used to pump the mercury vapour and the irradiated volume, which was confined to a thin sheath adjacent to the input window, was probed with the various (chopped) visible and ultraviolet lines emitted by the Ar+ laser. The fluorescent signal was greatly reduced compared to laser-pumping, and no induced signal changes could be detected in the fluorescent spectrum.

Since none of the continuous excitation schemes produced any measurable results, the entire approach was abandoned. The first cell, which had been prepared as outlined, ultimately failed after several months of continuous operation at about 400°C; the failure became evident from the appearance of $\text{HgH}$ molecular fluorescence near 401.7 nm (Pearse and Gaydon 1950). Total failure of the
vacuum integrity of the cell followed shortly. A new cell was made and tested according to the procedures outlined above, except that pure mercury with no added buffer gas was used.

vi) Pulsed Pump-and-Probe Experiments on Mercury Vapour

Because of the lack of promise shown in the cw experiments, a different experimental approach was adopted. Radiation produced by means of a high-power pulsed YAG laser was made incident on pure Hg. vapour in a sealed-off fluorescence cell, in order to produce large transient populations of excited metastable mercury molecules. A second pulsed dye-laser was used to further excite the molecules to higher (Rydberg) states, and the resulting fluorescence was detected and resolved with a spectrometer. The fluorescent signal was recorded with a transient digitizer and accumulated in a microcomputer. The resulting time-evolution spectrum was stored and analyzed for the presence of vibrational structure in the fluorescent bands.

1) Atomic Lifetimes

The 'pump' laser was tuned to 560.586 nm and the frequency-doubled output at 38666.591 cm\(^{-1}\) was focussed into the fluorescence cell; the side-arm was cooled to approximately 22°C and the main oven was kept at about 40°C. The resulting (atomic) fluorescence at, \(\lambda = 579.066\) nm was detected with the spectrometer, and the photomultiplier
pulses were accumulated and analyzed by the transient digitizer to generate a time-decay spectrum of the Hg $6^1D_2$ state. The experiment was repeated using the TAC and MGA; detected photon-to-pump pulse ratios were kept below 1:10 to reduce pile-up corrections (Atkinson 1977). The accumulated time-evolution was analyzed by computer and the decay rate was calculated and compared to the results obtained with the transient digitizer. The experiment was repeated for the Hg $6^3D_2$ atomic level; two-photon excitation of the Hg vapour was produced with 35698.11 cm$^{-1}$ radiation, and resonance fluorescence at $\lambda = 365.5$ nm was detected. Since the two methods produced virtually identical time-evolutions, I concluded that transient digitization was a satisfactory technique for the recording of fast transient fluorescent spectra, and used it in most subsequent experiments.

The 'Boxcar' integrating procedure was used to assess the degree of collisional excitation transfer between the $6^1D_2$ and $6^3D_J$ states. Scans of the spectral regions from 312 nm to 314 nm and from 364 nm to 370 nm were carried out; the total accumulated fluorescent signal corresponding to transitions from both $6^1D_2$ and $6^3D_2$ states to the $6^3P_1$ state was analyzed to determine the extent of collisional transfer between the excited states. This procedure was carried out with both the $6^1D_2$ and $6^3D_2$ states being populated in turn. A scan of the same spectral region from a low-pressure mercury lamp was also accumulated to determine the relative strength of each line under thermal equilibrium.
conditions. Extensive collisional mixing would suggest the presence of impurities which would affect the atomic and molecular measurements.

ii) Time Evolution of Hg\textsubscript{2} Molecular Fluorescence

The YAG laser-pumped dye-laser (pump laser) was used to excite the Hg \(6^{1}\text{D}_2\) state, and after a suitable delay the molecules were probed with the second pulsed laser. The fluorescence was detected with a spectrometer, and the fluorescent signal was registered with the transient digitizer and a microcomputer. The time-evolution spectrum was stored for later retrieval and analysis with a large computer.

The pump laser was tuned to 560.586 nm and the output was frequency doubled to produce short pulses of ultraviolet light. The unfocussed beam was directed into the sealed-off quartz fluorescence cell which contained mercury vapour at moderate pressure. The laser was then adjusted for resonant two-photon excitation of the Hg \(6^{1}\text{D}_2\) state. The tuning of the laser was monitored by maximizing the intensity of the atomic fluorescence emitted in any of the various cascade processes that were always present. The dye laser, frequency-doubler and the 'Q-switch' delay were adjusted to produce optimal fluorescent signal. The fluorescence detection optics were then adjusted to produce the maximal signal.

The YAG laser was designed to work optimally at 10 Hz, and since the microcomputer was limited to a maximum
repetition rate of 12 Hz for the transfer of the transient digitizer memory, the pump laser was always operated at 10 Hz. The nitrogen laser-pumped dye-laser (probe laser) was synchronized to the pump laser repetition rate; when timing was not too critical, the 'Q-Switch sync-pulse' available from the YAG laser was used, and for events which required more stringent timing uniformity, the pump laser output was sampled with a photodiode to produce precise synchronization. The initial delay during preliminary alignment was usually adjusted to about 5 μs.

The probe laser was tuned to the required wavelength and, when necessary, frequency-doubled. Its output was directed into the fluorescence cell and adjusted to overlap the region of excitation produced by the pump laser. The wavelength of the probe laser was then adjusted to maximize the induced fluorescent signal. Good overlap of the two beams in the mercury cell was found to be essential, and long focal length Suprasil lenses were used in the probe laser beam to keep the two beams of about the same size at the cell (2-4 mm cross section); the laser beams were never tightly focussed.

The delay between the two lasers was adjusted for highest intensity of the molecular fluorescence. When sufficient 335 nm band fluorescence was available, its time evolution was used to adjust the time delay; otherwise, the delay was optimized visually by manually setting the delay for maximal probe-laser induced signal. It was found that
the exact delay time was not very critical in producing maximal intensity of the molecular fluorescence.

When strongly emitting dyes were used in the probe laser, a spectral filter consisting of a diffraction grating and an aperture was frequently inserted in the probe laser beam to eliminate scatter at adjacent wavelengths and to suppress pumping of secondary transitions by the background dye fluorescence. This arrangement was never used when the probe laser was frequency-doubled, because of the substantial loss of laser power and the self-filtering characteristics of the non-linear process in the frequency doubling crystal.

For each molecular transition, the spectrometer was adjusted for maximal fluorescent signal and then the pump laser was rendered temporarily inoperative by inserting a beam block into the oscillator stage of the pump dye-laser. The fluorescent signal was monitored to ensure that the observed fluorescence was indeed due to excited Hg\textsubscript{2} molecules, and not a consequence of fluorescence induced in any of the components of the pump dye-laser. The pump laser beam was restored and its power reduced to suppress unwanted effects such as energy pooling. The probe laser power was also lowered to reduce non-linear effects while retaining adequate accumulation rates for the induced molecular fluorescence whose time-evolution was being recorded.

The accumulated decay spectrum was stored on magnetic disk and was also printed out and plotted graphically for
visual inspection. The probe laser beam was then spatially adjusted to illuminate the cell wall and a quartz lens was inserted in the detection path to offset the small change of distance from the source of scattered light to the spectrometer. After suitable attenuation, a time-evolution spectrum of the scattered probe light was recorded using the same trigger level on the transient digitizer for reference. The power settings and the operating wavelengths for both lasers were recorded. The time-delay was measured by detecting the probe laser light with the transient digitizer while triggering it from the pump laser; the temperatures of both compartments of the oven were recorded and the Hg vapour density estimated using the vapour pressure data given by Nesmeyanov (1963). These parameters were measured for each recording of a time-evolution spectrum.

For the more intense fluorescent bands, measurements were performed at various vapour pressures so that effects due to collisions could be assessed. The pressure was usually changed by about a factor of three between measurements, and was limited at low Hg densities by low fluorescent intensities, and at high densities by very short decay times due to collisional quenching.

c) Time Evolution of Atomic Emission Accompanying Molecular Excitation

The radiation from the pump laser caused enormous amounts of energy from numerous excited atomic states,
which was usually filtered out in order not to damage or saturate the photomultiplier. During the experiments on the ultraviolet \( \text{Hg}_2 \) bands, it was found that the molecular fluorescence was accompanied by 546.1 nm, 435.8 nm, and 404.7 nm atomic fluorescence of unusually high intensity.

The time-decay spectra of this atomic fluorescence were investigated using methods described above, except that the fourth harmonic of the YAG laser at 266 nm was used for pumping. The pump beam was reduced to approximately 3 mm in diameter to increase the power density incident on the mercury vapour, and to accommodate more efficient detection by the spectrometer. The use of the fourth harmonic greatly reduced atomic fluorescence induced by the pump laser but did not eliminate it completely.

d) Vibrational Structure of the Fluorescent \( \text{Hg}_2 \) Bands

In addition to the experiments concerned specifically with the time-evolution of the molecular and atomic fluorescence components, an additional series of experiments was carried out to investigate vibrational structures of the molecular (electronic) fluorescent bands. Similar procedures were employed as described above, but relatively high pump and probe laser powers were used. The grating spectral filter was used in the probe beam for all measurements which did not employ frequency doubling. The spectrometer was scanned under computer control and the spectral intensity at each wavelength setting was integrated by the microcomputer.
The wavelength setting was advanced automatically in 0.1 nm or 0.2 nm increments after a predetermined number (usually 50) of laser pulses. Whenever long wavelengths were examined, a 400 nm cut-off filter was inserted in the detection optics to eliminate second-order ultraviolet light in the spectrometer. The acceptance window of the boxcar integrator was adjusted for approximately 5 mean lifetimes of the expected signal. Signal-to-noise ratios were improved by signal averaging techniques. The accumulated data were plotted out to display the band structures, and were analyzed to yield molecular parameters; since the individual band-heads were not readily located in fluorescence, the band-centres were used when calculating molecular parameters.
V. RESULTS AND DISCUSSION.

