DYNAMICS OF OPTICALLY-PUMPED
PULSED MID-INFRARED NH₃ LASERS

By

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ABSTRACT

An extensive theoretical and experimental study of the dynamics of optically-pumped pulsed NH$_3$ lasers is presented. The results completely characterize the small-signal gain of NH$_3$ lasers operating on rotational-vibrational transitions in the mid-infrared wavelength range from 10 to 21 μm. Two gain mechanisms are identified from the experiments: single-photon inversion gain and two-photon Raman gain.

Raman gain is described by a density-matrix model as a coherent interaction of two radiation fields with three molecular levels. Raman emission is offset in frequency from the line center of the emitting transition, and is the dominant process both at large pump offsets and in pure NH$_3$. The Raman process and the ac Stark effect, which shifts the optimum gain frequency, are always present in NH$_3$ lasers and affect all transitions which have one level in common with the pumped transition.

Significant population transfer produces inversion gain which is the dominant gain process in mixtures of NH$_3$ with a buffer gas. A rate-equation model is developed based on the assumption of rapid rotational thermalization in all vibrational levels within, but not between, ortho-NH$_3$ (K=3n) and para-NH$_3$ (K=3n±1). The model accounts for the observed distributions and magnitudes of inversion gain for a wide range of pumping conditions. The thermalization concept makes it possible to characterize a gain distribution by the ratio of vibrational populations.
Another important consequence of rotational thermalization is the prediction and demonstration of a new line-tunable NH₃ laser. A two-step pumping process produces lasing from 16 to 21 µm on many ortho-NH₃ 2ν₂ transitions.

A final interesting prediction of the rate-equation model is that a 10-atm NH₃ laser is feasible. At this pressure, there is a potential for tuning the laser emission across 36% of the wavelength range from 10.5 to 13.8 µm, and for producing pulses as short as 10 ps.
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CHAPTER 1

INTRODUCTION

Optical pumping of molecular gases by high-energy lasers has proven to be the most successful method for creating high-power coherent sources across the mid-infrared wavelength region from 2-20 \( \mu \text{m} \) [1,2]. A few molecules, such as \( \text{NH}_3 \) and \( \text{CF}_4 \), have been established as "winners" (a term coined by Coleman [1]) for this technique and there has been considerable progress in the experimental development of lasers based on "winner" molecules. However, there have been very few reports on the development of quantitative models of the laser dynamics. Predictive models of the gain dynamics of mid-infrared optical pumping are necessary to exploit fully the potential of molecular gas lasers. In this thesis, the pulsed \( \text{NH}_3 \) gas laser is examined in detail and models of the gain dynamics are developed which account for all the major experimental features of mid-infrared optically-pumped \( \text{NH}_3 \) lasers. The models are validated by detailed comparisons with experiments and can be used to predict scalability and optimum operating conditions for a variety of \( \text{NH}_3 \) lasers. In particular, a new \( \text{NH}_3 \) laser, operating at longer wavelengths than most other \( \text{NH}_3 \) lasers, is developed based on the predictions of one of the models. With minor modifications the models can easily be applied to other molecules. Thus, the results described here provide a basis for understanding the dynamics of all optically-pumped molecular lasers.
In 1970, Chang and Bridges first used optical pumping by an infrared laser to produce far-infrared lasers [3]. That discovery revolutionized the development of coherent sources for the entire infrared spectrum. Two years later the first coherent optical pumping of mid-infrared lasers was demonstrated [4]. The mid-infrared region is of particular interest as the vibrational frequencies of most molecular gases lie in this range. Thus, optically-pumped molecular lasers in the mid-infrared provide a convenient tool for studying vibrational processes in molecules, as well as providing efficient, high-power sources for laser isotope separation, atmospheric monitoring and many other applications.

Prior to the discovery of optical pumping the major method for producing mid-infrared lasers was an electric discharge. The electric discharge method is highly successful for some molecules, such as CO₂ and HF, but is less successful with molecules such as N₂O and OCS which dissociate easily. Furthermore, a discharge pumps all the vibrational levels simultaneously and produces significant heating in the gas necessitating the use of elaborate cooling systems or rapid gas flow to achieve high pulse repetition rates. On the other hand, optical pumping is a very energy specific pumping technique. The pump radiation is narrowband so most of the pump energy is used for creating gain rather than gas heating. The chief disadvantage of optical pumping is that it requires a coincidence of the pump laser frequency and an absorbing transition in the molecular gas being pumped. This has not been a severe drawback, however, as witnessed by the hundreds of emission lines produced by optical pumping of tens of molecules [5]. Another source of mid-infrared radiation is
the tunable-diode-laser, but its use is generally restricted to high-precision spectroscopy because of its limited output power. Mid-infrared laser applications such as laser photochemistry, laser isotope separation and atmospheric monitoring require the high powers available by optical pumping with high-power lasers.

The pulsed NH$_3$ laser pumped by a TE CO$_2$ laser was discovered in 1976 [6]. That same year there were three other reports of mid-infrared NH$_3$ lasers pumped by single CO$_2$ laser beams [7-9], and one report of two CO$_2$ lasers used simultaneously to pump NH$_3$ [10]. Those reports included recognition of the two basic mechanisms of NH$_3$ laser operation, single-photon inversion gain [9] and two-photon Raman gain [7,8]. The addition of a non-absorbing buffer gas to enhance the laser performance and create multi-line operation from 10 to 14 μm was also demonstrated at that time [9]. Since 1976, the pulsed NH$_3$ laser has become one of the most powerful and efficient sources in the mid-infrared. Peak pulse energies of 1.5 J [11] and average powers of 20 W [12] have been produced with efficiencies comparable to that of the CO$_2$ laser. There have been many other reports of experimental improvements, but very few reports have addressed the need for developing a quantitative model both to explain the operation of mid-infrared NH$_3$ lasers and to develop the necessary tool for optimizing these devices [13-15]. The complexity of the laser dynamics, especially the presence of two gain mechanisms, may well account for the lack of comparison between theory and experiment.

The purpose of this thesis is to elucidate the principles of laser-pumped pulsed mid-infrared NH$_3$ laser operation by a combination of theory and experiment. Two models of the gain dynamics of NH$_3$ lasers are
developed and the predictions of these models are compared with the results of an extensive series of experiments. The first model employs a density-matrix approach to describe the two-photon Raman gain mechanism. This model is discussed in Chapter 4 and used in the first detailed comparison between theory and experiment for the Raman gain process in mid-infrared lasers. Single-photon inversion gain is modelled by a simple rate-equation theory based on the assumption of rapid rotational thermalization, and on the distinction between ortho-NH$_3$ and para-NH$_3$, the significance of which was not considered by previous researchers. The full implications of the rate-equation model are explored in Chapters 5 through 8 and the model is compared with experiments using several pumping transitions. The experiment described in Chapter 8 illustrates the utility of the concept of rotational thermalization in the design and demonstration of a line-tunable hot-band NH$_3$ laser produced by two-step optical pumping. A more detailed overview of the thesis is provided in the following paragraphs which summarize the contents of all of the chapters.

Chapter 2 is intended to provide the background information necessary for understanding the discussions in the rest of the thesis. It begins with a review of the spectroscopy of NH$_3$ relevant to optical pumping. Transition selection rules are presented and applied to a discussion of the vibrational bands accessible to CO$_2$ laser pumping. The optical-pumping process is described in detail for a typical pump transition to distinguish clearly the origins of the two gain processes. This chapter concludes with an examination of the actual pumping transitions used in the experiments and gives reasons for their choice.
The experimental apparatus and techniques used for most of the experiments are described in Chapter 3. The first part of the chapter contains details of the CO₂ pump laser and discusses how the laser construction influences the pump pulse characteristics. The second part is mainly a discussion of a typical NH₃ oscillator-amplifier configuration used for gain measurements. Precise details of the set-up for each experiment are left to the pertinent chapters. The measurement of small-signal gain coefficients is the basis of most of the experiments, and the techniques employed are fully described.

An extensive discussion of Raman gain and related coherent effects in pulsed NH₃ lasers is provided in Chapter 4. A review is given of the solution to the density matrix equations as formulated by Heppner et al. [16]. The solution is applied first to a case where Raman gain is the dominant process affecting the gain dynamics of the NH₃ laser. The good agreement between the experimental results and the model predictions for this case provides a firm basis for examining a more complex case where population inversion and Raman processes are both present. For a wide range of pumping conditions it is shown that coherent effects cannot be ignored for the laser transitions coupled directly to the pumped transition. Furthermore, the density matrix model predicts and explains the experimental measurements of gain coefficients and ac Stark shifts on all the directly-coupled transitions for well-characterized pumping conditions.

A proper treatment of inversion gain requires a rate-equation theory to handle the transfer of vibrational populations adequately. A rate-equation model based on a few simplifying assumptions is developed
fully in the first part of Chapter 5. The main assumptions are that the rotational populations are always thermalized at the ambient gas temperature except for the levels of the pumped transition, and that there is no interconversion between ortho-NH₃ and para-NH₃. The predictions of the model are investigated theoretically and one parameter, the ratio of the upper and lower vibrational populations (N₁/N₀), is used to characterize the distribution of small-signal gain coefficients. The model is validated by gain measurements performed with two pumping transitions. The two transitions were selected to compare pumping at different points in the rotational population distribution, and to compare pumping ortho-NH₃ and para-NH₃. The last section of Chapter 5 examines the effect of different buffer gases on NH₃ laser operation and suggests a figure of merit, based on molecular relaxation rates, for predicting buffer gas effectiveness.

Chapter 6 provides a more detailed examination of inversion gain dynamics in NH₃ lasers. One pumping transition is employed in extensive measurements of small-signal gain coefficients as a function of gas mixture, pump intensity, and laser transition. The difference in performance between a-type and s-type transitions noted by previous researchers [9,17] is finally resolved by these measurements, and the results are confirmed by comparison with calculations of the rate-equation model. In general, very good agreement is obtained between the model predictions and the experimental results. The results described in Chapter 6 can also be directly applied to optimize NH₃ lasers operating at total gas pressures up to ~100 Torr, which is the optimum pressure range for pulsed line-tunable operation.
To obtain greater tunability or short pulses from NH₃ lasers, the operating gas pressure must be increased. Chapter 7 examines the consequences of working at pressures of several hundred Torr. At these high pressures the gain lineshapes of adjacent transitions begin to overlap, but there are also overlapping absorptions due to transitions in other vibrational bands. It is shown that increases in pressure result in significant gas heating which tends to reduce the gain coefficients. Calculations of the rate-equation model are used to evaluate the maximum operating pressures that are possible in accord with the physical limitations of optical pumping of NH₃ (i.e., optical breakdown of gases and optical materials at high pump intensities).

Chapter 8 investigates another model prediction—that an NH₃ laser can be made to lase on the hot-band transitions in buffered gas mixtures. The basis for this prediction is that the rotational levels are thermalized throughout the optical pumping pulse. Thus, a two-step pumping process can invert the population on the hot-bands by using the best available pumping transition for each step. First, the small-signal absorption of the second pump is examined to confirm the thermalization process. Then, two optical-pumping schemes are demonstrated which culminate in fine-tunable operation on the hot-bands producing wavelengths from 16 to 21 μm. Preliminary measurements of energy extraction and efficiency are reported with suggestions for improving the laser operation.

Chapter 9 summarizes the conclusions of this thesis and includes recommendations for future investigations.
CHAPTER 2
OPTICAL PUMPING OF NH$_3$

2.1 Introduction

This chapter reviews the fundamentals of NH$_3$ spectroscopy and the properties of NH$_3$ relevant to optical pumping of rotational-vibrational transitions with a CO$_2$ laser. The information presented here is intended to provide a basis for understanding the discussions in subsequent chapters. The first two sections examine the vibrational and rotational energy level structure of NH$_3$ and present the selection rules for transitions. These sections are followed by a general discussion of the optical pumping process and of criteria for choosing transitions to optimize gain coefficients. Finally, the pump transitions employed in the experiments are presented along with the reasons for their choice.

2.2 NH$_3$ Molecular Structure

NH$_3$ is an oblate symmetric-top molecule with three-fold rotational symmetry (point group C$_{3v}$) [18]. There are four normal modes of vibration. Modes $v_1$ and $v_2$ are totally symmetric vibrations (species A$_1$), and modes $v_3$ and $v_4$ are degenerate vibrations (species E). The fundamental frequencies of these modes are $v_1 = 3337$ cm$^{-1}$, $v_2 = 950$ cm$^{-1}$, $v_3 = 3443$ cm$^{-1}$ and $v_4 = 1627$ cm$^{-1}$. Thus, only the $v_2$ mode is directly accessible in the 9-11 μm emission region of the CO$_2$ laser. Hence, NH$_3$ lasers optically pumped by CO$_2$ lasers have only operated on transitions within the $v_2$ mode of the ground electronic state. All of the modes are doubled by the
inversion of the molecule, which corresponds to the passing of the N atom through the plane of the H atoms. The inversion splitting is largest in the $v_2$ mode, and the $v_2$ vibrational levels are strongly anharmonic. The parity of the lower inversion level is symmetric (s) and that of the upper level is anti-symmetric (a). Vibrational-infrared transitions can only occur between levels of opposite parity. Thus, there are only four transition bands of interest here: two fundamentals with frequencies $v_2 s = 968$ cm$^{-1}$ and $v_2 a = 932$ cm$^{-1}$, and two hot bands ($2v_2 - v_2$) $2v_2 s = 950$ cm$^{-1}$ and $2v_2 a = 629$ cm$^{-1}$. In each case the parity label is associated with the lower vibrational level of the band. Most of the experiments described in this thesis concern the $v_2$ fundamental transitions, simply termed $v_2$ from now on. In Chapter 7 and 8 the two hot bands, called $2v_2$ from now on, are discussed.

