OPTICALLY PUMPED METAL VAPOR LASERS

MASTER

FINAL TECHNICAL REPORT

For the Period

15 April 1978 - 15 July 1980

A. Mandl and H. Hyman

September 1980

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Final Technical Report
for the Period
15 April 1978 - 15 July 1980

A. Mandl and H. Hyman

AVCO EVERETT RESEARCH LABORATORY, INC.
a Subsidiary of Avco Corporation
Everett, Massachusetts 02149

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FOREWORD

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ABSTRACT

The properties of optically-excited Hg/NH_3 and Hg/ND_3 mixtures have been studied as a function of mercury pressure in the range 1 - 40 torr. At low mercury pressures, ≤ 1 torr, the well-known UV emission band due to HgNH_3^* is dominant; this regime has been investigated extensively over the past ten years. However, at higher pressures the UV band disappears and is replaced by a strong green emission band, centered near 500 nm. From a detailed study of the spectral and temporal characteristics of the green band, it is concluded that it arises from the formation of the Hg_2NH_3^* (or Hg_2ND_3^*) excited molecular complex. The lifetime of this exciplex has been measured and is found to be 3.8 μsec ($\pm 25\%$). Because of interest in the system as a potential energy storage laser medium, optical transmission measurements have been carried out at selected wavelengths. Net absorption has been observed across the green band at high mercury density, as well as in the UV band in the low density regime.

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PHASE I

I. INTRODUCTION

This report is a summary of the work completed for the Department of Energy in which we attempted to develop an energy storage laser suitable for inertial confinement fusion. The approach is to use the high efficiency, scalable KrF laser to optically pump the mercury-ammonia exciplex. This long-lived exciplex can be used in a MOPA configuration to store the energy from a 1 μ sec KrF laser and subsequently extract the energy in a short ~ 1 nsec pulse. Our initial calculations projected that this laser could meet the D.O.E. goals for a laser to generate inertially confined fusion.

A key unknown which we identified, however, was intrinsic absorption of this system. Thus, the main objective of the program was to measure the net gain coefficient for the mercury ammonia exciplex (i.e., gain-absorption due to all species). Since all storage lasers have very small gain coefficients, it is necessary to have large optical path lengths in order to accurately measure the net gain. For this reason, a 1 meter device had to be built.

This report is divided into two sections: Phase I, describing the first portion of the program, i.e., building and testing of the apparatus, and Phase II, which is a

scientific paper that is being submitted for publication in the Journal of Chemical Physics. In Phase II, we summarize the various technical accomplishments of the program during its second phase.

A schematic diagram of the apparatus built under this program is shown schematically in Fig. I-1. The apparatus consists of several distinct parts. A 450 kV, 34 kJ Marx Bank capable of delivering a 1 μ sec pulse with a 150 nsec rise-time drives a cold cathode consisting of a set of 1" tantalum blades. The emitting area of the 12 cm x 1 m cathode is pictured in Fig. I-2. The resulting e-beam is compressed in a drift region by two magnetic field coils. The e-beam passes through a kapton foil and enters the XeI fluorescence cell. This fluorescence is used to optically pump Hg in the Hg/NH₃ suprasil quartz cell located at the center of the fluorescence cell. The XeI fluorescence cell, Hg/NH₃ suprasil quartz cell, and the gas handling system all had to be kept at high temperature so that high Hg vapor densities could be achieved. The fluorescence cell and closely coupled gas handling system with its remotely operated valves can be seen in Fig. I-3. The control systems for the vacuum, gas handling, ovens and magnets were wired into two panels which are shown in Fig. I-4 together with the System, Science and Software Marx Bank control panel.

A milestone for this program was to achieve very high e-beam currents so that XeI fluorescence pumping of the Hg/NH₃ system

H7883

Fig. I-1 Schematic Diagram of Experimental Apparatus of XeI*/HgNH₃* Optical Pumping

Fig. I-2 Photograph of Cold Cathode Inside E-Beam Box

Fig. I-3 Photograph of Fluorescence Cavity with Closely Coupled Gas Handling System

Fig. I-4 Photograph of Panels for Controlling Temperature, Vacuum and Gas Flow, Magnetic Field Coil and Marx Bank

would produce exciplex densities sufficient for a gain measurement. The goal was to produce an e-beam current density of $\sim 40 \text{ A/cm}^2$. It is for this reason that a magnetic field was used to compress the e-beam by a factor of ~ 4 .