1. Atomic Lifetimes

The radiative lifetimes of both the $\mathcal{D}^1_{2}$ and $\mathcal{D}^3_{2}$ Hg atomic states were measured by recording the time-decay spectra accompanying pulsed two-photon excitation; the measurements were carried out using both delayed coincidence and fast analogue-to-digital conversion techniques. Figure 12 shows a time-decay spectrum for the Hg $\mathcal{D}^1_{2}$ state and Fig. 13 shows a time-decay for the Hg $\mathcal{D}^3_{2}$ state; both plots are semilogarithmic and the straight lines indicate the slopes calculated using the weighted least-squares fitting computer program (FRANTIC). The peak signal channel for the digitized recording corresponds to approximately 8000 photons; the peak signals obtained with delayed coincidences are about an order of magnitude lower.

A computer analysis of the recorded time-evolutions yielded the atomic lifetimes which are summarized in Table III; the delayed coincidence results were corrected for pile-up. The lifetimes obtained using the transient digitizer represent the average of 5 separate measurements. Accumulation times were about 20 min for the digitized spectra, and about 6 h with delayed coincidences. Cell temperatures were 22°C at the side-arm, and 40°C in the main oven. This corresponded to a Hg vapour pressure of 1.5 × 10^{-3} torr (about 5.0 × 10^{13} atoms/cm^3). Also included in Table III are the lifetimes of the $\mathcal{D}^1_{2}$ and $\mathcal{D}^3_{2}$ states obtained by other groups. Since Faisal et al (1980) found no

61
Figure 12. Time-decay spectra of the Hg $^1D_2$ state. (a) - recorded using the transient digitizer; (b) - recorded using delayed coincidences.
Figure 13: Time-decay spectra of the Hg $^3D_2$ state. (a) - recorded using the transient digitizer; (b) - recorded using delayed coincidences.
TABLE III

Radiative lifetimes of the Hg $^1D_2$ and $^3D_2$ atomic states, measured at 313 K and at a density of approximately $5 \times 10^{13}$ cm$^{-3}$. (a) - transient digitizer results; (b) - results from delayed coincidences. The quoted errors in my results correspond to two standard deviations.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg $^1D_2$</td>
<td>10.8</td>
<td>10.9(3)</td>
<td>10.8</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.3$</td>
<td>$\pm 0.4$</td>
<td>$\pm 0.3$</td>
<td></td>
</tr>
<tr>
<td>Hg $^3D_2$</td>
<td>9.0</td>
<td>9.1</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\pm 0.3$</td>
<td>$\pm 0.4$</td>
<td>$\pm 0.2$</td>
<td></td>
</tr>
</tbody>
</table>
systematic variation of the $^6\text{D}_2$ lifetime with vapour density, the experiment was not repeated at other temperatures. It was found that two-photon excitation of the Hg $^6\text{D}_2$ state was much more efficient than of the $^6\text{D}_2$ state; at least an order of magnitude higher power levels were required when pumping the $^6\text{D}_2$ state, to achieve acceptable fluorescent accumulation rates; this is generally in accordance with the observations of Faisal et al (1980).

The extent of mixing between the states of the Hg $^6$s$^6$d atomic manifold was measured at the completion of the experiments on molecular fluorescence. This was done primarily to determine the presence of contamination in the cell after extended periods of operation at high temperatures (since the Boxcar integrating routine was not available at the start of the molecular measurements, no comparison with initial amounts of mixing could be made). The results are shown in Fig. 14 for the spectral lines arising from the decays of both the $^6\text{D}_2$ and $^6\text{D}_2$ Hg states. The 'A-values' for these two transitions are reported to be about the same (Lecler and Lanier 1976). Figure 14(a) shows a high-resolution spectrum obtained from a low-pressure Hg spectral lamp and shows the transitions from the $^6\text{D}_2$, $^6\text{D}_1$ and $^6\text{D}_2$ states to the $^6\text{P}_1$ state; (b) and (c) show the fluorescent signals accumulated when the $^6\text{D}_2$ and $^6\text{D}_2$ states, respectively, were two-photon pumped. In each case the signal originating from the sensitized state is multiplied by a scaling factor. In Fig. 14(b) and (c) the
Figure 14. Boxcar trace of the spectrum emitted in the decay of the Hg $6^1D_2$ and $6^3D_1$ states. (a) emission from a low-pressure spectral lamp; (b) trace recorded with the $6^1D_2$ state two-photon pumped; (c) trace recorded with the $6^3D_2$ state two-photon pumped.
the two components at 313.16 nm and 313.18 nm are not resolved; consequently the signal near these two wavelengths contains contributions from the decays of the $6^1D_2$ and $6^3D_1$ states (the energy splitting is approximately 3 cm$^{-1}$).

The measured intensity ratio of about 1:900, as shown in Fig. 14(b), is similar to the intensity ratio of the sensitized-to-direct components for the $6^1D_2$ and $6^3D_2$ states measured by Leclerc and Lanierpce (1976) but they could not attribute the observed intensity ratio solely to fine-structure mixing. Approximately the same population ratios in the pumped state and the sensitized state were obtained when transitions to the $6^3P_2$ atomic state were analyzed. My results are also consistent with those of Lukasiewski and Leclerc (1978) who measured an intensity ratio (sensitized-to-direct) of approximately 1:300 for transitions from the $6^3D_1$ and $6^1D_2$ states to the $6^3P_1$ state. If an unknown contaminant existed in the cell, the measured intensity ratios would have reflected its presence by collision-induced fine-structure mixing, an effect which was not detected. The test using an Ar$^+$ laser (Drullinger et al. 1977) produced negative results, indicating that no detectable amount of contamination was present. Also, the measured lifetimes of the Hg $6^1D_2$ and $6^3D_2$ states were about the same (within experimental error) when results obtained before high-temperature operation of the cell were compared to the results obtained after prolonged high-temperature operation of the cell, providing further evidence for the
absence of contaminants. I believe that the fluorescence intensity ratio of a sensitized state compared to a directly excited state is a more valid test for the presence of impurities than the procedure outlined by Drullinger et al (1977). The measured intensity ratio (sensitized to direct) implies a $^1D_2 - ^3D_2$ mixing cross section, induced by collisions with ground-state Hg atoms of approximately $7 \times 10^{-14}$ cm$^2$.

The influence of the collisional mixing on the measured Hg lifetimes was calculated to be less than 1%, and I concluded that the measured lifetimes were not affected by collisions to any significant degree.

ii) Molecular Lifetimes and Vibrational Band Structures

Several molecular Hg$_2$ Rydberg bands were excited and the resulting time-evolution spectra were recorded by means of the transient digitizer. The molecular bands were investigated using absorption of dye-laser probe pulses subsequent to pulsed excitation (pumping) of the Hg vapour. Unless otherwise indicated, populations of Hg$_2$ states were produced by resonant two-photon pumping of the Hg $^1D_2$ atomic state.

a) The 420 nm Band

The 420 nm fluorescent band was readily excited, particularly at the higher Hg densities, by dye-laser radiation of the same wavelength. The band was found to possess extensive vibrational structure and corresponds to
the bands seen by Takeyama (1952) in emission, and Callear and Lai (1980, 1982) in absorption. Figure 15(a) shows a time-decay spectrum of the 420 nm band recorded by detecting the $v' = 0 - v'' = 1$ vibrational transition at 422.7 nm while probing the $\text{Hg}_2^+$ excimers on the 0-0 transition; (b) shows the time-evolution of the 420.20 nm probe laser pulse. The calculated slope of the decay spectrum yields an effective lifetime of about 7.8 ns at a vapour pressure of 0.3 torr and temperature of 600 K. Figure 16 shows the decay rates of the 420 nm system measured at 600 K for various Hg vapour pressures. The error bars are shown for the 420 nm band data and represent $\pm/\mp$ two standard deviations of the computer-generated least squares fit of the decay rate at each pressure. The broken line is an unweighted least squares fit to the 420 nm data points; the decay rates at higher pressures were essentially too fast to be analyzed reliably.

The vibrational components of this band were doubled, with a splitting of not more than 20 cm$^{-1}$. While this splitting was not readily seen in fluorescence, it could be easily detected by tuning the probe laser wavelength across the vibrational band while monitoring the emission in a different vibrational transition. It appears that this band arises from $A_0^g \leftarrow 1_u$ transitions as shown in Fig. 27, the $1_u$ state correlating with the $7^3S_1$ atomic state. The $0_g^+ - 0_g^-$ splitting corresponds to the splitting reported by Callear and Lai (1982). The long wavelength component of the
Figure 15. Time-evolution of the 420 nm fluorescent band, (a) - Fluorescence emitted in the \( v''=1 \leftarrow v'=0 \) decay, following 0–0 excitation; (b) - scattered 420.2 nm probe light. The intensities in parts (a) and (b) are not plotted to the same scale.
doublet, \( A_0^+ \leftrightarrow 1_u \), seemed to be about a factor of two or three stronger than the short-wavelength component, \( A_0^+ \leftrightarrow 1_u \), but this aspect was not investigated quantitatively; no measurable difference in the decay rates of the two components could be detected.

The decay rates corresponding to higher vapour pressures were significantly larger and could only be estimated (see Appendix II) because of the limitations imposed both by the recording electronics, and by the long pulse-width of the probe laser (compared to the effective lifetime). The extrapolated intercept of the the plot in Fig. 16 corresponds to an effective lifetime of the \( 1_u \) Rydberg state of approximately 7.6 (±0.7) ns. A cross section of \( 1.3 \times 10^{-14} \) cm\(^2\) was calculated from the slope of the pressure-dependent decay rate and corresponds to collisional quenching of the \( 1_u \) state induced by collisions with ground state Hg atoms. Stock et al (1978a) measured a similar cross section for collisional quenching from the lowest \( 1_u \) state to the \( A_0^+ \) states.