The strength of a vibrational transition (i.e., gain and absorption coefficients) is proportional to the square of the vibrational transition dipole moment. The $v_2$ transition dipole moments in NH$_3$ are relatively large: 0.24 D [19] for the fundamental bands, 0.29 D for the $2v_2 s$ band [20, 21] and 0.40 D for the $2v_2 a$ band (compare with 0.037 D for the 10-um regular CO$_2$ bands [22]). The fact that NH$_3$ has a permanent dipole moment of 1.47 D along its axis in the ground state, and that the $v_2$ vibration is parallel to the axis, contributes to the size of the $v_2$ transition dipole moments. Thus, very high gain coefficients are possible on the mid-infrared transitions in NH$_3$.

---

*Not to be confused with population inversion which produces inversion gain. The context should make the meaning clear.

*Calculated from absorption measurements with a tunable-diode-laser.
2.3 Rotational Levels and Transition Rules

Each vibrational state consists of a set of rotational levels with energies specified by rotational constants. In NH$_3$, the principal rotational constants, B$_V$, and C$_V$, are inversely related to the moments of inertia perpendicular and parallel to the molecular axis respectively (the superscript $V$ denotes that B and C are functions of the vibrational state). The rotational energies, E, are given by [23].

$$E(J,K) = B_V J(J+1) + (C_V - B_V) K^2 - D_{JV} J^2 (J+1)^2$$ \[2.1\]

$$-D_{JK} J(J+1) K^2 + B_K K^4 + \ldots$$

where $K = |k|$ and k is the projection of the total angular momentum quantum number J on the molecular axis. Thus k takes on integral values from -J to J, and E(J,K) would be doubly-degenerate in K except that the vibrational inversion doubling removes that degeneracy. The presence of D$_{JV} J^2 (J+1)^2$ and higher order terms in Eq. 2.1 is a result of centrifugal and Coriolis effects in the non-rigid NH$_3$ molecule. These distortion terms are small with respect to the first two terms.

The populations of the rotational levels are described by a Boltzmann distribution. Thus the population density n$_{JK}$ at temperature T is given by [24]

$$n_{JK} = N f_V g_J g_K \left( \frac{B^2 C}{\pi} \frac{hc}{k_B T} \right)^{3/2} \exp\left[-E(J,K) hc / k_B T \right]$$ \[2.2\]

where N is the total population density, $f_V$ is the fractional population of the vibrational state (including inversion), $g_J$ and $g_K$ are statistical weights, and the other symbols take their standard meaning. Equation 2.2 was derived assuming that B$_V$ and C$_V$ are much smaller than $k_B T / hc$, \ldots
which is generally the case for NH$_3$. The factor $g_J = 2J+1$ accounts for the different orientations of J. As the spin of the identical hydrogen nuclei is 1/2, Fermi statistics apply to $g_K$. The rotational levels with $K = 3n$ (species A, ortho-NH$_3$) have twice the statistical weight of the levels with $K = 3n \pm 1$ (species E, para-NH$_3$). In addition, only half of the levels with $K=0$ are present depending on the inversion parity and on J: symmetric and J odd are present, as are antisymmetric and J even. For the allowed levels $g_K = 3$ for $K = 3n$ and $g_K = 3/2$ for $K = 3n \pm 1$.

Radiative transitions in the $\nu_2$ mode follow dipole-like selection rules:

$\Delta J($upper-lower$) = -1, 0, +1$;  \hspace{1cm} \Delta K = 0

A$\leftrightarrow$s, a$\leftrightarrow$a, s$\leftrightarrow$s

A$\leftrightarrow$A, E$\leftrightarrow$E, A$\leftrightarrow$E

where $\leftrightarrow$ means "allowed", and $\not\leftrightarrow$ means "not-allowed". Collision-induced transitions in pure NH$_3$ and in buffered mixtures relax these rules, in particular $\Delta k = 3n$ is allowed. The only rule which is strictly followed in all transitions is that ortho-NH$_3$ does not convert to para-NH$_3$ (A$\leftrightarrow$E)* [25-27] at least on the microsecond time-scale of the experiments described in later chapters. This rule plays an important part in the understanding of inversion gain dynamics in the NH$_3$ laser (see Chapters 5 and 6). The rotational-vibrational infrared transitions are denoted

*The overall symmetry of the levels is determined by the rotational symmetry since the $\nu_2$ vibrational mode is totally symmetric.
by the quantum numbers and parity of the lower level and by the branch
letter P (ΔJ = -1), Q (ΔJ = 0), or R (ΔJ = +1). The three branches
exist in all the bands. Thus a transition between the two levels
Gs(5,0) and ν2a(6,0) is labelled sR(5,0). The 2ν2 transitions are
distinguished by the prefix 2, such as 2sR(4,3).

2.4 Optical Pumping and the Effect of Pump Offset

The operation of pulsed NH3 lasers is complicated by the presence
of two gain mechanisms: single-photon inversion gain and two-photon
Raman gain. Usually one process or the other dominates the gain dynamics,
depending on the pumping conditions. A typical optical-pumping scheme
is shown in Fig. 2.1 to illustrate the essential features of the two
gain mechanisms and the conditions under which they appear. Pumping
occurs between rotational levels 2 and 0 with a pump laser whose
frequency differs from the molecular transition frequency ω2 by an
offset δω ≪ ω2. For sufficiently high pump powers gain is created on
the transition between levels 0 and 1. The frequency-dependent gain
coefficient g(ω) can be expressed

\[ g(ω) = σ_{01} [S_1(n_0 - n_1) + S_R(n_2 - n_1)] \]  \hspace{1cm} (2.3)

where σ_{01} is the absorption cross-section at frequency ω, S_1 and S_R
are lineshape factors (positive functions of δω and the transition
linewidths) for the inversion and Raman emissions respectively, and
n_0, n_1 and n_2 are the level populations. Thus, the first term cor-
responds to population inversion gain, and the second term corresponds to
Raman gain which is discussed next.
Fig. 2.1: Diagram of energy levels and radiative transitions for a typical optical-pumping scheme.
Raman gain is the dominant process under conditions of negligible population transfer from level 2 to level 0. This gain mechanism usually dominates at low pumping powers in pure gases at low pressures. Raman gain is a coherent process simultaneously involving two radiation fields and three molecular levels. The net result of the Raman process is the conversion of a pump photon at frequency $\omega_2 - \delta\omega$ to a photon at frequency $\omega_1 - \delta\omega$, and the transfer of a molecule directly from level 2 to level 1. Thus, the Raman gain coefficient, $g_R$, peaks at a frequency $\omega_1 - \delta\omega$, and will be positive as long as $n_2$ exceeds $n_1$. The difference $(n_2 - n_1)$ increases with increasing energy separation of levels 1 and 2 because of the Boltzmann distribution. The largest separation is obtained by pumping in the R-branch and lasing in the P-branch, hence maximizing the Raman gain coefficient. In general, $S_R$ is inversely proportional to the square of the pump offset, hence $g_R$ is maximized by minimizing the pump offset. Conditions of negligible population transfer occur in cases where the pump offset exceeds both the linewidth of the pump transition and the Rabi frequency ($\mu E/h$ where $\mu$ is the transition dipole moment) associated with the pump field, $E$. These conditions are dramatically illustrated in Fig. 2.2. The figure shows a scan of probe beam transmission as a function of frequency for two transitions pumped at different offsets by the same pump field. Note that there remains a strong absorption at the line center of both transitions, and that the Raman gain is peaked at frequencies offset from the line centers with the higher gain obtained at the smaller offset. The scan in Fig. 2.2 was obtained under cw pumping conditions and relatively small pump offsets. In order to examine the Raman gain processes independently of
Fig. 2.2: Tunable-diode-laser scan of the sP(7,0) and sP(7,1) transitions in the presence of CO$_2$ radiation. The two sharp spikes offset from the line center absorptions are the Raman transitions associated with off-resonant pumping of the sP(7,0) and sP(7,1) lines. The pump and TDL beams are copropagating in a 60 cm long waveguide. Pump intensity is $\sim$1 kW/cm$^2$ at an NH$_3$ pressure of $\sim$0.8 Torr. (From Ref. 28).
confounding effects in pulsed lasers, much larger pump offsets are required to compensate for the generally higher pump intensities. Hence, the 9P(34) pump is used to investigate Raman gain in isolation from all other processes for pulsed conditions. Table 2.1 lists the five CO₂ pump laser frequencies used in the experiments, and their corresponding offsets from the NH₃ transitions.

Let us return now to Eq. 2.3 to examine the conditions required for inversion gain. The inversion gain coefficient will be positive if \( n_0 \) exceeds \( n_1 \) (i.e., population inversion of the normal distribution). This requires a significant transfer of population from level 2 to level 0. Gain due to population inversion is regarded as a single-photon process because the absorption of a pump photon by a molecule is uncorrelated to the subsequent emission of an NH₃ laser photon. Thus the inversion gain coefficient peaks at frequency \( \omega_1 \), the line center of the molecular transition. The pump absorption coefficient directly affects the transfer of population and has an inverse square dependence on the pump offset. Thus population transfer can be increased either by increasing the pump transition linewidth (increase the gas pressure) or by reducing the pump offset. The effect of the pump offset can also be reduced by increasing the pump intensity which increases the effective linewidth of the pump transition by power broadening. In general, appreciable population transfer occurs in buffered mixtures at high pump intensities. The maximum population inversion occurs when the pump absorption is saturated so that \( n_0 \) and \( n_2 \) are equal (neglecting degeneracies). If rotational relaxation is sufficiently rapid for \( n_1 \) and \( n_2 \) to maintain a Boltzmann distribution then the inversion gain
**TABLE 2.1**

NH₃ transitions optically pumped by CO₂ lasers in this work.

<table>
<thead>
<tr>
<th>NH₃ Transition</th>
<th>NH₃ Wavelength [µm]</th>
<th>CO₂ Transition</th>
<th>Pump Offset (ν₉₃ - ν₉₄₀) [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>aR(1,1)</td>
<td>10.29</td>
<td>10R(14)</td>
<td>-1446ᵇ</td>
</tr>
<tr>
<td>aR(4,2)</td>
<td>9.67</td>
<td>9P(34)</td>
<td>-5164ᶜ</td>
</tr>
<tr>
<td>sR(5,0)</td>
<td>9.22</td>
<td>9R(30)</td>
<td>-190ᵈ</td>
</tr>
<tr>
<td>aR(6,0)</td>
<td>9.29</td>
<td>9R(16)</td>
<td>1355ᵇ</td>
</tr>
<tr>
<td>2sR(4,3)</td>
<td>9.59</td>
<td>9P(24)</td>
<td>-475ᶜ</td>
</tr>
</tbody>
</table>

ᵃ All transitions are in the regular $^{12}$C₁₆O₂ bands.
ᵇ Sattler et al. [29].
ᶜ Sattler and Worchesky [30].
ᵈ Rolland et al. [31].
coefficient will be positive if \( n_1 \) is initially less than half of \( n_2 \). This condition is most likely to occur for pumping in the R-branch and lasing in the P-branch of light molecules (large \( b^V \)) such as \( \text{NH}_3 \). Thus, the optimum choice of pump and emission transition branches is the same for both Raman and inversion gain.

One important difference between the two gain processes lies in the distribution of emission transitions. As the Raman process is a coherent interaction, Raman gain only appears on transitions which have one level in common with the pump transition. On the other hand, inversion gain can appear on many other transitions due to the collisional thermalization of the rotational population distribution, as shown in the upper part of Fig. 2.3. The lower portion of Fig. 2.3 illustrates the relative absorption strength for all the \( \nu_2 \) transitions between 11 and 13 \( \mu \text{m} \) for a dilute concentration of \( \text{NH}_3 \) in \( \text{N}_2 \) (see Appendix A for a sample calculation). This spectrum also represents the relative gain available on these transitions for a suitably high population inversion.