A typical set of current plate and I/V Marx characteristics is shown in Fig. I-5. The lower trace shows the Marx voltage which is seen to rise to $\sim 90\%$ of its maximum in $\sim 150 \text{ nsec}$. The voltage then levels off and over the $1.2 \text{ } \mu\text{sec}$ pulse shows some "droop." The Marx current pulse on the upper trace also rises rapidly but even though the Marx voltage droops somewhat the current continues to rise due to diode closure. The transmitted e-beam current, also shown on the upper trace of Fig. I-5, follows the Marx current and peaks at $\sim 41 \text{ A/cm}^2$ as the crowbar is applied, meeting our goal for e-beam intensity.

When comparison was made between the measured and calculated Marx current transmitted through the foil and into the fluorescence cell, agreement to better than $\pm 10\%$ was found. Thus, the e-beam entering the XeF fluorescence cell is well characterized and sufficient for this program.

The measurements of scientific interest culminating in the gain/absorption measurements on both the visible (green) band and the UV band are described in detail in the Phase II section of this report. A photograph showing the apparatus during a typical gain/absorption measurement is shown in Fig. I-6 (#4684-2).

J1618

Fig. I-5 Measurement of the Transmitted E-Beam Current. The e-beam current peaks at about 41 A/cm². Also included are the I/V characteristics of the Marx bank.

Fig. I-6 Photograph of Overall Experiment as seen During a
Gain/Absorption Measurement

I. INTRODUCTION

The mercury-ammonia system has been the subject of extensive investigation over the past decade, with results reported in a continuing series of papers, primarily by Phillips and his associates¹ and by Callear and co-workers², as well as by Hikida, et al.³⁻⁵ and Umemoto, et al.⁶ All of these studies were aimed at understanding the Hg-photosensitized luminescence of NH₃ as a function of NH₃ pressure, and were thus carried out at room temperature with [Hg] ~ 2 x 10⁻³ torr. The single exception appears to be the work of Callear and Connor⁷, who reported seeing green emission (the usual HgNH₃^{*} band is in the UV, centered at λ ~ 342 nm) which increased in intensity with increasing [Hg], and which they attributed to Hg₂^{*} formed by the reaction HgNH₃^{*} + Hg → Hg₂^{*} + NH₃. However, no discussion was given in their paper of the temperature or Hg density where this green emission became prominent, nor are we aware of any subsequent investigation of this result.

The primary purpose of the present work was to examine the mercury-ammonia molecule as a potential laser candidate (see Sec. II). Since the HgNH₃^{*} exciplex has a very small stimulated emission cross section (≈ 2.7 x 10⁻¹⁹ cm²), large excited-state densities are required to observe gain and/or obtain laser action, which in turn requires large initial ground-state mercury densities. The present work thus comprises the first detailed investigation of the mercury-ammonia system at high mercury densities, with [Hg] in the range of 1-40 torr. Of particular interest in this operating regime is the formation of a new species, Hg₂NH₃^{*}, which emits a strong green band, as will be discussed further in Sec. IV.

The plan of the paper is as follows. Section II briefly summarizes the existing Hg/NH₃ results relevant to the present study, and outlines the optical pumping scheme. The experimental apparatus is described in detail in Sec. III. Our results, including fluorescence spectra, lifetime measurements, and optical transmission (i.e. gain/absorption) measurements at selected wavelengths are presented and discussed in Sec. IV. Finally, Sec. V contains a summary and conclusions.