A small amount of radiation was also emitted from higher vibrational levels in the upper state; this could be due either to collisional mixing or to ‘direct’ excitation from some high rotational level in the lower state to correspondingly high rotational levels in the upper state. Limited resolution of the probe laser did not permit further investigation of this effect. A vibrational spectrum corresponding to transitions from the \( v' = 0 \) vibrational level
Figure 16. Pressure-dependent decay rates of the fluorescent bands following 420.2 nm probe-laser excitation: • - 422.7 nm \( v''=1 \leftarrow v'=0 \); X - 509.7 nm \( v''=0 \leftarrow v'=0 \), Δ - 632.6 nm \( v''=0 \leftarrow v'=0 \).
to various $v''$ levels is shown in Fig. 17. Vibrational analysis of the band maxima is shown in Fig. 18 and the wavelengths, assignments, and vibrational spacings are listed in Table IV. The analysis yielded the molecular constants $\omega''_e = 144 \text{ cm}^{-1}$ and $\omega''_x = 0.5 \text{ cm}^{-1}$. The doublet structure was not resolved and, consequently, the molecular constants are effectively an average for both the $\Omega_g^+$ and $\Omega_g^-$ states. The value of $\omega''_e$ agrees well with the value $\omega''_e = 143 \text{ cm}^{-1}$ deduced by Callier and Lai (1980) for both the $\Omega_g^+$ and $\Omega_g^-$ states.

b) The 509.7 nm Band

The 509.7 nm fluorescent band which also possesses extensive vibrational structure, was readily emitted upon excitation with 420 nm laser radiation, but even at the highest temperatures and high power levels of the pump and probe lasers, this band could not be excited directly by resonance absorption. The band had a high intensity, even at the lowest Hg densities, comparable to the 420 nm band. Such strength indicates substantial branching of the decay of the $1_u$ state.

The measured decay time and observed time-evolution of the fluorescence, measured by detecting the $v'=0-v''=0$ transition at 509.7 nm while probing the $\Delta \Omega_g^{-} \rightarrow 1_u^+$ transition at 420.20 nm, were identical (within experimental error) with those of the 420 nm band, suggesting a common emitting molecular state for the two bands. The 509.7 nm band fluorescence could readily be produced by exciting
Figure 17. Vibrational structure of the 420 nm $0_g^+ \leftrightarrow 0_u$ band excited by 420.2 nm probe-laser radiation. $v'-v''$ assignments of the vibrational peaks are shown.
Figure 18. Approximate separations between successive $v''$ vibrational levels in the 420 nm system. The probe-laser was tuned to the $4t \rightarrow 1u$ $v' = 0 - v'' = 0$ transition at 420.20 nm. The separations are averages of the unresolved $0t \rightarrow 1u$ and $0t \rightarrow 1u$ components.

**TABLE IV**

Vibrational analysis of the 420 nm system. The wavelengths are the mean values for the two components.

<table>
<thead>
<tr>
<th>$v' - v''$</th>
<th>$\lambda$ (nm)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\Delta\nu$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 0</td>
<td>420.20</td>
<td>23791</td>
<td>143</td>
</tr>
<tr>
<td>0 - 1</td>
<td>422.75</td>
<td>23648</td>
<td>142</td>
</tr>
<tr>
<td>0 - 2</td>
<td>425.30</td>
<td>23506</td>
<td>140</td>
</tr>
<tr>
<td>0 - 3</td>
<td>427.85</td>
<td>23366</td>
<td>139</td>
</tr>
<tr>
<td>0 - 4</td>
<td>430.4</td>
<td>23227</td>
<td>139</td>
</tr>
<tr>
<td>0 - 5</td>
<td>433.0</td>
<td>23088</td>
<td>138</td>
</tr>
<tr>
<td>0 - 6</td>
<td>435.6</td>
<td>22950</td>
<td></td>
</tr>
</tbody>
</table>
either of the two components of the $A_0^+ \rightarrow 1_u$ transition, indicating that the band is emitted in the decay of the $1_u$ state. Figure 16 shows the decay rates measured at 600 K for various Hg vapour pressures; the error bars are not shown but in general are slightly larger than those for the 420 nm band (the background signal was substantially larger since this band is located near the middle of the intense Hg 485 nm continuum). The extrapolated zero-pressure lifetime corresponding to this transition is 7.7 (±0.8) ns, and the cross section for Hg-induced collisional quenching is $1.5 \times 10^{-14}$ cm$^2$. I believe that this transition is emitted in the $E_2^g \leftarrow 1_u$ decay, as shown in Fig. 27. The energy difference between the $A_0^+$ states and the $E_2^g$ state is about 4190 cm$^{-1}$; this energy difference and the associated Boltzmann factor account for the inability to resonantly excite this transition. The position of the $E_2^g$ state can now be fixed with respect to the $O^+_g$ states as indicated in Fig. 27. This assignment differs from that of Callear and Lai (1980, 1982) who postulated different upper states for the two bands.

A vibrational spectrum of this band corresponding to transitions from the $v'=0$ vibrational level to various $v''$ levels is shown in Fig. 19. Vibrational analysis of the band maxima is shown in Fig. 20 and the wavelengths, assignments, and vibrational spacings are listed in Table V. The analysis yielded the molecular constants $\omega''_e = 142$ cm$^{-1}$ and $\omega''_e - \omega''_e x''_e = 0.5$ cm$^{-1}$. The $\omega''_e$ value is approximately the same as
Figure 19. Vibrational structure of the 509.7 nm band excited by 420.2 nm probe-laser radiation. $v'-v''$ assignments of the vibrational components are shown.
Figure 20. Approximate separations between successive $v''$ vibrational levels in the 509.7 nm system. The probe-laser was tuned to the $A^0 g \rightarrow 1 u\ v'=0 - v''=0$ transition at 420.20 nm.

| $v' - v''$ | $\lambda$ (nm) | $\nu$ (cm$^{-1}$) | $\Delta \nu$ (cm$^{-1}$) |
|------------|----------------|-----------------|----------------|-----|
| 0 - 0      | 509.7          | 19614           | 142            |     |
| 0 - 1      | 513.4          | 19472           | 139            |     |
| 0 - 2      | 517.1          | 19333           | 137            |     |
| 0 - 3      | 520.8          | 19196           | 139            |     |
| 0 - 4      | 524.6          | 19057           | 137            |     |
| 0 - 5      | 528.4          | 18920           | 135            |     |
| 0 - 6      | 532.2          | 18785           | 136            |     |
| 0 - 7      | 536.1          | 18649           |                |     |
that obtained by Callear and Lai (1980, 1982), based on an analysis of the emission spectra of Takeyama (1952). The intensities of the first three components are approximately equal, although the $0 \rightarrow 1$ component seemed to be the strongest. This may be due to instrumental effects and is not meant to imply any conclusions concerning Franck-Condon factors.

c) The 632.6 nm Band

The 632.6 nm band, which has not been previously reported in fluorescence or in absorption, is also emitted upon irradiating the Hg$_2$ dimers with 420 nm probe pulses. The band is very weak, even at the highest vapour densities and pump laser power, and exhibits substantial vibrational structure. The time-decay spectrum is virtually identical with those of the 420.0 nm and 509.7 nm bands; the extrapolated zero-pressure lifetime corresponding to this transition is 7.0 (±1 ns). It appears that this band is also emitted from the $1_u$ state; based on this assumption, I assign this band to the $F1_g \leftrightarrow 1_u$ decay as indicated in Fig. 27. This assignment is somewhat speculative since at the higher vapour pressures needed to accumulate a time-evolution spectrum, various collisional effects could cause rapid transfer to a different upper state and thus give rise to this fluorescent band. The potential energy curves of Mies et al (1978) show that the $F1_g$ molecular state correlates with the Hg $6^3P_2$ atomic state. The intensity of this band was somewhat lower than would be
expected from molecular states that correlate with a fully allowed atomic transition, but an unfavourable transition moment could account for this effect. No theoretical estimates of the transition moments between Rydberg and low-lying states are currently available.

A vibrational spectrum of this band is shown in Fig. 21 with a tentative assignment of the components. The fluorescent signal on the short-wavelength side of the 0-0 transition was strongly masked by the intense emission from the Hg\textsubscript{3} band. Vibrational analysis of the band maxima is shown in Fig. 22 and the wavelengths, assignments, and vibrational spacings are listed in Table VI. The analysis yielded the approximate values of $\omega'^{\prime} = 152$ cm\textsuperscript{-1} and $\omega''^{\prime} = 0.9$ cm\textsuperscript{-1}. Although both values are subject to considerable uncertainty, they are close to other vibrational constants for most of the low-lying Hg\textsubscript{2} states (Callear and Lai 1982). Based on the assignment $F1 \leftrightarrow u'$ and the location of the 0-0 band centre at approximately 632.6 nm, the location of the $F1$ potential energy curve can be fixed as shown in Fig. 27.

d) The 451.4 nm Band

The 451.4 nm fluorescent band was excited with some difficulty, particularly at low Hg densities, and was only observed at relatively high temperatures. The band exhibited some vibrational structure which, unlike the 420 nm band, was not doubled, and was produced by resonance absorption of dye-laser light, or by excitation with 420 nm light. In the
Figure 21. Vibrational structure of the 632.6 nm band excited by 420.2 nm probe-laser radiation. "v" assignments of the vibrational components are indicated.
Figure 22. Approximate separations between successive $v''$ vibrational levels in the 632.6 nm system. The probe-laser was tuned to the $A_{0g^+} \rightarrow 1u^+ \quad v'=0 - v''=0$ transition at 420.20 nm.

### Table VI

Vibrational analysis of the 632.6 nm system.