The \( 9\text{R}(5,0) \) transition pumped by \( 9\text{R}(30) \) is used for a detailed examination of inversion gain in buffered gas mixtures under almost resonant pumping conditions so that the pump absorption is maximized. For these conditions, population transfer dominates the laser dynamics and coherent processes are obscured. The \( 9\text{R}(16) \) pump is used to investigate an intermediate regime of pumping conditions where both the inversion gain and Raman gain processes can be clearly identified. In this regime the Rabi frequency of the pump is comparable to the pump offset, and both of these frequencies exceed the linewidth of the pump transition. These conditions are easily obtained in pure \( \text{NH}_3 \) and buffered mixtures at high
Fig. 2.3: Upper: A partial energy-level diagram of NH$_3$ showing typical emissions available in the $v_2$ mode by pumping aR(6,0). The curved arrows illustrate the initial population transfer within the vibrational levels.

Lower: Absorption spectrum of $v_2$ transitions between 11 and 13 $\mu$m. The solid lines represent transitions in ortho-NH$_3$ ($K=0,3,6,...$) and the dashed lines represent transitions in para-NH$_3$ ($K=1,2,4,5,...$).
pump intensities with the 9R(16) pump. The gain dynamics of the intermediate regime involve population transfer, Raman effects and ac Stark shifts.

The other two pump transitions listed in Table 2.1 are both used in further studies of inversion gain. The 10R(14) pump provides conditions suitable for testing the effectiveness of different buffer gases for enhancing inversion gain. It is also used in comparison with the 9R(16) pump to test the concept of rotational thermalization and to examine the distinction between ortho-NH₃ and para-NH₃. The final pump frequency, 9P(24), is used to create inversion gain on the 2ν₂ transitions by a two-step pumping process which also employs the 9R(30) pump. This pumping technique relies entirely on rotational thermalization, and thus it represents an important demonstration of that concept.

2.5 Summary

The spectroscopy and properties of NH₃ relevant to rotational vibrational transitions in the ν₂ mode have been presented. This information was applied to a simple view of the optical pumping process to examine the optimization of the Raman and inversion gain coefficients. In particular, the effect of the pump offset was discussed with reference to the pump transitions actually used in the experiments.
CHAPTER 3
EXPERIMENTAL APPARATUS AND TECHNIQUE

3.1 Introduction

In this chapter the experimental apparatus and techniques common to all the experiments are discussed. The basic experimental configuration consists of an \( \text{NH}_3 \) oscillator and amplifier pumped by a single \( \text{CO}_2 \) laser. A physical description of the apparatus is given, emphasizing the aspects which simplify the experimental measurements and subsequent analysis. The general techniques of \( \text{NH}_3 \) laser operation and gain measurements are described with reference to a typical experimental set-up. Exact details of equipment and conditions for each of the experiments are described later in the pertinent chapters.

3.2 The \( \text{CO}_2 \) Pump Laser

The pump source is a pulsed hybrid \( \text{CO}_2 \) laser constructed at McMaster and consists of two electric discharge sections, one at high pressure and the other at low pressure, placed end-to-end in an optical cavity 275 cm long. The high-pressure section is a transversely-excited-atmospheric (TEA) discharge* with an excitation volume of \( 110 \times 6 \times 2.5 \) cm\(^3\) formed by two solid aluminum electrodes (from Tachisto Inc.).

*The design is a scaled-down version of a TEA \( \text{CO}_2 \) laser in use at the Laser and Plasma Physics Section, Division of Physics, National Research Council of Canada, in Ottawa.
mounted in a sealed acrylic box. The main electrical circuit, illustrated in Fig. 3.1, employs two low-inductance 0.1 µF capacitors in parallel charged to 37 kV and discharged across the electrodes by a triggered spark gap. About 3 µs before the main circuit is fired the CO₂ laser gas mixture (7% CO₂: 5% N₂: 88% He, flowed at ~4 l/min) is preionized by the ultraviolet emission of a sliding spark array mounted on two glass rods. The preionization rods run the length of the main electrodes, and are centrally positioned above and below the discharge volume. The electrical circuit for the preionization rods is similar to the main circuit and employs a single 0.1 µF capacitor charged to 50 kV. The ends of the TEA section are sealed by NaCl windows mounted at the Brewster angle (≈56°). The low-pressure section is a 72 cm long glass tube of 50 mm id with NaCl Brewster-angle windows glued on the ends. The gas mixture is the same as for the TEA section and flows slowly at ~10 Torr. A longitudinal discharge is formed by two electrodes mounted at each end in the side arms, and supplied by a simple pulse-transformer circuit [32]. A delay generator triggers the low-pressure discharge first, and triggers the TEA section ~300 µs later. The low-pressure discharge narrows the CO₂ laser gain bandwidth from ~1 GHz to ~50 MHz, so that at most two longitudinal modes can oscillate in the cavity.

The optical cavity is formed by an original diffraction grating (135 l/mm, blazed for 10.6 µm), and a 25 m-radius of curvature partially-transmitting Ge mirror (35% transmission at 10 µm). The mirror is mounted on a translation stage at a slight angle to the transverse axis of the cavity to provide fine cavity-length tuning with 0.5 µm resolution. This resolution is sufficient to provide single longitudinal mode operation of
Fig. 3.1: Schematic diagram of the main discharge circuit for the TEA CO$_2$ laser.
the laser within 20 MHz of the line center of the CO\textsubscript{2} transition. Apertures in the cavity at each end confine lasing to a single transverse mode (TEM\textsubscript{00}). Thus the output pulse of the CO\textsubscript{2} laser has a spatially and temporally smooth profile which is well-characterized, and is at a known offset frequency from the absorbing transition in NH\textsubscript{3}. Peak pump energies of 1 J are available on the strongest lines in microsecond-long pulses.

In a typical experimental set-up for gain measurements the CO\textsubscript{2} laser is used to simultaneously pump an NH\textsubscript{3} oscillator and amplifier, as shown in Fig. 3.2. The CO\textsubscript{2} output beam is split into two approximately equal parts: one part is used to pump the NH\textsubscript{3} oscillator and the other pumps the NH\textsubscript{3} amplifier. A small fraction of one CO\textsubscript{2} beam is reflected from a NaCl flat onto a Ge:Au or photon-drag detector to monitor the pump beam and to check for single-mode operation. The pump repetition rate is \(\approx 15\) pulses per minute. The precise pulse shape varies with the CO\textsubscript{2} transition but is generally a gain-switched spike followed by a long tail. The 9R(16) and 10R(14) pulse shapes are almost triangular (\(\approx 1.5\) \(\mu\)s full width at half-maximum, FWHM) as shown in Fig. 3.3(a), whereas the other CO\textsubscript{2} transitions listed in Table 2.1 produce an initial spike of \(\approx 250\) ns FWHM having a peak intensity about 3 times that in the tail.

3.3 The NH\textsubscript{3} Oscillator and Amplifier

The gas cells used in the NH\textsubscript{3} oscillators and amplifiers are simple glass tubes of various lengths and are all 22 mm id with gas flow connections at both ends. Windows of NaCl are either glued directly on
Fig. 3.2: Schematic diagram of the experimental apparatus for gain measurements of NH$_3$. 
Fig. 3.3: Oscilloscope traces of typical pump and probe signals.

Electrical noise is present at the beginning of each trace.

(a) CO$_2$ laser pump pulse, 9R(16) transition.
(b) Lower trace is an unamplified NH$_3$ sP(7,0) signal.

Upper trace is the amplified signal.
the ends or attached to demountable fittings, and are usually set at the Brewster angle. The NH$_3$ gas is anhydrous grade from Matheson used without further purification. Initially, mixtures of NH$_3$ and various buffer gases were made by flowing the gases through calibrated flowmeters. Later, a 5 L flask was used to pre-mix the gases thereby allowing more accurate mixing, especially at low NH$_3$ concentrations. The gas cells are filled to the required pressure and then used for several shots before flushing and refilling. The difficulty with sealed-off operation is that NH$_3$ is easily adsorbed on the cell walls, thus changing the NH$_3$ partial pressure.

In most of the experiments the NH$_3$ oscillator consists of a 33 cm cell in a 50 cm long optical cavity formed by a diffraction grating (100 l/mm, blazed for 10.6 μm) and a dielectric-coated output mirror. The CO$_2$ beam enters the NH$_3$ cavity either by the first-order reflection from the grating as illustrated in Fig. 3.2, or by transmission through the end mirror to pump the NH$_3$ cell collinearly with the cavity axis. The output mirror is mounted on a piezo-electric translator (PZT) to provide cavity-length tuning over at least two modes. The cavity mode spacing of ~300 MHz is sufficiently large to ensure single-longitudinal mode operation of the NH$_3$ laser under most conditions. Operation at the line center for inversion-gain transitions is obtained by detecting the transmission of the NH$_3$ radiation through an external cell containing NH$_3$ at pressures <1 Torr. By tuning the PZT, the laser can be set within 30 MHz of the center of the Doppler-broadened absorption feature, and then the cell is removed. Gain measurements are performed in a separate amplifier cell of length either 11, 33 or 110 cm, depending on the magnitude of the gain coefficients being measured. The probe beam from the NH$_3$ laser
is attenuated and combined with part of the CO$_2$ pump beam by a NaCl flat. Complete overlap of the two beams is assured by tightly focusing the probe beam in the cell while maintaining a larger diameter collimated pump. This also minimizes the variation in pump intensity in the region probed by the NH$_3$ beam. The output from the amplifier cell is directed through a 1/4-m monochromator onto a HgCdTe detector monitored by a digital storage oscilloscope. Absolute gain coefficients are evaluated from the ratio of the probe signal with the pump beam in the cell to the signal through the unpumped cell with no NH$_3$ present. The use of attenuating filters just before the HgCdTe detector increases the dynamic range of the signal detection without disturbing the rest of the apparatus. Typical probe pulses are up to 1.5 μs FWHM as shown in Fig. 3.3(b). The width of the pulses enables the measurement of gain as a function of time by recording the signal at several points in the pulse. A constant time reference is provided by the signal from the detector which monitors the CO$_2$ pump radiation before the amplifier cell.

### Summary

This chapter contains a detailed description of the experimental apparatus and techniques used for gain measurements in NH$_3$. The use of a single-mode pump laser minimizes complications in the optical pumping process and facilitates comparisons between theory and experiment. The oscillator-amplifier technique is the most direct method of gain measurement and allows the greatest range and control over the experimental conditions. This technique is used extensively in the experiments described in the next four chapters.
CHAPTER 4
RAMAN GAIN IN NH₃ LASERS

4.1 Introduction

As discussed in Chapter 2, the Raman process is a coherent interaction of two radiation fields with three molecular levels. Thus, Raman gain only appears on laser transitions which have one level in common with the pumped transition. A quantum-mechanical theory based on the density-matrix formalism is required to describe such a system and several theories have been developed [16,32-36]. However, detailed comparisons with experiment have been carried out only for far-infrared lasers operating on rotational transitions [16,37-40]. This chapter discusses experiments performed with two pumping transitions to examine the Raman process in mid-infrared pulsed NH₃ lasers for a wide range of pumping conditions. The results of these experiments are in good agreement with the predictions of a density-matrix model.

The next section reviews the density-matrix theory as applied to mid-infrared transitions in a three-level system. Section 4.3 discusses a series of experiments performed using the 9P(34) pump in which the Raman process completely dominates the NH₃ laser gain dynamics. Thus, Raman gain can be examined separately from all other confounding effects, such as ac Stark shifts and population transfer. At the smaller offset of the 9R(16) pump, these other effects become significant but the distinction between Raman and inversion gain is still clear. Section 4.4 discusses the experiments carried out with the 9R(16) pump in this
intermediate region. The experiments demonstrate that the two laser
transitions coupled directly to the pumped transition each emit two
frequencies, one due to Raman gain and the other due to population
inversion. A combined rate-equation and density-matrix model accounts
for the occurrence of gain at the two frequencies and also predicts the
observed ac Stark shifts.

4.2 Density-Matrix Theory

The density matrix is an ensemble-averaged approach to the
quantum-mechanical problem of determining the probability amplitudes of
energy level occupation. The basic problem is to solve the equation of
motion of the density matrix for the Hamiltonian governing the molecular
energy levels and the dipole-moment interaction with the radiation
fields. Relaxation rates are included phenomenologically. The density-
matrix solution used here was formulated by Heppner et al. [16] and is
a semi-classical model because the radiation fields are treated as
electro-magnetic waves. The density-matrix solution has been implemented
numerically and used to compare theory with experiment (a summary of
the equations and their solution is presented in Appendix B). The model
allows both fields to have arbitrary strengths, arbitrary offsets from
the pumped and emitting transitions. It includes Doppler and pressure
broadening, and sums over the M-degenerate states, assuming negligible
M-relaxation. The solution is time-independent, and as such is most

* Model neglecting M-relaxation have been used successfully to
explain gain spectra in NH$_3$ [39,40], but this assumption may not be
entirely reasonable in view of the measurements of Leite et al. [41].
suitable for the analysis of cw laser systems. However, the model can
be successfully applied to pulsed systems provided that the rate of change
of the radiation field strengths is slow relative to the population trans-
fer rates [34]; a reasonable approximation in the present experiments.