II. BACKGROUND

A. Hg/NH₃(ND₃) Kinetics

A schematic of the potential energy curves and the dominant kinetic pathway for HgNH₃^{*} formation is shown in Fig. II-1. In our experiment, ground-state Hg atoms are initially excited to the Hg^{*}(³P₁) resonance level; the optical pumping scheme will be described below. Subsequent spin-orbit relaxation to the Hg^{*}(³P₀) state occurs by the process

which has a measured⁸ rate constant of $8.8 \times 10^{-11} \text{ cm}^3/\text{sec}$ ($8.6 \times 10^{-11} \text{ cm}^3/\text{sec}$ with ND₃ substituted for NH₃). A competing process is

with the quantum yields for reactions (1) and (2) being⁹ $\phi(1) \approx 0.7$, $\phi(2) \approx 0.3$ for NH₃, and $\phi(1) \approx 1.0$, $\phi(2) \approx 0$ for ND₃. For our operating conditions, with [NH₃] near $3 \times 10^{19} \text{ cm}^{-3}$, the HgNH₃^{*} (or HgND₃^{*}) excited complex is then formed by the 3-body reaction

J6213

Fig. II-1 HgNH_3 Partial Potential Energy Diagram with Formation Channel Indicated

with a rate constant of $^{10} 2.6 \times 10^{-30} \text{ cm}^6/\text{sec}$ ($3.4 \times 10^{-30} \text{ cm}^6/\text{sec}$ for ND_3^{11}). Numerous measurements have been made for the HgNH_3^* lifetime over the past ten years with generally reasonable agreement, the average value being approximately $1.6 \text{ } \mu\text{sec}$ for both HgNH_3^* and HgND_3^* . The HgNH_3^* exciplex is apparently not quenched by high pressures of NH_3 , but instead forms excited clusters of the type $\text{Hg}(\text{NH}_3)_n^*$, a phenomenon pointed out and studied by Callear and Connor^{7,12}. At 295°K , clusters with n up to at least 5 were observed; however, cluster formation was found to be suppressed at elevated temperatures, with at most $n = 2$ at 404°K . Since our operating conditions are in the range $T \geq 500^\circ\text{K}$, we do not expect clustering to be a significant factor in our experiment.

The HgNH_3^* exciplex emits a broad, structureless band, centered at $\lambda \approx 342 \text{ nm}$ and with $\text{FWHM} \approx 42 \text{ nm}$. The emission spectrum from HgND_3^* is almost identical, but is shifted slightly to the red⁹ by about 4 nm . The lack of structure in the band is characteristic of a strongly repulsive lower-level potential energy surface, as shown in Fig. II-1, in which the HgNH_3 complex rapidly dissociates into the ground-state species. As a consequence of this dissociating lower level, the HgNH_3^* exciplex is automatically inverted. Knowing the radiative lifetime and bandwidth, we can estimate the stimulated emission cross section to be $\sigma_{\text{stim}} = \lambda^4/8\pi c \Delta \lambda \tau \approx 2.7 \times 10^{-19} \text{ cm}^2$. Although this is a very small value, it is appropriate for a short-pulse, high-power storage laser applicable to the laser-driven inertial confinement fusion problem. For this application, the inverted population could be built up over a period $\sim 1 \text{ } \mu\text{sec}$, and the energy subsequently extracted in a short ($< 1 \text{ nsec}$) intense pulse.

B. Optical Pumping

For our conditions, the resonance line of Hg is optically thick. In order to obtain large excited-state densities, it is thus necessary to optically pump the Hg atoms in the collision-broadened wings of the 253.7 nm line. For this purpose, we have taken advantage of the fortuitous overlap between the strong $\Sigma \rightarrow \Sigma$ emission band of the XeI molecule¹³ and the Hg resonance transition. XeI is one of a class of molecular species -- the rare gas-monohalides -- which have been the source for several efficient, high-power UV lasers (e.g. KrF, XeF, XeCl, etc.). Although XeI has itself not yet been made to lase, it is a very bright fluorescence source and therefore well-suited to our application. The details of the XeI emission spectrum can vary somewhat, depending on the particular gas mixture and excitation source. In our experiment, in which a 99% Xe/1% HI mixture, at a total number density of $\sim 8 \times 10^{18} \text{ cm}^{-3}$, was irradiated by an intense 450 kV electron beam, the $\Sigma \rightarrow \Sigma$ band of XeI peaked at 253.2 nm with FWHM $\approx 2 \text{ nm}$, thus spanning the broadened Hg resonance line.