<table>
<thead>
<tr>
<th>$v' - v''$</th>
<th>$\lambda$(nm)</th>
<th>$\gamma$(cm$^{-1}$)</th>
<th>$\Delta\gamma$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 0</td>
<td>632.6</td>
<td>15803</td>
<td>151</td>
</tr>
<tr>
<td>0 - 1</td>
<td>638.7</td>
<td>15652</td>
<td>148</td>
</tr>
<tr>
<td>0 - 2</td>
<td>644.8</td>
<td>15504</td>
<td>146</td>
</tr>
<tr>
<td>0 - 3</td>
<td>650.9</td>
<td>15359</td>
<td>147</td>
</tr>
<tr>
<td>0 - 4</td>
<td>657.2</td>
<td>15212</td>
<td>143</td>
</tr>
<tr>
<td>0 - 5</td>
<td>663.4</td>
<td>15069</td>
<td>141</td>
</tr>
<tr>
<td>0 - 6</td>
<td>669.7</td>
<td>14928</td>
<td></td>
</tr>
</tbody>
</table>
latter case, the 451.4 nm intensity was lower by at least an order of magnitude than the 420 nm or 509.7 nm intensities. Conversely, excitation with 451.4 nm light also resulted in weak 420 nm and 509.7 nm fluorescent emission. The time-evolution of the fluorescence was measured over a range of Hg vapour densities and it was found that the decay-time decreased at higher vapour pressures, suggesting the presence of collisional quenching effects. An effective lifetime of 6.2 (+0.6) ns was measured at a pressure of 0.7 torr. The extrapolated zero-pressure lifetime of the upper state associated with this transition is 7 (+1) ns.

Figure 24 shows the decay rate measured at 775 K for several Hg vapour pressures. The large error bars (corresponding to two standard deviations of the computer analysis) are a consequence of fast decay times and large background signal levels. The cross section for collisional quenching of the upper state associated with this transition is $3 \times 10^{-14}$ cm$^2$.

The decay spectra used to determine this value were obtained at moderately high pump levels and may have been affected by energy pooling which would inflate the calculated quenching cross section.

Callear and Lai (1982) deduced that the lower molecular state associated with this band lay approximately 1700 cm$^{-1}$ above the $0^2$ reservoir states, and identified it as the $1^2$ state. This leads to the conclusion that the upper state must lie within a range extending from 100 cm$^{-1}$ below to 200 cm$^{-1}$ above the $1^1$ state (the emitting state for the
Figure 23. Variation of the fluorescent decay rate for the 451.4 nm band with Hg vapour pressure.
420 nm band), well within kT at the temperatures used in this experiment. Contrary to the Callear and Lai assignment (1982), the 420 nm and 451.4 nm bands do not appear to have their origins in a common upper state, though there is probably fairly close collisional coupling between the two emitting states.

Assuming that the B1 \( \text{g} \) assignment for the lower state is correct, an \( 0^+_u \), \( 1_u \) or \( 2_u \) state might, in principle, be considered as the upper state. The \( 2_u \) state is unlikely since it would correlate with high-lying atomic states and would require more than 2 eV of binding energy. Since the band has a reasonably large transition moment (Callear and Lai 1982; Takeyama 1952), the molecular transition should correlate with a fully allowed atomic transition. Accordingly, if the 420 nm band corresponds to the transition \( A0^+_g \left( 6^3P_1, 6^1S_0 \right) \leftrightarrow 1_u \left( 7^3S_1, 6^1S_0 \right) \), the 451.4 nm fluorescent band which terminates on the \( B1 \left( 6^3P_1, 6^1S_0 \right) \) level, must be emitted from a molecular state which correlates with the \( 7^3S_1 \) atomic state \( \left( 1_u, 0^+_u, 0^+_g \right) \). The \( 1_u \) state is the emitting state for the 420 nm band, and the \( 0^+_g \) state is ruled out by selection rules; consequently, the \( 0^+_u \) state remains as the only candidate and the 451.4 nm band is tentatively assigned to the transition \( B1 \left( 6^3P_1, 6^1S_0 \right) \leftrightarrow 0^+_u \) as shown in Fig. 27. As has already been pointed out, the assignment is based on the assumption that \( B1 \left( 6^3P_1, 6^1S_0 \right) \) is the lower level; should the lower state assignment prove to be incorrect, the previous arguments would not be valid.
No vibrational analysis of this band was attempted, since its fluorescent intensity was substantially lower than the strong fluorescent signal corresponding to the long time-decay of the 485 nm Hg triplet band excited by the pump laser. Only a few vibrational components could be distinguished from the background noise. Excitation of the 451.4 nm band by resonance absorption produced no measurable amount of emission in the 632.6 nm band. This indicates that the 632.6 nm band does not arise as a consequence of collisional mixing between the $1_u$ and $0_u^+$ states; were this the case, the 632.6 nm band should be stronger when the $0_u^+$ state was excited, than when the $1_u$ state was probed.

e) The 330 nm Band

Band fluorescence at this wavelength was excited by resonant absorption of frequency-doubled probe laser pulses. The band had a short decay time of less than 5 ns at 1 torr, which was measured with some difficulty, and a relatively low intensity which was at least in part due to the low efficiency of the probe dye-laser in the 660 nm region; this resulted in very low frequency-doubled output. The band was also obscured by the intense Hg$_2$ 335 nm band arising from transitions from the $1_u$ state to the ground state. Callendar and Lai (1982) reported that the 330 nm band was doubled and assigned this band to $A_0^+ \rightarrow 1_u$ transitions, the upper state correlating with an element of the $7^3P$ manifold. The doubled nature of this band was not observed in this investigation, presumably because of its extremely low intensity.
f) Absorption and Fluorescence
in the 258 nm - 281 nm Region

Initial experiments with the Hg²⁺ absorption systems were carried out on the 261.2 nm molecular transition since it seemed to be the strongest and broadest absorption feature (Callear and Lai 1982). Band fluorescence was produced with some difficulty, and this was ascribed to the fact that the power of the frequency-doubled probe-laser was not nearly as high as when the dye-laser was used without frequency doubling.

The experiments were carried out using the fourth harmonic from the YAG laser at 266 nm to produce the metastable excimer population. When the Hg vapour was probed with laser light in the range 258 nm to 281 nm, several features were observed. As the probe radiation was scanned over the spectral region, it appeared to be exciting transitions into a continuum. This continuum absorption was accompanied by extremely intense atomic fluorescence of wavelengths 404.7 nm, 435.8 nm, 546.0 nm, and much weaker emission at 407.7 nm. These components correspond to the transitions $6^3P_{0,1,2} \leftarrow 7^3S_1$ and $6^3P_1 \leftarrow 7^1S_0$. Since the induced emission disappeared when the pump laser was turned off, the UV absorption was clearly associated with the Hg excimers.

Superimposed on this continuous absorption were three sharp bands at 259.0 nm, 261.2 nm, and 271.8 nm. When the probe radiation was tuned to either 259.0 nm or 261.2 nm,
the resulting fluorescence included some vibrational structure as well as a faint component corresponding to the other band, in addition to the intense atomic emission associated with the continuum absorption. The three bands correspond to the absorption bands described by Callear and Lai (1982). On the other hand, no band fluorescence was detected corresponding to the 280 nm band, even though there was evidence of strong absorption of the probe laser pulses accompanied by intense atomic emission from the $7^3S_1$ state. Callear and Lai (1982) reported a strong absorption band at this wavelength and assigned it to the $A_0^+g$ states. The absence of this band in fluorescence may be due to the rapid non-radiative decay of the upper excited state.

Figure 24 shows the time-evolution spectrum of the 261.2 nm band recorded by detecting the $v'_i=0 \rightarrow v'_i=1$ transition while probing the $0-0$ vibrational component. Also shown in the same figure is the time-evolution of the 435.8 nm atomic emission induced by the probe laser. The molecular fluorescence decayed very rapidly, the time-profile being virtually identical to that of the probe laser pulse, and the observed decay time (see Appendix II) of less than 2 ns was of the order of the time-resolution capability of the electronics. The decay time of the molecular fluorescence appeared to be independent of the Hg vapour pressure, but the atomic decay time was much longer and decreased with increasing vapour pressure. It may also be seen in Fig. 24 that the atomic emission was delayed by
Figure 24. Time-evolution of the fluorescent emission following excitation with 261.2 nm probe-laser radiation at Hg vapour pressure of 0.3 torr and temperature of 600 K. (a) - 435.8 nm atomic fluorescence; (b) - 262.2 nm molecular fluorescence.
about 8 - 10 ns and this delay seemed to be almost independent of vapour pressure over the range 0.3 - 40 torr. The 407.7 nm emission was delayed by a somewhat longer time compared to the 435.8 nm emission and decayed much more slowly; a computer analysis of the 407.7 nm decay spectrum for multiple components was unsuccessful.

All three ultraviolet fluorescent bands had similar time-evolution spectra. Their decays were very rapid and they were accompanied by atomic emission whose decay was somewhat slower and vapour density-dependent. The time-evolution of the atomic emission did not change when the probe laser was detuned from resonance with the molecular bands. None of the ultraviolet absorptions associated with the Hg₂ bands produced any significant amount of fluorescence at longer wavelengths, corresponding to transitions to states above the A0⁺₈ levels. A specific search was made for these to establish an alternative check on the various fluorescent bands detected when the 420 nm band was excited.

The rapid decay and low intensity of the molecular fluorescence suggests the possibility that the UV bands may be emitted in the decay of a predissociating state. The potential energy diagrams of Mies et al (1978) show bound states with potential energy barriers at large internuclear distances due to anticrossings of pairs of PE curves. An Hg₂ molecule excited to such a state may predissociate by tunneling through the potential barrier onto the repulsive
slope of the potential energy curve. The tunneling process would determine the decay rate of the bound molecular state accounting for the very short decay time and low intensity of the band in emission. Callear and Lai (1982) indicated that the 261.2 nm band was strong in absorption, and yet I found that very little of the probe laser energy was re-emitted in the form of molecular fluorescence at that wavelength. Once the Hg₂ molecule finds itself on the repulsive part of the PE curve, it dissociates producing excited Hg atoms which ultimately decay emitting the 404.7 nm, 435.8 nm, and 546.1 nm components, as well as a much smaller amount of 407.7 nm radiation.