The input parameters for the model consist of spectroscopic
constants (frequencies, dipole moments and offsets), the equilibrium
populations of the three molecular levels, and two types of relaxation
rates, population decay and coherence decay. All the parameters, other
than the relaxation rates, are well known. If we number the levels from
highest to lowest energy as 0, 1 and 2 (as in Fig. 2.1), then the population
decay rates are $\gamma_0, \gamma_1$ and $\gamma_2$. Assuming hard-sphere collisions such that
every collision causes a change in energy and phase then the coherence
decay rates $\gamma_{01}$ and $\gamma_{02}$ can be identified with the corresponding pressure-
broadened widths, and $\gamma_{ij} = (\gamma_i + \gamma_j)/2$. To obtain the individual $\gamma_i$
and $\gamma_{12}$ we set $\gamma_2 = 4\gamma_0$. The factor of four is based on rates published for
the aQ(8,7) transition [41-43] and is in qualitative agreement with other
studies which show that $\gamma$(ground state) > $\gamma$(excited state) in the $\nu_2$ mode
of NH$_3$ [44]. Variations in this ratio have been shown to have a minor
effect on the model predictions [28]. The collisional broadenings of the
transitions are taken from Taylor [45] (see Appendix C) and from our own
measurements of pressure-broadened absorption with both a cw CO$_2$ laser
and a tunable diode laser.

The initial populations for most calculations are the thermal
equilibrium values at room temperature. However, these populations can
be any set of values to which the levels would decay in the absence of
the radiation fields. Since the density-matrix calculation maintains
the sum of the populations at a constant value the three coupled levels are essentially isolated. At high pump intensities which induce significant population transfers it is inadequate to treat the three levels in isolation from the vibrational manifolds. A satisfactory solution is to use a rate-equation model (developed in Chapter 5) to predict the integrated pump absorption and hence the vibrational populations and rotational temperature at the required pump intensity. The rotational partition function can then be used to evaluate the level populations. The pump absorption predicted by a rate-equation model will correspond very closely to the coherent calculation provided that the probe signal intensity does not perturb the populations significantly [34], as is the case in our experiments.

4.3 Experiments Using the 9P(34) Pump

4.3.1 The aR(4,2) Laser System

The P(34) 9-um CO₂ line is used to pump the aR(4,2) transition in NH₃, and lasing takes place on the aP(6,2) transition at 12.26 μm, as illustrated in Fig. 4.1. Note that this is the first report of lasing on this particular pump-emission pair in NH₃. This pump transition was chosen for the large value of frequency offset between the CO₂ pump and the NH₃ absorption - the pump is 5.16 GHz off resonance [30]. At typical pump intensities of 1 MW/cm² the Rabi frequency is ~1.2 GHz while the pressure broadened linewidth in a few Torr NH₃ is ~100 MHz. Consequently, as the offset greatly exceeds both of these frequencies for all applicable experimental conditions, we are able to measure true Raman gain separately from all other confounding effects. Figure 4.1
Fig. 4.1: Partial energy level diagram of NH₃ showing the vibrational-rotational transitions relevant to 12.26 μm lasing, and NH₃ spectra in the region of the pump and emission lines. Both the pump and emission frequencies are offset by 5.16 GHz from the line center absorption. Note that the nearest interfering transitions are more than 10 GHz away.
RELATIVE LINECENTRE ABSORPTION

\[ \text{OUTPUT} \]

\[ \text{WAVELENGTH (cm}^{-1}\text{)} \]

\[ \text{ENERGY (10}\text{em}) \]

\[ \nu_2 \text{ MODE} \]

\[ \text{V=1} \]

\[ \text{GROUND STATE} \text{ V=0} \]

\[ \text{s(5,2)} \]

\[ \text{a(6,2)} \]

\[ \text{a(4,2)} \]

\[ \text{P(3,4)} \]

\[ \text{PUMP 9.67}\mu\text{m} \]

\[ \text{aR(4,2)} \]

\[ \text{aP(6,2)} \]

\[ \text{12.26}\mu\text{m} \]

\[ \text{OUTPUT} \]

\[ \text{814.5} \]

\[ \text{815.5} \]

\[ \text{816.5} \]
also illustrates a further advantage of the chosen transitions - there are no nearby lines in either the 9-μm or 12-μm region to cause interference [23].

A schematic diagram of the experimental apparatus is shown in Fig. 4.2. The single-mode CO₂ laser emits pulses with energies of ~0.5 J on the P(34) 9-μm line, with half the energy in the initial 250 ns FWHM pulse. The NH₃ laser cavity is formed by a dichroic mirror M₁ (reflectivity 99% at 12 μm, 25% at 9.67 μm) and a high-reflectivity mirror M₂ (~95% at 9 and 12 μm) mounted on the piezo-electric translator (PZT). The laser gain cell is 33 cm long and contains NH₃ at ~10 Torr. The 12.26 μm output pulses are delayed 80 to 100 ns from the onset of the CO₂ laser pulse and have a duration of ~200 ns FWHM. A series of dichroic and salt beamsplitters are used to combine approximately half the CO₂ pump pulse with a strongly attenuated 12.26 μm pulse in the 110 cm amplifier tube in either co- or counter-propagating directions. The 12.26 μm probe pulse and the CO₂ pump pulse are detected with a HgCdTe detector (risetime < 50 ns) and a photon drag detector (risetime < 2 ns) and displayed simultaneously on a dual-beam oscilloscope.

An initial experiment was carried out to determine the frequency of the 12-μm output, and confirm that emission was taking place via a Raman process. The 12-μm pulses were directed into a 1/2-mi monochromator, and by careful calibration we were able to determine that the emission frequency was not at line center of the aP(6,2) transition, but shifted 0.2 cm⁻¹ higher in frequency. The next step was to measure the lasing frequency more precisely in order to compare the 12-μm offset with the
Fig. 4.2: Schematic diagram of the experimental apparatus for measuring gain in optically pumped NH$_3$. 
well-known pump offset. To this end we measured the small signal absorption of the NH$_3$ pulses in an external absorption cell in which the NH$_3$ pressure was varied. Results are shown in Fig. 4.3, and compared with calculations based on Taylor's values of the aP(6,2) line strength and linewidth [45]. The offset frequency is varied to give a best fit between experiment and theory. The best-fit value of 5.14 ± 0.1 GHz is in excellent agreement with the known pump offset of 5.16 GHz. This measurement clearly demonstrates that lasing takes place by means of a Raman process.

4.3.2 Gain Measurements

In the next series of experiments we used the 12-μm pulses to probe the Raman gain in the 110 cm amplifier as a function of NH$_3$ pressure. For convenience, we chose to measure the small-signal gain coefficients at the time of peak 12-μm output. At this time the CO$_2$ pump intensity had fallen to ~0.5 MW/cm$^2$ (70% of its peak value), and had a pulse-to-pulse stability of ±5%. Gain measurements were made by comparing the probe peak intensity with and without the pump beam present. Hence, the experiment actually measures the increase in 12-μm transmission induced by the presence of the intense 9-μm field. We call this "differential gain" to distinguish it from the true gain which must also account for any absorption of the 12-μm beam by the unpumped NH$_3$ molecules (see Fig. 4.3). Each experimental point is the average of several measurements with an absolute accuracy of ±0.1% limited chiefly by the pulse-to-pulse stability of the 12-μm laser. Figure 4.4 displays the results of the differential gain measurements as a function
Fig. 4.3: Absorption coefficient of the 12.26 μm NH₃ laser as a function of the square of the NH₃ pressure in an external cell. The solid line is a fit to the experimental data using a lasing offset frequency of 5.14 GHz and Taylor's calculated values for line strength and linewidth [45].
12.26 μm NH₃ LASER

![Graph showing small signal absorption vs. \( P^2 \) (10² Torr²)](image)
Comparison between theory and experimental measurements of small-signal gain. The dashed and solid lines are the theoretical predictions calculated using a best fit value of pump intensity of 0.5 MW/cm² at the entrance to the amplifier. The drop in gain at high pressure is caused by pump absorption.
of NH$_3$ pressure for both co- and counter-propagating 9- and 12-$\mu$m beams. For all these measurements care was taken to ensure that the gain was probed at the optimum optical frequency. We tuned the probe laser output frequency using the PZT and made gain measurements over an interval of $\approx$150 MHz. This procedure has the added advantage that an approximate value for the gain linewidth can be determined.

In Fig. 4.4 we compare the experimental measurements with calculations based on a theoretical model of the laser system. Calculations were performed for the experimental case of parallel linear polarization of the 9-$\mu$m and 12-$\mu$m fields, and numerical results were obtained for differential gain as a function of NH$_3$ pressure and pump intensity. Table 4.1 lists the input parameters [23,41,45] used to calculate the gain. There are no free parameters in the model. The experimental parameter with the largest uncertainty is the 9-$\mu$m pump intensity. For the data shown in Fig. 4.4, the CO$_2$ pump beam was gently focused towards the far end of the amplifier tube to compensate partially for the 9-$\mu$m absorption. This absorption is particularly severe at higher pressures of NH$_3$; with 20 Torr NH$_3$ in the amplifier $\approx$70% of the CO$_2$ energy was absorbed. We made measurements of the pump absorption as a function of NH$_3$ pressure, and then used the average pump intensity along the length of the amplifier tube to compare theory to experiment. In comparing experiment and theory in Fig. 4.4, we used a pump intensity value of $\approx$0.5 MW/cm$^2$ which gave the best overall agreement with experiment.

The theoretical predictions are shown in Fig. 4.4 by dashed and solid lines. In general, there is excellent agreement between calculation and experiment. In all cases, the model predicts absorption at the
### TABLE 4.1

NH₃ molecular data for the density-matrix model.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency [cm⁻¹]</th>
<th>Vibrational Dipole Moment [D]</th>
</tr>
</thead>
<tbody>
<tr>
<td>aR(4,2)</td>
<td>1033.32</td>
<td>0.24</td>
</tr>
<tr>
<td>aP(6,2)</td>
<td>815.59</td>
<td>0.24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level</th>
<th>Fractional Population</th>
<th>Decay Rate [s⁻¹ Torr⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₂s(5,2)</td>
<td>1.10 × 10⁻⁴</td>
<td>γ₀ = 2.51 × 10⁷</td>
</tr>
<tr>
<td>Ga(6,2)</td>
<td>6.48 × 10⁻³</td>
<td>γ₁ = 1.57 × 10⁸</td>
</tr>
<tr>
<td>Ga(4,2)</td>
<td>1.28 × 10⁻²</td>
<td>γ₂ = 1.83 × 10⁸</td>
</tr>
</tbody>
</table>

*aγ₀ from Ref. 41; γ₁ and γ₂ from γ₀j = (γ₀ + j/2) with γ₀j from Ref. 45, and γ₀2 from absorption measured in this work.*
aP(6,2) line centre, and gain only at the Raman frequency which is offset by \( \pm 5.2 \) GHz. At high pressure the calculated Raman gain is the same for co- and counter-propagating beams. However, at low pressure the Raman peak gain is different in the two cases, as is the linewidth. For the co-propagating case the limiting linewidth is the difference in the 9-\( \mu \)m and 12-\( \mu \)m Doppler widths (\( \approx 20 \) MHz) while the counter-propagating beam produces a limiting linewidth equal to the sum of the two Doppler widths (\( \approx 70 \) MHz). By tuning the probe laser using the PZT, we were able to confirm that the Raman linewidth is substantially narrower for the co-propagating case relative to the counter-propagating case at low pressure. The narrower linewidth in the co-propagating case makes it difficult to tune the probe laser to the gain line center and probably accounts for the observed disagreement between experiment and theory at low pressure.

As mentioned above, the 9-\( \mu \)m intensity was varied in the calculation to give a best fit in Fig. 4.4. In a separate series of experiments we made careful measurements of gain under conditions where the 9-\( \mu \)m intensity was spatially uniform and so could be well characterized. On average, our experimental gain measurements were \( \sim 30\% \) lower than the model predictions. In view of the uncertainties in many of the parameters in Table 4.1, and the residual uncertainties in the pump intensity measurement, this constitutes good agreement.

4.3.3 Conclusions

The experiments with the 9P(34) pump represent the first quantitative comparison between theory and experiment for a mid-infrared optically-pumped Raman laser. The experimental conditions were chosen to
emphasize the Raman processes, and minimize the effects of ac Stark shifts, power broadening and population transfer. Theory and experiment are found to be in very good agreement over a wide range of experimental conditions. These results give us confidence that the theoretical model can be applied to characterize more complex laser systems having smaller pump offsets where the above effects become significant, as discussed in the next section.