III. EXPERIMENTAL APPARATUS

As shown in Fig. II-2, our experiment consists of a coaxial arrangement, with an outer cell filled with the Xe/HI mixture and an inner cell containing the Hg/NH₃ mixture. The outer cell is irradiated by an intense e-beam, forming the XeI* exciplex. The XeI* fluorescence then acts as a bright optical pumping source for the Hg atoms in the inner cell, providing reasonably uniform spatial deposition. The various components of the experimental apparatus are described in detail below.

J1689

Fig. II-2 Setup for Optically Pumping HgNH_3^*

A. Electron Beam

The 12 x 100 cm cold cathode e-beam is driven by a 450 kV, 34 kJ Marx Bank capable of delivering a 1 μ sec pulse with a $\sim$ 150 nsec risetime. In order to obtain high current densities, a set of magnetic field coils in a Helmholtz arrangement was used to both guide and compress the e-beam. These coils can be run with currents greater than 2 kA and have been built with an inner water cooled Cu conductor to prevent overheating from the high temperature fluorescence cell and gas handling systems. The system is designed to compress the e-beam by a factor of 4.

The current density through the foil and into the fluorescence cell was measured in two ways. In order to test for spatial variation of the current along the foil a series of Faraday cups was set up and simultaneous current measurements into several cups were made. Small variations $\sim \pm 10\%$ were observed. The total current passing through the foil was measured by inserting a 1-m current plate at the back of the fluorescence cavity, connecting the plate to ground, and measuring the current with a Pearson transformer. In order to convert these measurements into a current density, a separate set of experiments was performed to determine the cross sectional area of the e-beam at the foil. In these experiments, blue cellophane was placed in front of the current plate. The e-beam discolours the cellophane leaving a clear exposed area where it strikes. From these measurements it was determined that the e-beam had been compressed to a 3 cm height inside the fluorescence cell, yielding current densities of 20-40 A/cm² into the cell. The e-beam voltage is $\sim$ 300 kV, and the pulse duration is typically 1 μ sec with a 150 nsec risetime.

B. Fluorescence Cells

The heart of the experiment is the two coaxial fluorescence cells (see Fig. II-2). The outer cell is 8 x 7 x 100 cm and is filled with a mixture of Xe and HI. At the center of this cell is a suprasil quartz cell with an I.D. of 0.8 cm and length of 100 cm, which is filled with Hg and NH₃ (or ND₃).

The e-beam entering the outer (XeI) cell is 3 x 100 cm with a current density $\leq 40 \text{ A/cm}^2$. The e-beam excites a mixture of Xe and HI (typically 300-400 torr Xe with 1% HI). The HI cylinder was initially cooled to liquid N₂ temperature and pumped to remove any H₂ formed from HI. After the HI cylinder was brought back to room temperature the gas was trapped at 0°C to remove any water present. It was found that the HI must be kept dry to maintain the mixture at high temperatures $\sim 275^\circ\text{C}$. The XeI cell is heated because the Hg/NH₃ cell located at its center has to be at a temperature sufficient to maintain the high Hg densities needed for the experiment. If any water were allowed into the XeI cell the fluorescence fell significantly at temperatures above about 100°C. Various other iodine donor molecules were tried, but at the high operating temperatures, none gave as much fluorescence as HI. The Xe density was also varied and it was found that the fluorescence peaked for Xe ~ 350 torr. At the temperature of the experiment, this corresponds to an Xe density of $\sim 8 \times 10^{18} \text{ cm}^{-3}$. At lower pressure the stopping power of Xe is too low and at higher pressure Xe apparently quenches XeI*. Using the lifetime of XeI*, which was recently reported as 15 nsec,¹³ our measurements indicate a quenching rate for XeI* by Xe of $8.2 \times 10^{-12} \text{ cm}^3/\text{sec}$, in good agreement with Hammati and Collins.¹³

In order to maximize the fluorescence absorbed by the Hg, the Hg/NH₃ cell was filled with a buffer gas (typically N₂) in order to broaden the Hg absorption line. Either the NH₃ alone or the NH₃ + buffer gas was maintained at pressures of 2 atm or greater. When the inner cell was filled to pressures above an atmosphere, a buffer gas (typically He) was added to the outer XeI cell to balance the pressure and reduce the strain on the inner cavity.