The presence of three such PE curves would account for the properties of the three molecular bands. Since the 261.2 nm band exhibited doubling which corresponded to the the $A_0^+ \rightarrow g$ splitting, the emitting state is likely a $1_u$ state. The 259.0 nm and 271.8 nm bands did not exhibit doubling and consequently are likely emitted in the decay of $0_u^+$ and/or $0_u^-$ states. Because of the high density of excited states in this energy range, collisional transfer between the two states corresponding to the 259.0 nm and 261.2 nm bands should be relatively easy.

While such a mechanism would account for the presence of three sharp molecular bands exhibiting very short decay times, it does not explain the noticeable delay of approximately 8-10 ns between the emission of the molecular and atomic fluorescence. If the decay of the
molecular states was as rapid as the measurements indicated and predissociation of the excited state produced atoms directly in the $^3S_1$ atomic state, no delay between the atomic and molecular fluorescences would be expected. However, if an atomic state intermediate between the dissociating molecular state and the radiating atomic state were populated directly as a result of the tunneling process, either a collisional or radiative cascade would be required to form the $^3S_1$ state. Since collisional mixing tends to be rapid, the predominant process is likely a radiative cascade from some higher state which produces the $^3S_1$ and $^1S_0$ atomic states.

The time-evolution of the atomic fluorescence at 435.8 nm exhibits the characteristic behaviour of a level populated by cascade transitions from higher-lying levels. The curve in Fig. 24 was fitted to a difference of two exponential terms, one corresponding to the decay rate of the $^3S_1$ state and the other corresponding to the upper (feeding) state. At 0.3 torr Hg vapour pressure, the longer decay time was about 14 ns and the shorter decay about 7.5 ns but both had substantial uncertainties (±2 ns). At 9.0 torr the decay times were reduced to about 8 ns for the long decay time and 6 ns for the short decay time but both values were subject to fairly large uncertainties.

Simple Coulomb approximation calculations (Bates and Daamgård 1949) of the radiative atomic lifetimes yield 17 ns for the $^3S_1$ state, 49 ns for the $^3P_2$ state, 67 ns for the
$7^3P_1$ state, 71 ns for the $7^3P_0$ state, and 2.11 ns for the $6^1P_1$ state. The experimentally determined lifetimes for the $7^3S_1$ and $6^1P_1$ states are both approximately one-half of these calculated values (Boriso and Osherovich 1981; Lurio 1965). It seems reasonable to assume that the true $7^3P$ lifetime should be in the range 20–35 ns and, accordingly, the measured long time-decay of 15 ns would correspond to the $7^3P$ decay. By similar reasoning, the 'true' lifetime of the $7^1P_1$ state should be about 5 ns and, accordingly, this state could not contribute to the population of the $7^3S_1$ and $7^1S_0$ states. Furthermore, the $7^1S_0$ state can be populated by an intercombination transition from the $7^3P_1$ state, and another intercombination transition to the $6^3P_1$ state could account for the 407.7 nm emission. The process of multiple intercombination transitions would also account for the much weaker measured intensity of the 407.7 nm emission.

Subsequent experiments indicated that the $8^3S_1$, $8^1S_0$, $6^1D_2$ and $6^3P_1$ atomic states were not populated as a result of the continuum absorption and it seems that the $7^3P$ states most likely constitute the reservoir of excitation energy which is primarily responsible for the observed atomic emission. Because of collisional mixing, all the $7^3P$ states will be populated to some extent and the particular $7^3P$ state which is connected to the repulsive molecular level cannot be determined. The contribution from the tunneling process to the atomic emission is considered to be much smaller and may account for some of the slight
irregularities that were seen in the decay spectra.

The relative strengths of the atomic emissions at 404.7 nm, 407.7 nm, and 435.8 nm, induced by the probe dye-laser operating at 261.2 nm, as well as the same atomic emission intensities obtained from a low-pressure Hg spectral lamp are shown in Fig. 25. In Fig. 25(a), the spectrum obtained from a Hg spectral lamp, the states responsible for the atomic emission are assumed to be in thermal equilibrium. By comparison, in Fig. 25(b) where the fluorescence was induced by the probe dye-laser, the intensity of the 407.7 nm emission is approximately an order of magnitude lower than in the case of the spectral lamp. This strengthens the argument that the process which leads to the transfer of excitation energy into the atomic states is specific to the Hg triplet states.

Since the multiple exponential fit to the measured time-decay spectra was very sensitive to irregularities in the data and tended to produce rather large uncertainties in the computed decay rates, the time-evolutions for the atomic emission produced by UV probe laser pulses was analyzed using only the data which corresponded to the fluorescence at late times and fitting the data to a single exponential decay rate. This approach should provide at least a rough estimate of the kinetics associated with this fluorescence since the decay rate at long times is determined primarily by the slower component of a double exponential decay. Figure 26 shows the decay rates,
Figure 25. Boxcar trace of the atomic fluorescence induced by UV probe-laser radiation. (a)- line intensities from a low-pressure Hg spectral lamp; (b)- fluorescent intensities of the corresponding components excited by 261.2 nm probe-laser light. The intensity of the 407.79 nm component is multiplied by a 10X scaling factor.
Figure 26. Variation of the Hg 435.8 nm fluorescent decay rate with Hg vapour pressure.
calculated by means of this approach. The extrapolated lifetime of the slowly decaying state is 15 ns and the cross section for collisional quenching induced by collisions with Hg ground-state atoms is about $7 \times 10^{-15}$ cm$^2$. The values are expected at best to be accurate to $\pm$ 50% because of the limitations of this treatment. There may have been some radiation trapping effects involved in the transitions out of the $^3S_1$ state since all of the lower ($^3P$) states are either metastable or radiation trapped.

Figure 27 shows the pertinent potential energy curves that are now thought to be fairly accurate with respect to their relative location on the energy scale. The shapes of the curves corresponding to the low-lying states, which are still qualitative, are as given by Mies et al. (1978), as is the ordering of the states; the positions of the $^3P_g^+$ and $^1P_u$ states are quoted from Drullinger et al. (1977). The ordering of the PE curves associated with the $^3S_1$ Rydberg state are still speculative since I was not able to determine conclusively which Rydberg state, the $^1P_u$ or the $^3P_g^+$, was lower in energy. The transitions which were observed in this investigation are shown in Fig. 27. The UV transitions are not shown since I did not determine conclusively which Rydberg molecular level correlates with which particular atomic state.

iii) Extraneous Effects and Sources of Experimental Error

An attempt was made to discover whether energy pooling effects might have been evident in some of the experiments.
Figure 27. Potential energy curves for Hg₂.
In particular, when some of the weak molecular bands were being investigated, it became necessary to operate the pump laser at moderately high power levels, which resulted in some irregularities in the time-evolution of the Hg\textsubscript{2} 335 nm fluorescence. Figure 28 shows a part of the early time-decay of the 335 nm band produced by 280.3 nm laser radiation (two-photon pumping of the \textit{6^1D_2} state). As may be seen, there is a change by about a factor of three in the decay rate, between the non-exponential early times and the exponential late times of the time-evolution spectrum. The decay spectrum was obtained at a temperature of 790 K and a Hg vapour density of $1.2 \times 10^{17}$ cm$^{-3}$ (12 torr); the laser power density incident on the Hg vapour was about 2 MW/cm$^2$. Similar results were obtained using the fourth harmonic of the YAG laser, but substantially higher power densities were required; this reflects the much higher effective absorption coefficient of the Hg vapour when two-photon excitation is used. The presence of non-exponential components in the decay indicates the presence of energy-pooling effects in the Hg\textsubscript{2} system, similar to those observed by Komine and Byer (1977). These high power-levels were used only when observing the extremely weak features associated with the 632.6 nm and 451.4 nm fluorescent bands and, consequently, some of the observed properties of these bands may be partly due to energy-pooling effects.

There were several sources of systematic error in the experiments performed to measure fluorescent decay rates and
Figure 28. Time-evolution of the $\text{Hg}_2 \text{XO}_g^+ \leftarrow 1_u$ fluorescence at 335 nm, excited by two-photon pumping of the $6^1\text{D}_2$ atomic state.
hence lifetimes of the Rydberg states. In eq. 12, there is an implicit assumption that the fluorescent signal must be accumulated with respect to some fixed reference time. This means that any given position in the transient digitizer's memory (and thus in the microcomputer's memory) should always correspond to the same time after the excitation pulse. In the present case, a trigger signal generated by the probe dye-laser was used to start the accumulation of the fluorescent signal produced by each laser pulse. The transient digitizer had its own internal clock which was referenced to the probe laser pulses, and consequently, was subject to a built-in error of +/- 1 channel (+/-2 ns). As long as the analysis of the time-evolution of the decay started at a time at which the exciting pulse was off, no discrepancies in the decay rate were expected. However, for the short effective lifetimes encountered in this experiment, a reduction in the number of channels used in the analysis increased the statistical errors; this effect is negligible for long effective lifetimes.

Some of the dyes used in the probe laser, Stilbene 420, in particular, had a fairly short useful lifetime which caused an almost monotonic decrease in probe-laser power with time, as the dye was degraded by the UV N₂ pump laser. This caused a slow drift of the trigger level with respect to the peak of the recorded time-decay spectra, reducing the number of available channels for analysis. A much more severe problem was the occasional early triggering of the
recording electronics by as much as 50 - 100 ns, presumably due to electrical noise. This effect superimposed a 'hump' on the accumulated fluorescent signal at moderately late times and, consequently, limited the number of channels that could be employed in the computer analysis. Just a few of these early triggering events would produce substantial irregularities in the recorded time-evolution spectra.