4.4 Experiments Using the 9R(16) Pump

4.4.1 The aR(6,0) Laser System

The aR(6,0) system illustrated in Fig. 4.5 was selected to examine the effects of high pump intensity on Raman gain, and related coherent processes. As shown in Fig. 4.5 the frequency of the 9R(16) pump is 1.36 GHz below the NH₃ absorption line center [29]. Note that both the aP(8,0) and aP(6,0) transitions have one level in common with the pumped transition. First let us consider the three levels involving the pump transition and aP(8,0), which we call the directly pumped transition. At low pump intensities, the laser gain spectrum is characterized by a strong line center absorption and by Raman gain at a frequency offset from the emitting transition. At high pump intensities, where the Rabi frequency is comparable to the offset, there is significant population transfer which reduces the absorption at the line center of aP(8,0) and can even produce gain at line center. The intense pump field also induces an ac Stark shift which moves the Raman gain and the line center feature apart. Another three-level system is formed by the pump transition and aP(6,0). Theory predicts the appearance of coherent
Fig. 4.5: Partial energy-level diagram of NH$_3$ showing typical transitions relevant to pumping with the R(16) 9-μm CO$_2$ line. Transition (a) is the directly pumped Raman transition, (b) is a cascade inversion transition and (c) is the indirectly pumped Raman transition.
effects on this transition also. However, as will be discussed in
Section 4.4.3, the generation of emission on aP(6,0) first requires
significant population transfer and hence we term it the indirectly pumped
Raman transition. Population transfer is enhanced by the addition of a
buffer gas which increases the pump absorption.

4.4.2 Pure NH$_3$

The initial experiments of pumping with 9R(16) were carried out
in pure NH$_3$. The experimental configuration employed for all the 9R(16)
experiments is the one shown schematically in Fig. 3.2. Note once again
that the CO$_2$ pump laser operates in a single longitudinal and transverse
mode at a fixed frequency offset from aR(6,0). The majority of the
results obtained with 9R(16) and described in this chapter would not be
observed with a multi-mode pump pulse having a broad (~1 GHz) frequency
content. Over a wide range of pump intensities and gas pressures the
only transition that we have observed in pure NH$_3$ is Raman emission on
the aP(8,0) line. (Previous studies have reported up to three emitting
transitions from pure NH$_3$ pumped by 9R(16) [46,47].) Measurements of
gain coefficients for the aP(8,0) Raman emission were made with a peak
pump intensity of ~0.6 MW/cm$^2$ in both the oscillator and amplifier. We
have not made a detailed comparison with theory as this requires an
accurate knowledge of the level populations, the pump intensity, and the
probe frequency as a function of time. In addition, variations in the
pump intensity affect both the amplifier gain and the probe frequency
through the ac Stark effect. However, typical measured and estimated
gain coefficients were as high as 10 %cm\(^{-1}\) with values greater than 4 %cm\(^{-1}\) for pressures from 1 to 19 Torr. If we assume thermal populations initially and consider only the optimum frequency for the probe the model predicts a peak gain of 20 %cm\(^{-1}\) with values greater than 10 %cm\(^{-1}\) up to 20 Torr. This approximate agreement can be refined using an approach which permits more accurate specification of the input populations.

4.4.3 \(\text{NH}_3\) Buffered with \(\text{N}_2\)

A more careful study of the effects of high pump intensity is made possible by buffering the \(\text{NH}_3\) with an inert gas such as nitrogen. In this way many more lines are produced by the usual laser process of population inversion. These transitions are characterized by the emission of a single frequency component at line center. More interesting, though, are the two transitions \(aP(8,0)\) and \(aP(6,0)\) which each have one level in common with the pumped transition. They are distinguished by the emission of two distinct frequency components. One component is due to population inversion, the other is due to the Raman gain process. The two frequencies are identified by the differences in their absorption in an external cell of \(\text{NH}_3\) as shown in Fig. 4.6 for \(aP(6,0)\). Measuring the absorption while tuning the length of the \(\text{NH}_3\) laser cavity reveals that the two frequencies lie on opposite sides of line center. The higher frequency is the inversion component and lies about 200 MHz above line center. This offset is due to the ac Stark effect which is discussed later in more detail. The lower frequency for each transition is offset by approximately the pump offset, in agreement with the theoretical prediction for a Raman component.
Fig. 4.6: Emission on aP(6,0) contains both Raman and inversion frequency components simultaneously. The inversion component can be identified by stronger absorption in an external cell.

(a) The unattenuated aP(6,0) pulse.

(b) The aP(6,0) pulse after passing through a short cell containing pure NH$_3$. 
To understand the occurrence of aP(6,0) Raman gain, it is best to compare it to aP(8,0). For aP(8,0), the Raman process is directly due to the pump field transferring molecules between two levels in the ground vibrational state. The gain is proportional to the population difference between the lower pumped level and the lower laser level. Raman gain on aP(6,0) is proportional to the population difference between the upper laser level and the upper pumped level, i.e. levels s(5,0) and s(7,0), both in the excited vibrational state. At thermal equilibrium this difference is positive, but under intense pumping in pure NH₃ the difference is usually negative because the rotational relaxation rate is slow. In addition, there are generally insufficient molecules in the excited state to produce significant gain. However, by adding a buffer gas a large population is transferred to the upper vibrational state and the rotational relaxation rate can exceed the pumping rate. This process can thus be called an indirectly pumped Raman process because the population transfer to the ν₂ level must first be established by the pump before sufficient Raman gain can appear to produce lasing. Too much buffer gas reduces the peak gain by further broadening of the linewidth. Naturally, the indirectly pumped Raman gain is always accompanied by population inversion.

One measure of the magnitude of the gain is given by the inverse of the time delay, t_d, to lasing from the onset of the pump pulse since a higher gain implies a shorter time to threshold. Observations of t_d⁻¹ in an oscillator for the inversion and Raman components of the aP(8,0) and aP(6,0) transitions are shown in Fig. 4.7 as a function of NH₃ partial pressure in a mixture with N₂ at constant total pressure. The
Fig. 4.7: The inverse of the time delay, $t_d$, to lasing from the onset of the pump, as measured in a 12-μm oscillator, is a measure of the gain on the Raman and inversion components of aP(8,0) and aP(6,0). The values of $t_d^{-1}$ are shown as a function of NH$_3$ pressure in a mixture with N$_2$ at a constant total pressure of 80 Torr. The minimum $t_d$, 240 ns, is the same for each transition.
relative gain observations displayed in Fig. 4.7 were verified by direct
gain measurements in the amplifier for a mixture of 1 Torr NH₃ and 75
Torr N₂. At a time 0.7 μs after the peak of the pump pulse the gain on
the aP(6,0) inversion component was 0.2 %cm⁻¹ while the inversion gain
on aP(8,0) was 1.4 %cm⁻¹. At the same time the Raman gain on aP(6,0)
was slightly higher than that on aP(8,0), 0.4 %cm⁻¹ compared to 0.2
%cm⁻¹. By assuming initial level populations in accord with the
population transferred to the upper vibrational level the density-matrix
model can be used to calculate the gain on both transitions. The calcula-
tion confirms the relative value of the measured gain coefficients
and predicts absolute values of the same order. Clearly population
inversion is the dominant gain mechanism in the buffered gas mixture at
low NH₃ concentrations. However, the buffer gas also permits the
observation of an additional Raman line not obtained previously.

4.4.4 ac Stark Shifts

It was noted above that the inversion components of aP(8,0) and
aP(6,0) were not at line center but were offset to higher frequencies by
~200 MHz. Tuning the NH₃ laser cavity length could only move the
emission frequency to within 100 MHz of line center. The offset is
causd by an ac Stark shift in the NH₃ oscillator resulting from the
high pump intensity. The effect can be measured quantitatively in a
second NH₃ cell by noting the change in absorption of the NH₃ probe beam
in low pressure NH₃ induced by the presence of a pump beam. The
presence of the pump increases the absorption by as much as a factor of
4, which is consistent with a shift of the absorption profile towards
Fig. 4.8: The aP(8,0) and aP(6,0) inversion components are offset by 200 MHz from line center due to ac Stark shifts induced by the high pump intensity in the NH₃ laser. The offset can be measured by absorption in an external cell. (a) The unattenuated aP(8,0) inversion pulse. (b) Upper trace: The aP(8,0) inversion pulse after passing through 1.0 Torr of NH₃ in a 33 cm cell. Lower trace: Measurement repeated with a pump pulse of ~0.5 MW/cm² present in the 33 cm cell. Absorption coefficients are compared at the time indicated by the arrow. The presence of the pump induces additional absorption by the ac Stark effect. This shifts the absorption line towards the emission frequency. Electrical noise is present on the early portion of each trace.
Fig. 4.9: Log plot of absorption as a function of frequency in pure NH₃ for aP(8,0) and aP(6,0) calculated for three values of the pump intensity: (1) No pump, (2) 128 kW/cm², (3) 254 kW/cm². For each transition the experimental points, shown with appropriate error bars, were measured at a single frequency setting of the NH₃ laser.
the emission frequency. A typical observation is shown in Fig. 4.8 for the $aP(8,0)$ transition*. Thus experiment confirms the model prediction of an ac Stark effect that shifts the inversion emission to higher frequencies, away from the Raman frequency. Another prediction of the model is an increasing frequency shift with pump intensity which is almost linear for shifts up to 20% of the pump offset. The dependence on pump intensity was confirmed by measurements at two intensity values for both the $aP(8,0)$ and $aP(6,0)$ transitions. The model predictions and experimental measurements at a single probe frequency for each line are displayed in Fig. 4.9. The probe frequency in each case was determined from the signal attenuation in the unpumped gas. Satisfactory agreement with the density-matrix calculation is obtained for both transitions simultaneously with a single set of initial populations for each pump intensity. The initial populations in all of the relevant rotational levels were determined by a rate-equation calculation, as described in Section 4.2. All of the $M$ sub-levels are included in the calculation of the ac Stark shifts, but the shifted line-shapes do not appear distorted as the shifts are small and the absorption is dominated by the $M=0$ and 1 sub-levels.

4.5 Summary

This chapter examines the Raman process and related coherent effects for a wide range of pumping conditions obtained with two

*Experimental tests were carried out to ensure that the measured increase in absorption was not influenced by either beam deflection or thermal heating of the NH$_3$. 
separate pumping transitions. The results of the experimental measurements are in good agreement with the predictions of a density-matrix model. At high pumping intensities in buffered gas mixtures there is significant population transfer which creates inversion gain in addition to the Raman gain on the transitions directly coupled to the pumped transition. Population transfer and inversion gain is more easily discussed in terms of a rate-equation model, which is the subject of the next chapter.
CHAPTER 5
INVERSION GAIN IN NH₃LASERS

5.1 Introduction

Population inversion is the dominant gain mechanism in line-
tunable optically-pumped NH₃ lasers. The process requires appreciable
population transfer, which generally occurs in buffered gas mixtures at
high pump powers. In this chapter, a predictive model of the inversion
gain dynamics is developed which accounts for all the major experimental
features of 12-μm NH₃ lasers. The model is validated by detailed
comparisons with experiments, and can be used to predict scalability
and optimum operating conditions for a variety of optically-pumped mid-
infrared NH₃ lasers. The experiments involve measurements of gain
coefficients using two different pump transitions in mixtures of NH₃
with three separate buffer gases.

The two pump transitions studied in this chapter are the aR(6,0)
and aR(1,1) absorption lines. These transitions were selected to
compare pumping at high and low J, and to compare pumping ortho-NH₃ and
para-NH₃. Both transitions are well separated from any other absorption
lines in NH₃, and thus are easier to analyze than the more commonly
pumped sR(5,k) multiplet (see Chapter 6) [9,11,17,48]. We have measured
small-signal gain coefficients on several 12-μm transitions associated
with each pump transition over a wide range of gas mixture, pressure,
and pump intensity. These experiments enable us to recognize the
important operating parameters of the system, and hence to construct an
accurate rate-equation model based on a few simplifying assumptions. The chief assumption of the model is that the rotational populations are always thermalized; this assumption is shown to account for the observed gain distributions resulting from both transitions. In addition, we treat the two statistical forms of NH$_3$ separately, and allow no conversion from ortho- to para-NH$_3$ or vice-versa. This assumption is shown to be essential for any accurate modelling of pulsed NH$_3$ lasers. As far as we know, only one previous study has reported a measured gain coefficient for a pulsed NH$_3$ laser [49], and the theoretical analyses of the mid-infrared NH$_3$ laser have examined only single-line emission [13-15]. Previous researchers do not appear to distinguish between ortho- and para-NH$_3$, and the idea of rotational thermalization has only received passing mention [9,11,17]. Our research shows that these two concepts should be major features of models of NH$_3$ laser systems, and that a simple rate-equation model based on these assumptions gives good agreement between experiment and calculation over a wide range of experimental conditions.