The inner quartz cavity was also subjected to direct e-beam bombardment. This presents no physical danger to the cell but can act to reduce the optical transmission of the quartz cavity to the fluorescence pump. However, measurements on suprasil quartz witness plates exposed to the e-beam showed that after 40-50 shots the transmission decreased by only a few percent. The inner cell was replaced after a few hundred shots.

IV. RESULTS AND DISCUSSION

A. Fluorescence Spectra

The experimental apparatus for making fluorescence measurements of the optically excited Hg/NH₃ mixture is shown schematically in Fig. II-3. A typical XeI* fluorescence spectrum from our apparatus is shown in Fig. II-4. A significant fraction of this radiation is absorbed in the pressure-broadened Hg resonance line to produce Hg*(³P₁) in the central suprasil quartz cell. As discussed in Sec. IIA, the Hg*(³P₁) is relaxed by the NH₃ to form metastable Hg*(³P₀), which combines, in a 3-body reaction, to form the HgNH₃ excimer. A Tracor-Northern optical multi-channel analyzer (OMA) is used to monitor the fluorescence from the excimer. The OMA is gated so that the XeI* fluorescence has decayed and only the longer-lived mercury-ammonia excimer radiation is present.

Figure II-5 shows a series of measurements in which the fluorescence from a mixture of Hg/NH₃ is observed to change as the Hg pressure varies from 1 to 25 torr, with the NH₃ pressure held fixed at 2 atm. At the low Hg pressures (1-2 torr) the emission peaks at 342 nm and is identified as HgNH₃*. This is shown in Figs. II-5a and 5b. Figure II-5a is the raw data from the OMA. The response of the OMA is such that data below $\lambda \sim 400$ nm is skewed toward longer wavelengths. The data of Fig. II-5a has been corrected and replotted in Fig. II-5b, which shows the typical HgNH₃* spectrum peaking at 342 nm with a ~ 42 nm halfwidth. As the Hg pressure is increased (Fig. II-5c), the relative emission of

J4002

Fig. II-3 Schematic Diagram for Experimental Apparatus for Fluorescence and Lifetime Measurements

J6214

Fig. II-4 Measured XeT* Emission Spectrum Near the 253.7 nm Mercury Absorption Line

Fig. II-5 Measured Fluorescence from Hg/NH₃ Optically Pumped Mixtures as a Function of [Hg], [NH₃] = $3 \times 10^{19} \text{ cm}^{-3}$; (a) [Hg] = $3 \times 10^{16} \text{ cm}^{-3}$; (b) Corrected Spectrum of (a) Reflecting Change in Response of the OMA Around 350 nm (c) [Hg] = $2 \times 10^{17} \text{ cm}^{-3}$ (d) Hg = $5 \times 10^{17} \text{ cm}^{-3}$.

the 342 nm band is observed to decrease and a new band appears which peaks at ~ 500 nm. Since the response of the OMA is reasonably flat around 500 nm, the spectra taken in this region did not have to be corrected. The sensitivity of the OMA is such that the 342 nm signal is $\sim 1/5$ the sensitivity of the 500 nm signal, so the 342 nm UV band should be multiplied by ~ 5 when comparing it to the 500 nm green band. At $[\text{Hg}] = 25$ torr (Fig. II-5d), essentially all the radiation is from the green band. Similar emission has also been observed when deuterated ammonia, ND_3 , is substituted for NH_3 .