The statistical error was kept to a minimum by accumulating a large signal in the early time-channels, and was estimated to be 5%. The other major source of error was also statistical in nature, since the fluorescence signal induced by the probe laser was frequently embedded in a moderately large background signal (noise). This was particularly evident in the weak bands and in some of the atomic decay-rate measurements performed using the probe laser to excite the $3^3S_1$ emission. This type of error was most evident at long times after the exciting pulse, at which the data are most heavily weighted in the non-linear least squares fit of the decay parameters. On occasions, the data-fitting had to be limited to to about 3 or 4 mean decay times because of this effect, introducing a somewhat larger statistical error. The molecular lifetimes are estimated to be accurate within about 25%, and the atomic lifetimes measured using two-photon excitation are estimated to be accurate within about 5%.
VI. SUMMARY AND CONCLUSIONS

Pulsed 'pump-and-probe' techniques were employed to investigate the time-evolution of the decays of several Hg₂ fluorescent bands, permitting their assignment to particular molecular Rydberg states. In particular:

i) The 1_u Rydberg state was found to be the emitting state for the 420 nm, 509.7 nm, and the previously unseen 632.6 nm fluorescent bands. The assignment of these bands differs from that of Callear and Lai (1982) who proposed different upper states for the 420 nm and 509.7 nm bands.

ii) The radiative lifetime of the 1_u Rydberg state was measured to be approximately 7.6 (±0.6) ns and the cross section for its collisional quenching induced by collisions with ground-state Hg atoms was found to be approximately 1.4×10⁻¹⁴ cm².

iii) The 451.4 nm fluorescent band was found to originate from a different upper state than the 420 nm fluorescent band, in contrast to the assignment of Callear and Lai (1982), and the emitting state is tentatively assigned as the 0_u⁺ state which correlates with the Hg 7³S₁ atomic state. The radiative lifetime of the 0_u⁺ state was measured to be approximately 7 (±1) ns and the cross section for its collisional quenching induced by collisions with ground-state Hg atoms was found to be approximately 3×10⁻¹⁴ cm².

iv) The absorption bands near 259.0 nm, 261.2 nm, and
271.8 nm were found to have extremely short fluorescent lifetimes of less than 2 ns, and appeared to decay primarily in a non-radiative fashion, possibly either through tunneling or predissociation.

v) A previously unreported continuum absorption in Hg$_2$ excimers was discovered, extending from below 258 nm to beyond 281 nm. This is tentatively attributed to excitation $^+$ from the A$_0^+$ states to a repulsive state or (states) associated with the $^3P$ manifold. The associated $^3P$ state was found to have a lifetime of approximately 15 (±2) ns and a cross section for its collisional quenching induced by collisions with ground-state Hg atoms of approximately 7×10$^{-15}$ cm$^2$.

vi) Approximate vibrational constants for Hg$_2$ were found to be $\omega''_e=144$ cm$^{-1}$ and $\omega''_x=0.5$ cm$^{-1}$ for the $^1A_0^+$ states; $\omega''_e=142$ cm$^{-1}$ and $\omega''_x=0.5$ cm$^{-1}$ for the $^2E_2^g$ state; and, $\omega''_e=152$ cm$^{-1}$ and $\omega''_x=0.9$ cm$^{-1}$ for the $^2F_1^g$ state.

The lifetimes of the Hg $^1D_2^g$ and $^3D_2^g$ atomic states were determined using two-photon excitation techniques and found to be 10.8 (±0.3) ns and 9.0 (±0.4) ns respectively, in good agreement with values reported elsewhere. The fine-structure mixing cross section of $^1D_2^g$ – $^3D_2^g$ induced by collisions with ground state Hg atoms was measured to be approximately 7×10$^{-14}$ cm$^2$.

The pump-and-probe method used in these experiments hinged on the efficient population of the Hg$_2$ $^0_{1g}^+$ metastable states from which higher Rydberg states were excited by the
probe laser pulses. Two-photon excitation of the Hg $^6\text{D}_2$ state was found to be an efficient mechanism for the production of metastable Hg$_2$ molecules at intermediate and high mercury vapour pressures. This pumping scheme had the advantage that very much better penetration into the Hg vapour could be achieved at these vapour densities than with resonance line pumping.

There are several further experiments which suggest themselves as a consequence of this investigation. More precise measurements of the vibrational (and rotational) constants of the lower Hg$_2$ metastable states using high-resolution techniques and isotopically pure mercury would allow determination of the molecular constants with much higher accuracy. Their knowledge would assist in the definite assignment of several of the molecular transitions which are still in doubt, in particular those associated with the 451.4 nm band. Also, there is pressing need for the accurate determination of the energy (relative to the A0$^+_g$ states) of the upper and lower state associated with the 451.4 nm band; their knowledge would lead to the accurate location of both with respect to the known potential energy curves and would substantially add to our knowledge of the Hg$_2$ system.

The Hg $^7\text{S}_1$ state seemed to be moderately stable with respect to collisional quenching by ground state Hg atoms, an effect which could readily be tested. The Hg $^7\text{P}_\text{manifold, which appears, to be involved in the UV absorption
continuum which leads to the formation of Hg $^3S_1$ atoms, could be investigated using three-photon absorption techniques similar to those employed by Dalby and Sanders (1981), and possibly clarify the role which these states play in the decay of highly excited Rydberg atoms and molecules.
APPENDIX I

Quad-Prism Unidirectional Achromatic Beam Expander

The design of the dye-laser oscillator described below was based on the quad-prism beam expander initially developed by Novikov and Tertshnik (1975) and the achromatic quad-prism expander developed by Klauminzer (1978). It had the following advantages over other types of dye-laser oscillators:

i) the cavity length of the oscillator can be reduced substantially from that required for a telescope expander, permitting more passes through the amplifying dye-volume and producing significantly higher efficiencies;

ii) the air-glass interfaces can be designed for non-normal incidence to minimize spurious feedback and resulting in a reduced level of background radiation at other wavelengths;

iii) the magnification of the expander can be adjusted by simply orienting the prisms at slightly different angles when aligning the expander;

iv) the prism expander produces substantial polarization discrimination so that a high degree of linear polarization of the output is obtained without an expensive crystal polarizer;

v) the entire prism array is relatively inexpensive compared to an achromatic telescope of the same magnification;
vi) the mounting for the prisms, in contrast to a telescope, does not have to be highly accurate and expensive.

The following are the equations on which the design of the multiple-prism achromatic expander is based:

Snell's Law \[ \frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{n_2}{n_1} \]  (AI-1)

Magnification 'M' at an air/glass interface:

\[ M = \frac{W_2}{W_1} = \left\{ 1 + \left[ 1 - \left( \frac{n_1}{n_2} \right)^2 \right] \tan^2 \theta_1 \right\}^{\frac{1}{2}} \]  (AI-2)

Transmissions 'T_p' and 'T_s' for each polarization at an interface:

\[ T_p = 1 - \left( \frac{\tan(\theta_1 - \theta_2)}{\tan(\theta_1 + \theta_2)} \right)^2 \]  (AI-3)

\[ T_s = 1 - \left( \frac{\sin(\theta_1 - \theta_2)}{\sin(\theta_1 + \theta_2)} \right)^2 \]  (AI-4)

where \( \theta_1, \theta_2, n_1, n_2, W_1, \) and \( W_2 \) are defined in Fig. AI-1.

The objective of the design was to maximize the transmission for the preferred 'p-polarized' (parallel) component at the expense of the 's-polarized' (perpendicular) component, while maintaining the prism-pair essentially achromatic.

This was accomplished by the judicious selection of the prism apex angles and the angles of incidence at each prism.

Refractive indices and other glass properties were obtained from the Schott short-form catalogue. Only those
Figure AI.1: One-dimensional magnification \( n_1 \), \( n_2 \) at an air/glass interface.
glasses were considered which exhibited high optical homogeneity and had high 'internal' transmission (transmission minus surface reflection losses) in the required wavelength range (385 nm - 750 nm). Initial calculations indicated that glasses of high refractive index were required for optimal efficiency at a given magnification. Because of symmetry properties, only a single pair of prisms needed to be considered in the calculations; the second pair was similar to the first (except for size) and was inverted with respect to the first pair upon assembly. Any angular deviation introduced by the first pair of prisms would be offset by an opposite angular deviation in the second pair. Preliminary calculations also indicated that the first prism of each pair should have a moderately low Abbe-number, while the second prism should have a somewhat higher Abbe-number (the Abbe-number \( v_d \) is defined as \( v_d = (n_d - 1)/(n_F - n_C) \) where \( n_d \) is the refractive index at a specific spectral line; 'd' denotes the He 587.56 nm line, 'F' denotes the H 486.13 nm line, and 'C' denotes the H 656.27 nm line; \( v_d \) is a measure of the inherent ability of a particular glass to disperse light).

An analytic solution was initially sought which would represent the transmission of a prism-pair by a function of the variable parameters, but the complexity of the equations quickly assumed unreasonable proportions and, consequently, this approach was abandoned. A computer was used to provide numerical solutions to the problem so that general trends
could be recognized and a suitable configuration determined by inspection. When all other optical factors were essentially equal, preference was given to those glasses which were readily available, had high hardness for good polish acceptance and durability, and were chemically inert. If possible, combinations of materials which would permit an identical geometrical shape for each prism were sought in order to reduce construction costs.