Section 5.2 is a discussion of the two pump transitions used in the experiments. The following section develops the rate-equation model from first principles to final form. The predictions of the model and the method of calculating gain coefficients are examined in Section 5.4. The next three sections present and analyze the experimental results obtained from the two pump transitions. The final section is a brief summary of the chapter.
5.2 The aR(6,0) and aR(1,1) Laser Systems

The experiments on inversion gain in buffered mixtures of NH₃ were performed with two different pumping transitions. The first transition is aR(6,0), offset by 1.36 GHz from the 9-μm R(16) line of CO₂. The second transition is aR(1,1) which is offset by 1.45 GHz from the R(14) 10-μm CO₂ line [29]. These two systems are very similar in that they are both essentially isolated from interfering absorptions, and have similar pump pulse energy and power available at comparable pump offsets. These transitions were selected to compare the effect on the inversion gain of pumping the rotational Boltzmann distribution near its peak and at low J. Thus they serve to test the concept of rotational level thermalization. They also serve to examine the effect of pumping the two statistical forms of NH₃ as the aR(6,0) transition is in ortho-NH₃ and the aR(1,1) transition is in para-NH₃. More than 20 emission lines between 11.5 and 13.0 μm have been generated with these two systems from mixtures of ~1 Torr NH₃ and 50 to 300 Torr of N₂, Ar or He. This is the first known report of line-tunable emission over many transitions for both the aR(6,0) and aR(1,1) systems. Previous studies have reported at most three emitting transitions for the aR(6,0) system [46,47], and only one line when aR(1,1) is pumped [7,8,46]. The pumping scheme for aR(6,0) and some typical emission lines have been shown previously in Fig. 2.3. The experimental configuration employed for the two pump transitions is the one displayed in Fig. 3.2. The techniques applied to the experiments discussed in this chapter were described in Chapter 3, and further details are presented with the experimental results in later sections.
5.3 Rate-Equation Model

The dynamics of inversion gain are best described by a rate-equation theory which can treat the changes in vibrational and rotational populations. To model these processes in NH$_3$, we have made a few simplifying assumptions. We assume that all the population is contained in the ground, first and second excited levels of the $\nu_2$ mode. These vibrational levels are treated as harmonic with a fundamental frequency of 950 cm$^{-1}$, and the inversion doubling is neglected, as shown in Fig. 5.1. Since we are interested only in transitions between the ground and $1\nu_2$ levels we consider all energy transfer to higher vibrational levels as lumped into the $2\nu_2$ level. As long as the $2\nu_2$ population does not become comparable to the remaining population then this simplification is justified. Little is known about vibrational energy transfer in NH$_3$ except that there is rapid coupling between the lowest three levels in the $\nu_2$ mode, and less rapid coupling to higher levels and other modes [50]. This is probably due to the fact that only the $2\nu_2$ level is nearly harmonic with the $1\nu_2$ level. Neglecting the splitting due to inversion doubling is easily justified for the ground and $1\nu_2$ levels (split by 0.8 and 36 cm$^{-1}$ respectively) since the energy transfer between a and s states in these levels is fast relative to all other relaxation rates. The larger splitting of the $2\nu_2$ level, 285 cm$^{-1}$, is neglected on the basis of previous remarks, and to preserve the simplicity of the model.

An important assumption of the model is that the rotational populations of the ground and $1\nu_2$ levels are completely thermalized at the ambient gas temperature, with the exception of the two levels of the
Fig. 5.1: Schematic diagram of the energy levels and transitions included in the rate-equation model. The wavy lines indicate collisional transitions. The condition for complete saturation of the pump absorption, and hence for obtaining the maximum value of $N_1/N_0$, is contained in the inset.
Pump saturation

\[ r_0 = \left( \frac{g_0}{g_1} \right) r_1 \]

\[ \nu_2 = 950 \text{ cm}^{-1} \]
pumped transition which are treated separately. A thermalized rotational distribution is justified by the fast rate of rotational relaxation relative to the vibration-translation (V-T) relaxation rate and is confirmed by the good agreement with our experimental results. Finally, we assume that only one species, ortho or para, is pumped and so only that species is counted in the vibrational distribution of energy. The unpumped species only couples to the translational energy and thus contributes only to the pressure, heat capacity and molecular relaxation. We find that quantitative agreement with experiment can only be obtained by treating the ortho and para forms separately. Based on these assumptions we proceed with the development of the rate-equations. The notation and initial analysis follows that of Gordiets et al. in their review of vibrational gas kinetics [51].

The general form of the relaxation rate of vibrational level \( N_n \) within a single vibration mode is

\[
\frac{dN_n}{dt} = Z \sum_{m \neq n} \left[ P_{mn} N_m - P_{nm} N_n \right] + \sum_{i, j} \left[ Q_{ij} N_i N_j - Q_{ij} N_i N_n \right]
\]  

(5.1)

where \( Z \) is the gas kinetic collision rate, \( P_{mn} \) is the V-T transition probability from \( m \) to \( n \), \( Q_{mn} \) is the V-V transition probability from levels \( i \) and \( m \) to levels \( j \) and \( n \), and \( N \) is the total population density. If we only consider single-quantum transitions in an harmonic oscillator then
\[ P_{n+1,n} = (n+1)P_{1,0} \]

\[ P_{n,n+1} = \exp\left(-\frac{\hbar \nu}{k_B T}\right) P_{n+1,n} = x_\nu P_{n+1,n} \]

\[ Q^{m-1,m}_{n+1,n} = (n+1)mQ^{0,1}_{1,0} = (n+1)mQ \] (5.2)

\[ and \]

\[ Q^{m,m-1}_{n,n+1} = Q^{m-1,m}_{n+1,n} \]

where \( \nu \) is the harmonic frequency. For our case there are only three levels so that

\[ N = N_0 + N_1 + N_2 \] (5.3)

and only two rate equations are required

\[
\frac{dN_0}{dt} = ZP_{1,0} \left[ N_1 - x_\nu N_0 \right] + \frac{2ZQ}{N} \left[ N_1^2 - N_0 N_2 \right] \\
\equiv P_0 + Q_0
\]

\[
\frac{dN_1}{dt} = ZP_{1,0} \left[ 2N_2 - (1 + 2x_\nu)N_1 + x_\nu N_0 \right] - \frac{4ZQ}{N} \left[ N_1^2 - N_0 N_2 \right] \\
\equiv -P_1 - 2Q_0
\] (5.4)

Now consider the two rotational levels of the pumped transition: \( r_0 \) in \( N_0 \), and \( r_1 \) in \( N_1 \). Each level relaxes to its equilibrium value, \( r_i^e \), at the rate \( \tau_i \), and is affected directly by the pumping rate

\[
W_p \Delta r = (I_p / h \nu \sigma) [r_0 - r_1 (g_0 / g_1)]
\] (5.5)

where \( I_p \) is the pump intensity of the frequency \( \nu_p \), \( \sigma \) is the absorption cross-section and \( g_0, g_1 \) are the level degeneracies. As the populations \( r_0 \) and \( r_1 \) are counted in \( N_0 \) and \( N_1 \) we also must include the pumping term.
in the $N_i$ equations and a proportional value of vibrational relaxation in the $r_i$ equations. The complete rate-equations are therefore

\[
\begin{align*}
\frac{dN_0}{dt} &= P_0 + Q_0 - W_p \Delta r \\
\frac{dN_1}{dt} &= -P_1 - 2Q_0 + W_p \Delta r \\
\frac{dN}{dt} &= -\frac{[r_0 - r_0^e]}{\tau_0} - W_p \Delta r + \frac{r_0}{N_0} (P_0 + Q_0) \\
\frac{dr_1}{dt} &= -\frac{[r_1 - r_1^e]}{\tau_1} + W_p \Delta r - \frac{r_1}{N_1} (P_1 + 2Q_0)
\end{align*}
\] (5.6)

At thermal equilibrium, with no pump present $r_i^e = f_i N_i$. With the presence of the pump, because $r_i$ is included in $N_i$,

\[
r_i^e = f_i (N_i - r_i)/(1 - f_i) \tag{5.7}
\]

The structure of the model is illustrated in Fig. 5.1 with the pump and relaxation rates indicated. Actual values for the vibrational relaxation rates are obtained by the following identifications

\[
\tau_{VT}^{-1} = ZP_{1,0} \quad \text{and} \quad \tau_{VV}^{-1} = ZQ \tag{5.8}
\]

The values of $\tau_{VT}$ are given by Hovis and Moore [52] in the form

\[
\tau_{VT}^{-1} = k_{NH_3} p_{NH_3} + k_M p_M \tag{5.9}
\]

where the $k$'s are rates and the $p$'s are pressures of $NH_3$ and a buffer gas $M$. The $V-V$ rate is unknown but is no doubt faster than the $V-T$ rate in pure $NH_3$ and so was defined as
\[
\tau_{VV} = \frac{\tau}{(k_{\text{NH}_3}p_{\text{NH}_3})}, \quad 0 < \tau < 1
\] (5.10)

with \( \tau \) as a variable parameter. The rotational relaxation rates are defined by the pressure-broadened halfwidth at half maximum of the absorption line

\[
\Delta \nu = (\Delta \nu/p)_{\text{NH}_3}p_{\text{NH}_3} + (\Delta \nu/p)_M p_M
\]

\[= (1/4n)(1/\tau_0 + 1/\tau_1)\] (5.11)

with \( 1/\tau_1 = y/\tau_0 \). The rate in \( \nu_2 \) is known to be slower than in the ground state but the exact ratio is unknown. Therefore this ratio, \( y \), was also made a variable parameter but was usually maintained at 0.25, based on rates published for the aQ(8,7) transition [41-43]. Note that a buffer gas only affects \( \Delta \nu \) and \( \tau_{VT} \) besides increasing the heat capacity. This is a much simpler method of including the buffer gas than the two-component equations described by Gordiets et al. [51]. The effect of the buffer gas is discussed in more detail later.

To handle the problem of pumping only one species, ortho or para, very little modification is required. The sum of \( N_0 N_1 \), and \( N_2 \) is then only half of the total population and the initial values are defined appropriately. This completes the model. The equations were implemented using a predictor-corrector solution in a computer program (see Appendix D). The time development of the populations, from their initial values at thermal equilibrium, was investigated for a wide range of conditions using a typical pump pulse profile. For all the cases the rotational-translational temperature was maintained constant at the initial value of 300 K because the temperature changes, determined from
the absorbed energy and heat capacity, were always < 10 K.

5.4 Gain Calculation and Model Predictions

The evaluation of the gain spectrum is the final step in the modelling procedure. The gain spectrum is completely determined by the vibrational distribution under the assumption of rotational thermalization. Rather than use the values of \( N_0 \) and \( N_1 \) directly, we define two parameters which express the degree of vibrational inversion, \( N_1/N_0 \), and the fractional population in the ground and \( 1v_2 \) states, \( n_f = (N_0+N_1)/N \).

The value of \( N_1/N_0 \) specifies the gain distribution while \( n_f \) simply scales the gain magnitude. A separate program takes specific values of these two parameters together with the \( \text{NH}_3 \) partial pressure, the total pressure broadening due to a buffer gas, and the rotational temperature to evaluate the gain on the \( \text{NH}_3 \) transitions of interest (see Appendix A).

A perspective on the results of the model can be obtained by first evaluating the maximum vibrational inversion possible, and then investigating the gain spectrum as a function of \( N_1/N_0 \). The maximum value of \( N_1/N_0 \) is attained when the pump absorption is completely saturated. From Eq. 5.5 and Fig. 5.1, saturation occurs when \( r_0 = r_1(g_0/g_1) \). Complete rotational thermalization implies \( r_1 = r_1^e = f_i N_1 \), thus by substituting for the rotational partition function \^[24\] we obtain

\[
\left( \frac{N_1}{N_0} \right)_{\text{max}} = \left( \frac{f_0}{f_1} \right) \left( \frac{g_1}{g_0} \right) \\
= \exp(-E_0hc/k_BT) / \exp(-E_1hc/k_BT) \\
= \exp[(-E_1+E_0)hc/k_BT] \\
\]

(5.12)
TABLE 5.1
Maximum vibrational inversion for several 
CO₂ laser-pumped NH₃ transitions.

<table>
<thead>
<tr>
<th>NH₃ Transition</th>
<th>CO₂ Pump Transition</th>
<th>( \frac{N_1}{N_0} ) max</th>
</tr>
</thead>
<tbody>
<tr>
<td>aR(6,0)</td>
<td>9R(16)</td>
<td>1.96</td>
</tr>
<tr>
<td>sR(5,0)</td>
<td>9R(30)</td>
<td>1.78</td>
</tr>
<tr>
<td>aR(1,1)’</td>
<td>10R(14)</td>
<td>1.21</td>
</tr>
<tr>
<td>aQ(5,3)</td>
<td>10P(32)</td>
<td>1.00</td>
</tr>
</tbody>
</table>
where $E_i$ is the rotational energy of $r_i$. This ratio has been shown by Golger and Letokhov [53] and by Goela and Morse [54] to determine the relative effectiveness of pumping on P, Q, and R-branch transitions in any molecule. The general conclusion is that the optimum condition for gain is to pump on an R-transition to obtain the largest value of $N_i/N_0$ and hence maximum gain on the P-transitions. We can evaluate $(N_i/N_0)_{\text{max}}$ for NH$_3$ by recalling that, to first order of Eq. 2.1,

$$E_i(J,K) = BJ(J+1) + (C-B)K^2$$  \hspace{1cm} (5.13)

with $B = 10 \text{ cm}^{-1}$, and $K$ does not change in the transitions. Table 5.1 lists values of $(N_i/N_0)_{\text{max}}$ for several NH$_3$ transitions in near coincidence with CO$_2$ laser lines. The four systems have all produced lasing in NH$_3$, and the two with the higher values of $(N_i/N_0)_{\text{max}}$, aR(6,0) and sR(5,0), are most efficient.