When mercury vapor at ~ 25 torr was optically pumped in the presence of a nitrogen buffer gas alone, with no ammonia present, emission was also observed around 500 nm, which we attribute to the well-known¹⁴ green band due to Hg_3^* . We then performed a series of measurements in which Hg vapor at 25 torr was optically pumped in the presence of each of the buffer gases N_2 , NH_3 , and ND_3 . In all three cases bright green emission was observed, as shown in Fig. II-6. There was, however, a significant difference in the three spectra. The emission from the Hg/N_2 mixture (presumably due to Hg_3^*) is considerably broader than that from either the Hg/NH_3 or Hg/ND_3 mixtures. In addition, the peak of the band for the Hg/ND_3 case is slightly red-shifted, by ~ 2 nm, compared to that for the Hg/NH_3 mixture.

B. Lifetime Measurements

In order to more fully characterize the molecular species responsible for the green emission band, a series of lifetime

Fig. II-6 Measured Fluorescence Spectra at $[\text{Hg}] = 5 \times 10^{17} \text{ cm}^{-3}$
for Various Buffer Gases N_2 , NH_3 and ND_3 , each at
 $3 \times 10^{19} \text{ cm}^{-3}$

measurements were performed using a photodiode with a high pass filter ($\lambda > 420$ nm), as shown schematically in Fig. II-3. Typical oscilloscope traces for these measurements are shown in Fig. II-7. The top trace (Fig. II-7a) shows a background measurement with no Hg/NH₃ in the suprasil quartz cell, the observed signal being due to XeI* radiation scattered into the central cell. When a mixture of Hg/NH₃ is added to the central cell, a long time decay of the radiation is observed (Fig. II-7b). This decay is plotted on a semi-log chart in Fig. II-8 and gives a good fit to an exponential. The average of a series of measurements of the lifetimes for this emission with either NH₃ or ND₃ as the buffer gas is $\tau = 3.8$ μ sec ($\pm 25\%$). The lifetime we measured for Hg₃* (formed in the Hg/N₂ mixture) was much longer and in reasonable agreement with the previously reported^{15,16} values of ~ 15 μ sec. In addition, measurements were carried out with various ammonia pressures in the range 1 - 3 atm, and no significant difference in the 3.8 μ sec lifetime was observed.

We can now summarize our results as follows. For [Hg] > 10 torr, the optically-excited Hg/NH₃ (or Hg/ND₃) mixture emits a strong green band close to the position of the well-known Hg₃* band. However, from our lifetime measurements, as well as from a detailed comparison of the various spectra (Fig. II-6), it is apparent that the green-band emitter in the Hg/NH₃ and Hg/ND₃ mixtures is not Hg₃*. In addition, the spectral shift when ND₃ is substituted for NH₃ would imply that the emitting molecule

J4040

Fig. II-7 Typical Data Showing Fluorescence Lifetime of Hg/NH_3 Optically Pumped Mixtures. (A) gives background with no Hg/NH_3 in inner cell. XeI^* emission is scattered from fluorescence cell into inner cell. Upper trace of (A) is XeI^* side light emission. Lower trace (A) gives emission from inner cell looking down the 1 m optical axis. (B) gives signals when Hg/NH_3 mixture is added to inner cell.

J4001

Fig. II-8 Typical Semi-Log Plot of the Decay of Hg_2NH_3^* Fluorescence

contains ammonia. We therefore suggest that the green band arises from a new species: the Hg_2NH_3^* (or Hg_2ND_3^*) exciplex.

From the data shown in Fig. II-5, it is clear that the disappearance of the HgNH_3 UV band is correlated both with an increase in mercury pressure as well as with the appearance of the green band. This suggests that HgNH_3^* is the precursor of the Hg_2NH_3^* exciplex, and that the formation channel is either