The geometrical description of the problem is indicated in Fig. AI-2. Both prism apex angles $\theta_1$ and $\theta_2$ were initially chosen to have arbitrary and convenient values of $30^\circ$. The dispersion (here defined as the angular separation of light at different wavelengths) of a collimated beam of white light was calculated as it passed through the first prism; 404.7 nm and 656.3 nm were chosen as the wavelengths for which the dispersions of the two prisms were to be matched, and 486.1 nm was chosen as the wavelength at which transmissions and magnifications were calculated. The dispersion was then calculated for a beam of collimated white light which passed in the opposite direction through the second prism. The two dispersions were matched by an iterative procedure until they agreed to within a specified accuracy (usually $0.001^\circ$), the magnification was calculated at each surface and the total magnification compared to the design specification. When the dispersion and magnification were sufficiently accurate, the transmissions for each polarization component and the various angles ($\theta_1 - \theta_8$), $\theta_1$
Figure AI-2. A prism-pair representing one-half of the quad-expander. Angles at each interface, which are wavelength-dependent, are exaggerated for clarity.
and $\Theta_2$ were stored in the computer; the transmissions were also calculated for the case of anti-reflection coatings on the output surfaces with nominally zero reflectivity for normal incidence. The prism apex angles $\Theta_1$ and $\Theta_2$ were then varied in a systematic way (usually by increments of $1/2^\circ$ or $1^\circ$), and the process was repeated. The entire array of pertinent numbers was printed out in tabular form so that general trends could be deduced by inspection, and favourable configurations noted.

The entire sequence was repeated for different magnifications and combinations of materials. In order to accelerate convergence to the specified accuracy levels, learning routines were built into the program to make use of internally generated values every time the dispersion or magnification exceeded the required value. The resulting transmissions were plotted and inspected in order to locate a single set of prism apex angles which would fulfill the requirements.

The selection of the optimal configuration was based on the following criteria:

i) the preferred configuration should permit operation at any magnification in the range 28 - 48, with nearly optimal transmission;

ii) for any magnification in the design range, incidence angles at the near normal surfaces should, if possible, be greater than $1^\circ$, to reduce the chance of spurious feedback, but smaller than about $5^\circ$ so that standard anti-reflection
coatings could be used;

ii) standard angles (e.g. 30° or 45°) for the prism apex
angles would be given preference;

iv) if standard angles were not possible, the second

preference would be for configurations which used equal
non-standard apex angles.

The results of the calculations led to several
conclusions. For a given Abbe-number, a glass with a higher
refractive index usually yielded increased transmission. The
first prism of each pair should have a moderately low
Abbe-number and the second prism should have a somewhat
higher Abbe-number; very large or small values of this
parameter did not usually produce suitable designs. It was
found that the combination of F2 (620-364) and BK7 (517-642)
glasses ('620' indicates that n_d =1.620, and 364 indicates
that the Abbe-number is v_d =56.4) yielded about the best
results in the calculations (assuming anti-reflection
coatings only on surfaces used close to normal incidence).
If no coatings are to be used, the difference between an all
quartz array and the F2-BK7 configuration turns out to be
small, but the exit angles for the case of quartz prisms are
rather large (nominally 30° for optimal transmission).

The layout of an actual quad-prism expander is shown in
Fig. AI-3; the angles correspond to a magnification of 40X.
The 'dashed' position of prism P1 permits a reduction of the
length of the expander but introduces a slight displacement
of the optical axis between input and output. Figure AI-4
Figure AI-3. The layout of a Quad-prism Expander. The figure is approximately twice actual size; the arrangement of the second pair duplicates that of the first pair, but the pairs are inverted with respect to each other. The 'dashed' position of $P_1$ permits further shortening of the overall length of the expander, but introduces a net displacement of the optical axis between the input beam and the output beam.
Figure AI-4. One-way transmission through a quad-prism expander as a function of apex angle of the prisms. (a) Variation with apex angles of prisms $P_2$ and $P_4$ ($P_1$ and $P_3$ fixed at $43^\circ$); variation with apex angles of prisms $P_1$ and $P_3$ ($P_2$ and $P_4$ fixed at $38^\circ$). The magnification in both cases is 40X and the prisms have no AR coatings.
shows the one-way transmission through the expander as a function of prism apex angles; (a) is the variation with apex angles of prisms $P_2$ and $P_4$ ($\theta_{P_1}$ and $\theta_{P_3}$ fixed at $43^0$); (b) is the variation with apex angles of prisms $P_1$ and $P_3$ ($\theta_{P_2}$ and $\theta_{P_4}$ fixed at $38^0$). The graphs in Fig. AI-4 are based on calculations for a 40X expander with no anti-reflection coatings. Even though in both cases the transmission seems to be sharply peaked, its overall variation is only slight over a range of about $20^0$. When zero-reflectivity coatings are included on the exit surfaces (those used at nearly normal incidence), the single-pass transmission increases to about 80%.

Figure AI-5 shows a graph of the exit angle from prism $P_4$ for several wavelengths in the visible spectral region. The data correspond to the F2-BK7 combination with $37^0$ apex angles in all prisms, and the deviation is measured relative to the 656.3 nm exit angle from $P_4$ (the large prism). As shown in the figure, the quad-prism array is fairly achromatic over the entire visible spectrum, with deviations not exceeding $0.01^0$. Alternative values could readily be chosen for the zero-deviation wavelengths, but this was not pursued.

Another aspect which was noted, but not pursued extensively, was the possibility of anti-reflection coatings on the input faces (corresponding to large incidence angles) of the prisms. Figure AI-6 shows the division of the wavefront at a prism input face covered with an AR coating
Figure AI-5. A plot of the exit angle from prism P₄ in relation to wavelength. The apex angles of all prisms are 37°, and the magnification is 40X. The exit angle is shown relative to the exit angle for λ=656.3 nm.
Figure AI-6. Division of the wavefront at the air/coating and coating/glass interfaces. Interference takes place between reflections $R_1$ and $R_2$; the reflectivity is zero when $R_1$ and $R_2$ are 180° out-of-phase and of equal amplitude. Refractive indices for air, coating and glass are $n_1$, $n_2$ and $n_3$ respectively.
The thickness of the coating is exaggerated for clarity. The refractive indices are \( n_1 \), \( n_2 \), and \( n_3 \) for air, coating and glass, respectively. For prisms \( P_1 \) and \( P_3 \) all wavelengths of light are incident at approximately the same angle and the recombining wavefronts have an optical path difference of \( 2n_2(\lambda_b)L_1 - n_1(\lambda_b)L_3 \) for blue light and
\[
2n_2(\lambda_2)L_2 - n_1(\lambda_2)(L_3 + \Delta L_3)
\]
for red light. If \( R_1 \) and \( R_2 \) are \( 180^\circ \) out of phase and of equal amplitude (there is a \( 180^\circ \) phase shift at the air/glass interface if \( n_2 > n_3 \)) the recombining wavefronts will interfere with each other destructively and reduce the reflected energy to zero. The geometry for light incident on prisms \( P_2 \) and \( P_4 \) is slightly more complicated due to dispersion effects in the preceding prism; this causes blue light to be incident at a larger angle than red light. Since no information concerning the optical properties of coating materials was available, the aspects of anti-reflection coatings on the input faces was not pursued extensively. Coating manufacturers should be able to supply appropriate anti-reflection coatings for the input faces of the prisms. It is possible that a monolayer of the correct thickness and refractive index might prove adequate as an AR coating and be effective over a very large wavelength range due to the normal variation of refractive index with wavelength. If a coating with zero reflectance were applied to prisms \( P_1 \) and \( P_3 \), the single-pass loss for the p-polarized component would be reduced to about 5%.

Two expanders were assembled according to the design
outlined above, using all prisms with apex angles of 36.625°, coated with broadband anti-reflection coatings on the exit faces. Prisms P₁ and P₃ (see Fig. A1-3) were fabricated from Schott F2 glass, and prisms P₂ and P₄ from BK7 glass. The lengths of the exit faces were 10 mm for the first two prisms, 20 mm for the third prism, and 40 mm for the fourth prism. All prisms were nominally 10 mm-thick.

Since the achromaticy was rather sensitive to alignment, a calculation was performed to determine the angles that 488 nm light from an Ar+ laser would make with the various surfaces while propagating in the reverse direction through the expander. These angles were then used to align the expander by adjusting the individual prisms until the back-reflections from those surfaces at which light was close to normal incidence coincided with a mark on a reference plane. When all the prisms were correctly adjusted, the assembly was installed in our dye laser and its performance checked. One expander was adjusted for a linear magnification of 28X and the other for 32X. These values were selected because of the intended application (wavelength range) in the two dye lasers, and were appropriate to the grating order that was used.

The performance of the nitrogen laser-pumped dye laser was quite satisfactory. Using R6G in ethanol and an oscillator-amplifier configuration, the overall efficiency was found to be approximately 16% with a dye-laser bandwidth of 0.2 cm⁻¹ and about 10% with a bandwidth of less than
0.05 cm\(^{-1}\) at 580 nm. The spectral bandwidth properties of the pulsed dye-laser are shown in Fig. AI-7. The interferograms, obtained photographically by means of an etalon operated in the projection mode, were used to measure approximate bandwidths. Both pictures were obtained at a dye laser wavelength of \(\lambda=580\) nm and with about 2 s exposures at 10 Hz; the detection etalon had a FSR of 1.0 cm\(^{-1}\) and a specified Finesse of >15. Some mode-structure was apparent under visual observation, but small pulse-to-pulse fluctuations blended this structure into a virtually continuous distribution. The broadband output from the dye-laser, shown in the interferogram in Fig. AI-7(a), was recorded using a 32X expander in the oscillator stage. The narrowband output from the dye-laser, shown in Fig. AI-7(b), was recorded using a 32X expander and an etalon (FSR of 1.0 cm\(^{-1}\) and Finesse \(<10\) in the dye-laser oscillator stage. In both cases, the dye-laser was operated well above threshold. For narrowband operation, virtually only a single cavity mode is active, but the spectral characteristics of the output were beyond the resolution limit of the detection etalon. The optical path-length in the cavity was found to be approximately 17.5 cm, corresponding to a mode-spacing of slightly less than 0.03 cm\(^{-1}\).