An examination of the relationship between small-signal gain and $N_i/N_0$ is displayed in Fig. 5.2 for a typical gas mixture, and constant $n_f (=0.9)$. The selected transitions span the range of P-transitions found in experiments and include the first transitions of the Q and R-branches which show positive gain coefficients as $N_i/N_0$ is increased. Note that sufficient gain for laser action ($\sim 0.5 \text{ cm}^{-1}$) can be obtained at the relatively low value of 0.6 for $N_i/N_0$, well below the maximum values in Table 5.1. At this point the gain is centered on the high-J P transitions. As $N_i/N_0$ increases the peak gain shifts to lower J values which are nearer the peak in the rotational Boltzmann distribution. Gain on the Q and R-transitions appears for still higher $N_i/N_0$ and the gain coefficient of the Q-transition quickly approaches that of the
Fig. 5.2: Calculated small-signal gain coefficients for selected transitions in a typical gas mixture as a function of the vibrational population inversion parameter, $N_1/N_0$, with $(N_0 + N_1)/N = 0.9$. 
$N_2 : NH_3 = 80:1$.

76 Torr

1) $aP (8,0)$
2) $aP (6,0)$
3) $aP (4,0)$
4) $aP (2,0)$
5) $aR (0,0)$
6) $aQ (3,3)$
peak P-transition.

Figure 5.3 illustrates the calculated time dependence of $N_1/N_0$ for the $aR(6,0)$ pumped system with a gas mixture of $N_2$ and $NH_3$ in the ratio 80:1 at a total pressure of 76 Torr. The pump pulse shape and peak intensity, 0.7 MW/cm$^2$, used in the calculation correspond to the pump pulse used in the experiment. The two calculated gain spectra shown before and after the peak of the pump pulse illustrate how slight changes in $N_1/N_0$ can dramatically change the available gain. The value of $n_f$ during the slow decay of $N_1/N_0$ remained constant at $\sim 0.84$. Thus only 16% of the ortho population was elevated to the $2\nu_2$ level, justifying the initial assumption of a small population in that level.

The calculation in Fig. 5.3 was done with the V-V rate set a factor of 2.5 faster than the total V-T rate* and the rotational rate ratio set at $y = 0.25$. We investigated the effects of varying these parameters, as well as the ortho/para assumption, by running the model to evaluate the peak value of $N_1/N_0$ as a function of pump intensity. The same gas mixture and pulse shape as in Fig. 5.3 were used, and the major results are displayed in Fig. 5.4. The middle curve in Fig. 5.4 shows the variation in peak $N_1/N_0$ for $\tau_{VV}/\tau_{VT} = 0.4$ and $y = 0.25$. For a typical range of pump intensities $N_1/N_0$ remains less than 1.0, well below the maximum value predicted for this transition (i.e. 2.0, see Table 5.1). Experimentally, we find that pumping $aR(6,0)$ with a pump

*This corresponds to $t = 0.23$. It is more convenient for the discussion of Fig. 5.3 and 5.4 to represent $\tau_{VV}$ as a fraction of the total $\tau_{VT}$ and not as in Eq. 5.10. Later, for the comparison of different buffer gases, Eq. 5.10 will be the required definition.
Fig. 5.3: Upper: Typical pump pulse shape of the 9R(16) and 10R(14) CO₂ lines.

Lower: Vibrational inversion of ortho-NH₃ as a function of time for a typical gas mixture pumped by 9R(16). A partial gain spectrum is shown for two times. The horizontal line on the rising edge indicates when gain first appears.
Fig. 5.4: Calculated peak vibrational inversion as a function of pump intensity. The solid line indicates the same conditions as in Fig. 5.3. The dashed line shows the effect of increasing the V-V relaxation time. The dotted line shows the effect of including para-NH$_3$ in the pumped population.
aR(6,0) - 9R(16)
$N_2: NH_3 = 80:1$
76 Torr

$N_1/N_0$

$\tau_{vv}/\tau_{vt}$ SPECIES

- 1.0 ORTHO
- 0.4 ORTHO
- 0.4 ORTHO + PARA

PEAK PUMP INTENSITY (MW/cm$^2$)
intensity of ~0.6 MW/cm² produces gain coefficients and distributions consistent with a value of \( N_1/N_0 = 0.7-0.8 \), in general agreement with the middle curve.

The calculations were next modified to simulate pumping both the ortho and para components of NH₃. The bottom curve in Fig. 5.4 illustrates the results. At all pump intensities the ratio \( N_1/N_0 \) is substantially decreased, and negligible gain is predicted for pump intensities less than 1.5 MW/cm². Varying the unknown parameters in the calculation (i.e., \( t \) and \( y \)) within a physically reasonable range did not alter the conclusion that one must assume negligible coupling between ortho- and para-NH₃ if the calculations are to predict gain at intensities which agree with experiment. The absence of significant vibrational energy transfer between ortho- and para-NH₃ in the time-scale-of-interest is confirmed experimentally by the observation that pumping ortho-NH₃ produces lasing only on ortho-NH₃, and similarly for para-NH₃.

As a final step in examining the calculated ratio \( N_1/N_0 \), the computer simulation was run for the ortho-NH₃ case and the value of \( \tau_{VV}/\tau_{VT} \) varied from 0.01 to 1.0. For \( \tau_{VV}/\tau_{VT} = 1.0 \) the upper curve in Fig. 5.4 is obtained. By slowing down the rate of vibrational equilibration a higher value of \( N_1/N_0 \) is predicted at all intensities but is still less than 1.2 at 2 MW/cm². It is unlikely that \( \tau_{VV} \) would actually be as long as \( \tau_{VT} \), since in the mixture the contribution to \( \tau_{VT} \) by NH₃ and N₂ are about equal and it is well known that \( \tau_{VV} \) is much less than \( \tau_{VT} \) in other gases [51].

Decreasing \( \tau_{VV}/\tau_{VT} \) from 0.4 to 0.01 reduces \( N_1/N_0 \) by ~14%. Changing the ratio of rotational rates, \( \gamma \) has a similar effect. Increasing 1/\( \tau_1 \) relative to 1/\( \tau_0 \) increases \( N_1/N_0 \) by
reducing the saturation of the pump absorption, allowing a larger population transfer to the $1_{2}$ level. For all of these cases the value of $n_f$ was never less than ~0.75, which reaffirms the assumption of a relatively small transfer of the population to the $2_{2}$ level. The more important result is that, despite the uncertainties in some of the relaxation rates, the model always predicts significant gain will occur when the pumping intensity exceeds ~0.5 MW/cm$^2$.

5.5 Results from Pumping aR(6,0)

Two methods for comparing the experimental observations to the predictions of the rate-equation model are readily suggested by the discussion in the previous section. One is an examination of gain as a function of time. The other is to determine the complete gain spectrum at a single time. The aR(6,0) system was chosen for both of these detailed tests because of the greater number of lines and higher gains available. It is more instructive to examine the gain distribution first, and thus obtain an overall picture of the real inversion gain.

Gain coefficients were measured on nine emission lines in the aR(6,0) system, at a time 0.7 ms after the peak of the pump pulse, for the gas mixture and pumping conditions indicated in Fig. 5.3. This particular gas mixture was chosen as it gave the highest measured gain on the greatest number of lines. Experimentally, we find that increasing (decreasing) the NH$_3$ pressure increases (decreases) the gain at high-J relative to low-J P-transitions. Decreasing the buffer pressure results in fewer lines, while increasing it just reduces all the gain coefficients by pressure broadening. These effects become apparent for changes in pressure of ~20%. Smaller variations in the mixture are
difficult to distinguish from the effect of pump intensity variations. For all the gain measurements on the aR(6,0) system the variations in gas mixture were maintained at <5% or less. The range of the experimental values are shown as solid lines in Fig. 5.5. The predicted gain coefficients, shown as broken lines, illustrate the effect of a ±10% variation in the pump intensity about 0.7 MW/cm², the value which gives the best fit to the shape of the gain distribution. The pump intensity measured experimentally lies <20% lower. This is satisfactory agreement considering the uncertainty in some model parameters and in experimental measurements of the intensity.

The most important point illustrated by Fig. 5.5 is that the gain spectrum represents a thermalized rotational distribution. The gain is not clustered near aP(8,0), the directly pumped transition, but is spread over many lower J-value transitions. Some of the highest gain coefficients were measured on aP(4,0), as expected for a thermalized rotational population and a reasonably high value of N₁/N₀. Having chosen the pump intensity in the calculation to fit N₁/N₀ (=0.78), the magnitude of the gain coefficients can still be scaled by the pressure-broadening of the buffer gas, in this case nitrogen. A constant value of 3.2 MHz/Torr was used for Fig. 5.5, which is consistent with values we have measured on several P-transitions with a tunable-diode-laser. In comparing the predicted to measured gain it must be realized that the model evaluates gain for a single point in space, whereas in the experiment the gain is averaged over a 33 cm length and a diameter of a few millimetres. A reasonable variation of 5% in the pump intensity longitudinally, transversely, and shot-to-shot can easily account
Fig. 5.5: Comparison between theory and experiment for small-signal gain coefficients of several P-transitions. The dashed bars are the model predictions for a variation in pump intensity of ±10%. The solid bars indicate the range of the measured values. The gain coefficients are evaluated at 0.7 μs after the peak of the pump pulse, which has a peak intensity of 0.6 MW/cm².
N₂ : NH₃ = 80:1
76 Torr
for the minor discrepancies in the comparison. An important aspect of
the pump intensity fluctuations is that the gain varies much more at
low \( J \) than high \( J \), both experimentally and theoretically. This can be
interpreted from Fig. 5.2 as being due simply to the difference in gain
dependence on \( N_1/N_0 \) for the various transitions.

As discussed in Chapter 4, two of the transitions, \( aP(8,0) \) and
\( aP(6,0) \), differ from the rest of the inversion lines because they each
have one level in common with the pump transition, \( aR(6,0) \) (shown in
Fig. 4.5). A complete discussion of the \( \text{NH}_3 \) laser operation on these
transitions was provided in Chapter 4, but two points will be repeated
here. First, the rotational levels of the pump transition are not in
thermal equilibrium with the other levels. The effect is to increase
the gain on \( aP(8,0) \) and \( aP(6,0) \) relative to the thermalized gain calcu-
lation. Second, the gain on both transitions is reduced and shifted
away from line center by ac Stark shifts induced by the high pump
intensity. Because the two effects tend to be counteracting the pre-
dicted gain coefficients for these two transitions were calculated in
the same manner as all the rest. Figure 5.5 shows that the observed
gains on \( aP(8,0) \) and \( aP(6,0) \) are similar to the gains on their
neighbouring transitions. Thus, despite the complication of having one
level in common with the pump transition the thermalized gain calcu-
lation is often adequate for these transitions in a buffered mixture.

One obvious discrepancy in Fig. 5.5 is that the measured value
of the gain on \( sP(5,0) \) is substantially less than the predicted value.
Further experiments confirmed that gain coefficients on the \( s \)-transitions
are significantly lower than gain coefficients on the corresponding
a-transitions. This difference arises from the inversion doubling which splits the $\nu_2$ level. To this point, our rate-equation model has neglected the inversion splittings in the calculation of vibrational populations. This is a reasonable approximation in estimating absolute gain coefficients, but in calculating relative gain coefficients on the a- and s-transitions one must take into account the 36 cm$^{-1}$ splitting of the $\nu_2$ level. At room temperature, this splitting produces about 16% difference between the degree of vibrational inversion for the s- and for the a-transitions. Consequently, the predicted gain coefficients for the sP transitions shown in Fig. 5.5 are too high, and a more detailed calculation results in good agreement with the experimental measurement on sP(5,0). Other researchers have noted that a-transitions are much easier to observe than s-transitions in line-tunable NH$_3$ lasers [9,17]; this point is examined quantitatively in Chapter 6.

The shape of the entire gain spectrum in Fig. 5.5 was used to determine a value for $N_1/N_0$. An alternative method is to examine the time-dependence of the gain. Figure 5.6 compares gain coefficients measured at several time points in a single typical pulse for each of two transitions, aP(4,0) and aP(8,3). The time is measured from the start of the pump pulse in Fig. 5.3. Note that there is a marked difference in the time development of the gain on the two transitions. The gain on aP(8,3) is practically constant over a 1 μs interval, while that on aP(4,0) starts much higher but goes to zero more swiftly. The curves in Fig. 5.6 are the predicted gain coefficients from the time-dependence of $N_1/N_0$ in Fig. 5.3. The important point is not the absolute magnitude of the predicted gain but the variation in time. The
Fig. 5.6: Gain coefficients as a function of time for two widely separated transitions under the same conditions as Fig. 5.3. The lines are the model calculations. The points are the experimental values measured from typical probe pulses.
two curves show essentially the same time-dependence as the corresponding experimental values. From Fig. 5.2, the gain coefficient for $aR(4,0)$ is very sensitive to the degree of vibrational inversion, more so than the gain on the other transitions, for $N_1/N_0$ less than 1.0. Hence the time-dependence of the gain on $aP(4,0)$ provides a sensitive test of the accuracy of the rate-equation model and of the input parameters. In general, the model predictions of the time-dependence of the gain are in good agreement with the experimental measurements. Thus we conclude that all the major dynamic processes are included correctly in the model.