or

We can obtain a rough estimate of the rate constants for processes (4) and (5) by noting that the UV band begins to disappear at $[\text{Hg}] \sim 10$ torr (corresponding to $2 \times 10^{17} \text{ cm}^{-3}$ at our operating temperature). If we take $\text{M} = \text{NH}_3$ in (4) with $[\text{NH}_3] \approx 2 \text{ atm}$, we must have $k_4[\text{Hg}][\text{NH}_3] \approx 1/\tau(\text{HgNH}_3^*) \approx 6 \times 10^5$, giving $k_4 \approx 10^{-31} \text{ cm}^6/\text{sec}$, which is a very reasonable value for this type of attachment or clustering process. Similarly, we have $k_5[\text{Hg}] \approx 6 \times 10^5$, giving $k_5 \approx 3 \times 10^{-12} \text{ cm}^3/\text{sec}$, which again is quite reasonable for the displacement reaction. Process (6), by direct analogy to the 3-body attachment of NH_3 to $\text{Hg}^*(^3\text{P}_0)$, would be expected to be fast. Further work would be required to determine which of the above two kinetic channels is dominant.

C. Optical Transmission Measurements for the Green Band

From the measured bandwidth and lifetime of the Hg_2NH_3^* and Hg_2ND_3^* exciplexes, we estimate a stimulated emission cross section of $\sim 2 \times 10^{-19} \text{ cm}^2$. Since this is a reasonable value for

a high-power storage laser (see Sec. II A), we have examined this system for gain. The measurements were performed using an Ar ion laser (Lexel Model 95-4) in a standard gain/absorption configuration.

Gain/absorption measurements have been previously performed¹⁷ on the Hg_3^* molecule which emits in the bandpass of interest. We repeated these measurements and found good agreement with the previous work. Using the cross section for absorption by Hg_3^* [$\sigma(514.5 \text{ nm}) = 1.6 \times 10^{-19} \text{ cm}^2$] given by McGeoch¹⁷, we were able to estimate the Hg_3^* excited state density. By taking ratios of the emission intensities of $\text{Hg}_3^*:\text{Hg}_2\text{NH}_3^*:\text{Hg}_2\text{ND}_3^*$, we could determine the Hg_2NH_3^* and Hg_2ND_3^* excited state number densities to be typically $\sim 5 \times 10^{14} \text{ cm}^{-3}$.

Gain/absorption measurements were performed on both the Hg_2NH_3^* and Hg_2ND_3^* systems. A typical measurement is shown in Fig. II-9. The upper oscilloscope shows the balanced gain-absorption signal through a differential amplifier when no Hg/NH_3 mix is in the cell. The e-gun voltage is displayed on the upper trace to show the timing of the e-gun pulse. The lower oscillogram gives the measured absorption at 488 nm. This is a differential signal showing the difference between the Ar ion laser signal and the laser signal through the excited medium.

Note that the absorption increases while the pump is on and then decays back to zero in a time equal to the Hg_2NH_3^* measured lifetime. Thus, the absorption is most likely intrinsic to Hg_2NH_3^* . The gain/absorption measurements of Hg_2NH_3^* for various

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Fig. II-9 Gain/Absorption Measurement on Hg₂NH₃*. Hg = 40 torr/
NH₃ = 200 torr/Ar = 1650 torr/ λ = 488 nm/T = 250°C
(fluorescence cell temperature). Upper trace marked
gain/abs shows run with no Hg/NH₃ in inner cell; lower
trace is gain/absorption measurement with Hg/NH₃ in
cell. On each oscillogram the upper e-gun voltage
trace is displayed as an indicator of when the system
was being optically pumped.

wavelengths across the emission band are plotted in Fig. II-10. The Hg_2NH_3^* fluorescence is shown for reference on the same figure. It can be seen that the maximum absorption occurs at 470 nm and then drops steadily toward the red to approximately $5 \times 10^{-5} \text{ cm}^{-1}$ at 568 nm. Since the Hg_2NH_3^* excited state density was determined as $\sim 5 \times 10^{14} \text{ cm}^{-3}$, this implies that the intrinsic absorption cross section from the excited Hg_2NH_3^* is $\sim 3 \times 10^{-19} \text{ cm}^2$ at 568 nm.

The measurements have been repeated for deuterated mercury ammonia, Hg_2ND_3^* , and the results are plotted in Fig. II-11. The peak absorption seems to be at $\sim 480 \text{ nm}$ with the absorption again dropping towards the red. The overall absorption in Hg_2ND_3^* is higher than for Hg_2NH_3^* , $\sim 10^{-4} \text{ cm}^{-1}$ at 568 nm, implying an intrinsic upper state absorption cross section of $\sim 4 \times 10^{-19} \text{ cm}^2$ at this wavelength.