Table AI-I shows several magnifications that can be obtained from a quad-prism expander; and the required incidence and exit angles at each prism; the calculations are based on F2-glass for prisms \(P_1\) and \(P_3\), and BK7-glass for
Figure AI-7. (a) - Interferogram of broadband 580 nm dye-laser output. A 32X expander was used in the oscillator stage; the bandwidth is approximately 0.2 cm\(^{-1}\).

(b) - Interferogram of narrowband 580 nm dye-laser output. A 32X expander and an etalon (FSR = 1.0 cm\(^{-1}\), Finesse 10) were used in the oscillator stage; the bandwidth is less than 0.06 cm\(^{-1}\). Both interferograms were photographed using a 2 s exposure at 10 Hz and a detection etalon with a FSR of 1.0 cm\(^{-1}\) and Finesse of about 15.
Angles of incidence and exit required to obtain various magnifications of an achromatic Quad Prism Expander. Prisms $P_1$ and $P_2$ are made of Schott F2 (320-364) Flint glass, and prisms $P_3$ and $P_4$ are made of Schott BK7 (517-642) Crown glass. Angles $\theta_1-\theta_8$ are defined in Fig. AI-2; $\theta_i$ for $i > 8$ is the same as $\theta_1$. All angles are in decimal degrees and '+' '-' indicates that the exit beam is directed toward / away from the apex of that prism. Transmissions are for a single pass of the p-polarized component, with zero-reflectivity AR coating on the exit face of each prism.

<table>
<thead>
<tr>
<th>Magn.</th>
<th>$\theta_1=\theta_9$</th>
<th>$\theta_4=\theta_{12}$</th>
<th>$\theta_5=\theta_{13}$</th>
<th>$\theta_8=\theta_{16}$</th>
<th>Trans.</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.00</td>
<td>71.77</td>
<td>-1.58</td>
<td>67.97</td>
<td>+1.13</td>
<td>84.28%</td>
</tr>
<tr>
<td>34.00</td>
<td>72.34</td>
<td>-1.36</td>
<td>68.01</td>
<td>+1.14</td>
<td>83.10%</td>
</tr>
<tr>
<td>36.00</td>
<td>72.86</td>
<td>-1.17</td>
<td>68.03</td>
<td>+1.16</td>
<td>81.94%</td>
</tr>
<tr>
<td>38.00</td>
<td>73.33</td>
<td>-1.00</td>
<td>68.06</td>
<td>+1.17</td>
<td>80.81%</td>
</tr>
<tr>
<td>40.00</td>
<td>73.77</td>
<td>-0.85</td>
<td>68.08</td>
<td>+1.18</td>
<td>79.70%</td>
</tr>
<tr>
<td>42.00</td>
<td>74.17</td>
<td>-0.71</td>
<td>68.11</td>
<td>+1.19</td>
<td>78.62%</td>
</tr>
<tr>
<td>44.00</td>
<td>74.54</td>
<td>-0.58</td>
<td>68.13</td>
<td>+1.20</td>
<td>77.57%</td>
</tr>
<tr>
<td>46.00</td>
<td>74.89</td>
<td>-0.47</td>
<td>68.14</td>
<td>+1.21</td>
<td>76.54%</td>
</tr>
</tbody>
</table>
prisms $P_2$ and $P_4$, and apex angles of $37^\circ$ for all prisms. The transmissions are for a single pass of p-polarized light and zero reflectance at the output face of each prism. Each configuration is achromatic and has nearly optimal transmission. When the apex angles are allowed to differ in each prism, a more favourable configuration, based on exit angle with respect to normal incidence, can be achieved.

I have used these dye-lasers successfully from about 385 nm to 750 nm and found them to be efficient and easy to align and maintain. Based on the results of this investigation, it was found that substantial improvement in dye-laser performance over the original Hänsch design could be achieved using the quad-prism expander.
APPENDIX II

Computer Simulation of the Decay of an Excited State Subjected to Pulsed Pumping

The time-evolution of an excited state population, caused by pulsed pumping, was simulated on a computer in order to better understand the properties of the excited HgI molecules. A good approximation for the time-evolution of the pump pulse is provided by a modified Gaussian shape, which adequately represents the time-evolution of our laser pulses. The pump pulse may be represented by the expression:

$$W(t) = W_0 \exp{-[(t-t_0)/\alpha]^2} - \exp{-[(t_0)/\alpha]^2} \quad (AII-1)$$

where:

$$W_0 = C \quad \text{for} \quad 0 < t < 2t_0$$
$$W_0 = 0 \quad \text{for} \quad 2t_0 < t < 0$$

$W(t)$ is the amplitude of the pump pulse at time $t$, and $W_0$ is a switching parameter which permits the pulse to be turned on at time $t=0$ and turned off at time $t=2t_0$; this is necessary to keep the pumping term from contributing to the simulation outside of the time interval $0 - 2t_0$, where the pulse is assumed to be turned off. $C$ is a constant to permit normalization of the pump pulse to a convenient value. The parameter $\alpha$ controls the rise-time and fall-time of the pumping pulse. The second term in eq. (AII-1) ensures that the pulse is turned on and off smoothly, with no sudden jump in amplitude at $t=0$ and $t=2t_0$. The representation of the pump pulse is not mathematically continuous at $t=0$ or $t=2t_0$, since the time-derivative of eq. (AII-1) is not continuous.
at the turn-on and turn-off points. This expression for the pumping term has the advantage that essentially, any Gaussian pulse can be represented by varying the free parameters $\alpha$ and $t_0$; contributions from the pumping term do not extend to $t=\infty$.

The problem was simplified by assuming that only first-order effects were present (no stimulated emission or further excitation out of the pumped level by the pumping pulse). The time-evolution of the excited state population can be represented by the differential equation:

$$\frac{d}{dt} N(t) = W(t) - \Gamma N(t) \quad \text{(AII-2)}$$

where $N(t)$ is the instantaneous population density and $\Gamma$ is the effective decay rate (reciprocal lifetime) of the excited state. The equation is a first-order inhomogeneous linear differential equation and can be solved using standard techniques. The solution of the homogeneous equation is:

$$N(t) = N_0 \exp(-\Gamma t) \quad \text{(AII-3)}$$

where $N_0$ is chosen to match the boundary conditions. The solution of the initial equation for $0 < t < 2t_0$ is:

$$N(t) = \left(\frac{W}{\Gamma}\right) \left\{ \exp[-(\Gamma + (t_0/\omega)^2)t] - \exp[-2\Gamma (t + (t_0/\omega)^2)] \right\} + \left(\frac{W}{\Gamma^2}\right) \left\{ \exp[\Gamma (t-t_0)](\Gamma/2) \right\} \left[ \text{erf} \left( \frac{\sqrt{\Gamma t}}{\omega} + \frac{\sqrt{\Gamma/2}}{2} \right) \right.$$

$$+ \text{erf} \left( \frac{\sqrt{\Gamma (t+t_0)}}{\omega} + \frac{\sqrt{\Gamma/2}}{2} \right) \left] \right.$$  

(AII-4a)

For $t > 2t_0$, the solution is:
\[ N(t) = N(t_0) \exp(-\Gamma t) \]  
\begin{equation}
(AII-4b)
\end{equation}

where \( \text{erf}(x) \) is the error function (a value determined by integrating the normal distribution function from 0 to \( x \)).

Solutions of (AII-4a) were generated on a computer ( \( \text{erfc}(x) \), the complementary error function, was used for better numerical accuracy) and the results for several different decay rates of the excited state are plotted semilogarithmically in Fig. AII-1; the various curves have been normalized to the same peak amplitude for clarity. The curves were generated using the values \( \alpha = 4.75 \text{ ns} \) and \( t_0 = 8.0 \text{ ns} \); these particular numerical values approximately represented the initial time behavior of the pulse shape of the output (frequency-doubled) from the probe dye-laser, as measured with the transient digitizer. The values used in the simulation were somewhat larger than expected since the limited rise-time and somewhat slower fall-time of the recording equipment substantially increased the measured pulse-width compared to the value obtained using the fast detector. Of particular interest is the shift of the curve peaks with increasing effective lifetimes of the excited state (all the curves for finite values of \( \Gamma \) are linear with slope \( -1/\Gamma \) for \( t \to 2t_0 \)). The shift in the peak was used to draw qualitative conclusions concerning several of the time-evolution spectra associated with the molecular fluorescent bands.

The mathematical representation of the pumping pulse is
Figure AII-1. Computer-simulated time-evolution of the decay of an excited state subjected to pulsed pumping. (a)-effective lifetime of 1 ns; (b)-effective lifetime of 3 ns; (c)-effective lifetime of 6 ns. Times corresponding to maximal amplitude for each effective lifetime are labeled \( t_a \), \( t_b \), and \( t_c \), respectively.
not wholly correct since measurements of time-evolution of the dye-laser pulses, carried out with our fastest detector, indicated that the actual decay was slower than predicted by the Gaussian time-profile used in this model. This may be due to the slow decrease of the 337.1 nm radiation from the $N_2$ pump laser as it self-terminates, an effect which was not included in the computer simulation. Corrections for this effect would slightly increase the shift of the peaks in Fig. AII-1.
BIBLIOGRAPHY


Franck, J. and Grotrian, W., 1921. Z. Physik, 4, 89.


VITA AUCTORIS

I was born on August 9, 1948 in Leamington, Ontario, and upon graduation from Kennedy Collegiate in 1970, I enrolled in the Honours Physics program at the University of Windsor. After graduation in 1975, I entered the Faculty of Graduate Studies at the University of Windsor. After receiving a Master of Science degree in 1977, I proceeded to work toward a Ph.D. in Physics. During some of my years of graduate study I was the holder of a Natural Sciences and Engineering Research Council Canada Postgraduate Scholarship.