We are thus measuring a very small absorption cross section which is monotonically decreasing to the red and on the order of, but slightly larger than, the stimulated emission cross section. It is, of course, possible (See Figs. II-10 and 11) that at some wavelength, $\lambda > 568 \text{ nm}$, net gain may be observable.

D. Optical Transmission Measurements for the UV Band

By operating at lower Hg pressures ($\sim 1 \text{ torr}$), where HgNH_3^* formation is still dominant, we made a series of optical transmission measurements for the UV band. The two UV lines of an

Fig. II-10 Gain/Absorption Measurements on Hg₂NH₃* at Various Wavelengths Across the Hg₂NH₃* Emission Band Which is Indicated by a Dashed Curve

Fig. II-11 Gain/Absorption Measurements on Hg_2NH_3^*

Ar ion laser were used and significantly greater absorption was observed when compared to the green band measurements. Within our 25% error estimate the HgNH_3^* and HgND_3^* absorption was the same. As in the green band case, the absorption fell toward the red with the resulting absorption coefficients: $0.2\% \text{ cm}^{-1}$ at 351 nm and $0.15\% \text{ cm}^{-1}$ at 364 nm. A significant difference between the UV and visible transmission measurements was that in the UV case the absorption did not decay with the $\sim 1.6 \text{ } \mu\text{sec}$ lifetime of the HgNH_3^* molecule, but lasted significantly longer ($> 10 \text{ } \mu\text{sec}$). It is therefore likely that this relatively large absorption is not due to self-absorption by HgNH_3^* but to some transient, long-lived species formed in the optically-pumped mixture.

V. SUMMARY AND CONCLUSIONS

The present work constitutes the first detailed investigation of the mercury-ammonia system as a function of mercury pressure. Our experimental results point to the existence of two distinct regimes. At low mercury pressures, ≤ 1 torr, the well-known UV emission band due to HgNH_3^* is dominant; this is the regime that has been studied extensively over the past ten years. However, at higher pressures, with $[\text{Hg}] \geq 25$ torr, the UV band completely disappears and is replaced by an intense green emission band centered near 500 nm. It is at first tempting to ascribe this green emission to the well-known Hg_2^* band. However, from a detailed study of both the spectral and temporal characteristics of the green band, we have concluded that 1) it is not due to Hg_2^* and 2) it is specific to the presence of ammonia in the system. We have therefore suggested that the green emission arises from the Hg_2NH_3^* (or Hg_2ND_3^*) exciplex, which is formed in mercury-ammonia mixtures at

high mercury pressure. Our measurements yield a lifetime of 3.8 μsec ($\pm 25\%$) for both the Hg_2NH_3^* and Hg_2ND_3^* excited molecular species. We have also identified the most probable kinetic channels for the formation of Hg_2NH_3^* and have estimated rate constants for the relevant processes.

As indicated earlier, the mercury-ammonia system is potentially interesting for use as an energy storage laser. In order to scale such a laser up to the energies required for practical applications, it is important to maximize the laser energy density and thus to operate at as high a mercury density as is feasible. The most attractive operating regime is therefore the one in which the Hg_2NH_3^* (or Hg_2ND_3^*) exciplex is dominant, and we have thus carried out gain/absorption measurements at selected wavelengths spanning the green emission band. Our results show net absorption across the band which, in addition, appears to be intrinsic to the Hg_2NH_3^* (or Hg_2ND_3^*) exciplex. A less detailed investigation of the low mercury density regime has also revealed net absorption in the UV band. Since the gain/absorption measurements were carried out at discrete wavelengths in both the green and UV bands, we cannot absolutely rule out the possibility that net gain may exist at some wavelength. However, although the mercury-ammonia system remains interesting from a basic kinetics viewpoint, we conclude that it does not look promising as a practical energy storage laser candidate.

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