5.6 Results from Pumping $aR(1,1)$

While the measurements shown in Fig. 5.5 are indicative of a thermalized rotational population distribution, they do not rule out a stepwise cascade mechanism from the pumped upper level $v_2=7,0$. A much more stringent test of the thermalization model is to pump a low-$J$ transition and see if gain still appears centered at $J=6$. Consequently, we pumped the $aR(1,1)$ transition in a mixture of 1 Torr $NH_3$ and 80 Torr $N_2$, and the resulting gain spectrum is shown in Fig. 5.7(a). Note that the directly pumped line, $aP(3,1)$, is entirely absent, and that the gain is centered on $J=5$ and 6 with emission out to $J=8$. Rather than make elaborate gain measurements we measured the time delay of the $aP(J,1)$ emission lines with respect to the onset of the pump pulse. Since a higher gain implies a shorter time to threshold a measure of the gain is given by the inverse of the time delay, shown normalized in Fig. 5.7(a). Clearly, the gain distribution from pumping $aR(1,1)$ is thermalized.
Fig. 5.7: Emission spectra of $aP(J,1)$ lines obtained by pumping $aR(1,1)$ in mixtures with three different buffer gases: (a) nitrogen, (b) argon, (c) helium. The pump is the $R(14)$ 10-μm line of CO$_2$. The inverse of the time delay to lasing from the onset of the pump is a measure of the gain. All time delays are normalized to the minimum $aP(6,1)$ delay (0.40 μs, in N$_2$ mixtures).
(c) $\text{He:NH}_3 = 290:1$, 300 Torr

(b) $\text{Ar:NH}_3 = 160:1$, 160 Torr

(a) $\text{N}_2:\text{NH}_3 = 80:1$, 80 Torr

NORMALIZED (TIME DELAY)$^{-1}$

$J = 3, 4, 5, 6, 7, 8$
In contrast to the previous case of pumping ortho-NH$_3$ (with aR(6,0)), pumping aR(1,1) excites para-NH$_3$. Only transitions in para-NH$_3$ were observed to lase in this case. The wavelength discrimination of the monochromator was sufficient to resolve clearly the positions of the orth-NH$_3$ lines aP(J,3), but none of these lines were seen. Since ortho-NH$_3$ has a higher statistical weight than para-NH$_3$, the absence of lines in ortho-NH$_3$ provides a striking confirmation of the absence of significant vibrational energy transfer from para to ortho-NH$_3$. It is particularly noteworthy that aP(6,4) was observed to lase, but not aP(6,3). If the ortho and para components had equal vibrational populations then the aP(6,3) line would have twice as much gain as aP(6,4). The evidence is thus very clear that para and ortho-NH$_3$ do not exchange vibrational energy, at least on the time-scale of the present experiment.

5.7 Effects of Different Buffer Gases

The only buffer gas used in the experiments described so far is N$_2$. There has been a previous study which suggests that the effectiveness of N$_2$ as a buffer gas is enhanced by rotational resonance with some of the levels in NH$_3$ [11]. If this were the dominant effect then atomic gases such as He and Ar should be much less effective than N$_2$. The aR(1,1) system provides a fairly sensitive test for the relative merit of a buffer gas since the maximum possible value of $N_1/N_0$ is much lower than for aR(6,0), and any slight decrease in efficiency will result in much poorer laser operation. The spectrum of aP(J,1) transitions obtained with Ar and He as buffer gases are displayed in Fig. 5.7(b) and 5.7(c). Argon was very similar in performance to N$_2$, but He was
much worse and only one line was emitted. The comparison was performed for identical pumping conditions by switching quickly between buffer gases. The partial pressure of NH$_3$ was maintained at ~1 Torr while the total pressure was varied to produce the optimum results. Note that Ar was best at twice the pressure of N$_2$, and He at almost quadruple the N$_2$ pressure.

A rate-equation analysis of the three buffer gases requires a knowledge of the V-T rates and pressure-broadening coefficients. The V-T rates have been measured by Hovis and Moore [52]. We conducted a series of absorption measurements with a cw CO$_2$ laser to determine the pressure-broadening rates of the aR(1,1) transition. A summary of the input parameters and the results of the rate-equation calculations for each gas is given in Table 5.2*. To provide a basis for comparison the gas mixture was set at 1.0 Torr NH$_3$ mixed with sufficient buffer gas to provide the same pressure-broadened linewidth of the pump transition for each gas. Note the similarity between these pressures and the optimum values determined experimentally. A typical value of the experimental pump intensity, 1.0 MW/cm$^2$, was used to scale the pulse shape of Fig. 5.3 for the calculation. The same V-V rate as in Fig. 5.3 was used for all three gases. The calculated peak values of $N_1/N_0$ and the associated peak gain coefficients for para-NH$_3$ transitions illustrate

*For simplicity we have chosen to use a N$_2$ pressure-broadening coefficient of 3.2 MHz/Torr for all transitions for which gain is calculated. However, there is evidence that the broadening coefficients are dependent on J and K in pure NH$_3$ [45]. Thus, it is not surprising that a specific measurement on the aR(1,1) transition gives a N$_2$ broadening coefficient of 4.3 MHz/Torr.


**TABLE 5.2**
Comparison of buffer gas effectiveness on aR(1,1) in NH₃ for equal absorption linewidth.

<table>
<thead>
<tr>
<th></th>
<th>NH₃</th>
<th>Buffer Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂</td>
<td>Ar</td>
</tr>
<tr>
<td>(\Deltaν/p^a) [MHz Torr⁻¹]</td>
<td>19.8±0.6</td>
<td>4.34±0.28</td>
</tr>
<tr>
<td>(k_{VT}^b) [ms⁻¹Torr⁻¹]</td>
<td>(1.3±0.2)×10³</td>
<td>12±1.3</td>
</tr>
<tr>
<td>((\Deltaν/p)/k_{VT})</td>
<td>15</td>
<td>362</td>
</tr>
<tr>
<td>Partial Pressure [Torr]</td>
<td>1.0</td>
<td>75</td>
</tr>
<tr>
<td>Peak (N_1/N_0^c)</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>Peak Gain [%cm⁻¹]</td>
<td>-</td>
<td>0.93</td>
</tr>
</tbody>
</table>

\(^a\)CO₂ laser measurements.

\(^b\)At 293 K, from Hovis and Moore [52].

\(^c\)Peak pump intensity 1.0 MW/cm² and pump pulse shape of Fig. 5.3.
that Ar is practically equivalent to N₂ while He is much less effective. The values of the ratio of the pressure-broadening coefficient to the V-T rate are listed in Table 5.2 for all four gases. The trend in this ratio for the buffer gases closely follows the trend in the peak value of N₁/N₂. The very low ratio for NH₃ agrees with the usual experimental observations of only one emission line from pumping pure NH₃. The effectiveness of N₂ as a buffer gas can be explained simply by its large pressure-broadening coefficient relative to its V-T rate contribution. Rotational resonance may help, but it is certainly not the dominant process.

5.8 Summary

In this chapter a simple rate equation model is shown to account for all the major features of gain dynamics in pulsed NH₃ lasers. The model accurately predicts the gain distribution as a function of rotational quantum number, and hence can be used to determine the line-tunability of high-pressure NH₃ lasers. The two major concepts embodied in the model are the assumption of rapid thermalization of the rotational populations and the absence of vibrational energy transfer between ortho- and para-NH₃. Both assumptions are clearly verified by experimental observations on pumping aR(6,0) and aR(1,1). The model is used to calculate absolute gain coefficients, and their time-dependence, for a variety of 12-μm transitions, and these calculations are shown to be in good agreement with experimental measurements. We also identify the parameters which determine the effectiveness of a buffer gas in pulsed
NH₃ lasers. \( N_2 \) and Ar are shown to be particularly effective buffer gases, while He is much less efficient.
CHAPTER 6

OPTIMIZATION OF INVERSION GAIN IN \textit{NH}_3 \textit{LASERS}

6.1 Introduction

Of all the pulsed \textit{NH}_3 lasers previously reported in the literature, only those pumped by the 9R(30) CO\textsubscript{2} line have provided multi-line and line-tunable operation over a wide range of transitions in the \nu_2 band [17,55]. All of the emissions generated with other pump transitions can be produced by an R(30)-pumped \textit{NH}_3 laser which employs a buffered gas mixture. Thus, it is not surprising that this \textit{NH}_3 laser has been the subject of much study and development [11,17,48,56,57] and consequently has been employed in several mid-infrared applications [48,58,59]. Despite the number of studies on the R(30)-pumped \textit{NH}_3 laser, the dynamics of its operation and the distribution of its emission frequencies had not yet been adequately explained prior to the work described here. In this chapter, we provide the first comprehensive examination of the small-signal gain in this \textit{NH}_3 laser system. The results clearly illustrate that the distribution of laser transitions is due to the thermalization of the rotational populations. In addition, we resolve the problem of the observed differences in laser operation between a-transitions and s-transitions noted by previous researchers [9,17], and demonstrate that distinguishing between ortho-\textit{NH}_3 and para-\textit{NH}_3 transitions is essential. Another series of measurements illustrate the effects of \textit{NH}_3 concentration and pump intensity on the small-signal gain. Significant increases in gas temperature due to pump absorption
are found to be responsible for reducing the gain in high concentration mixtures. The experimental measurements all confirm the predictions of the rate-equation model which was developed in Chapter 5, and which is extended in this chapter. Hence, this model can be applied with confidence to predict scalability and optimum operating conditions for a variety of optically pumped NH$_3$ lasers.

The principle reason for the success of the R(30)-pumped NH$_3$ laser is that 9R(30) is almost resonant with the NH$_3$ transition which it pumps, sR(5,0). Resonant pumping produces much higher population inversions and thus higher gain coefficients on the NH$_3$ laser transitions. At high pump intensities gain is created in the Q and R branches, in addition to the P branch. The wide range of available laser transitions includes both ortho- and para-NH$_3$ transitions, as sR(5,1) is also pumped efficiently by 9R(30) at high pump intensities. Section 6.2 discusses the sR(5,0) laser system and the apparatus used in the experiments. Section 6.3 examines gain as a function of transition, including the effects of inversion doubling and the distinction between ortho and para transitions. In Section 6.4 the aP(4,0) transition is selected to study the dependence of gain on the concentration of NH$_3$ in a gas mixture of constant total pressure. Section 6.5 examines the variation of the small-signal gain as a function of pump intensity. The detailed experimental results presented in this chapter can be utilized directly in the optimization of pulsed line-tunable NH$_3$ lasers.
6.2 The sR(5,0) Laser System

The sR(5,0) transition is offset 150 MHz from the 9R(30) CO₂ pump line [31]. For dilute gas mixtures of NH₃ with N₂ at total pressures greater than 50 Torr, the pump offset is less than the pressure-broadened half-width of the absorption line. Thus, for typical pumping conditions at pressures of 50 to 100 Torr the sR(5,0) transition is resonantly pumped. All of the sR(5,K) transitions lie within 1.6 GHz of 9R(30), and the pump offset for sR(5,1) is only 345 MHz [60]. Hence, at sufficiently high pump intensities 9R(30) pumps the entire sR(5,K) multiplet and creates gain in both the ortho and para species of NH₃.

The experiments discussed in this chapter involve measurements of small-signal gain coefficients in dilute mixtures of NH₃ with N₂. Nitrogen was used because the results of Chapter 5 show that N₂ is the best choice for the buffer gas. The general technique and apparatus employed have already been discussed in Chapter 3. There is a minor change in the experimental arrangement for pumping the NH₃ oscillator, as shown in Fig. 6.1. To facilitate switching from one laser transition to another, the NH₃ laser is pumped through a dichroic mirror M₁ which transmits ∼60% of the R(30) energy. Another dichroic mirror M₂ transmits ∼90% of the R(30) pulse, and is used to direct the NH₃ laser output to the amplifier cell. Both M₁ and M₂ have a reflectivity >95% between 790 and 940 cm⁻¹. This range covers most of the NH₃ laser transitions. Hence, the NH₃ laser can be tuned from line to line by turning the grating without disturbing the alignment of the CO₂ pump beam. For each new NH₃ transition, the NH₃ probe beam alignment is
Fig. 6.1: Schematic diagram of the experimental apparatus for measuring gain in NH$_3$ optically pumped by the 9R(30) CO$_2$ line.
checked to ensure proper overlap with the CO₂ beam in the amplifier cell. The gain measurements are performed at the line center of the NH₃ transitions, as explained in Chapter 3. For the range of pressures examined in this chapter (30 to 80 Torr, typical of most line-tunable NH₃ lasers), the transitions are pressure-broadened. A mixture of 1% NH₃ in N₂ is employed for most of the gain measurements as it limits the pump attenuation while allowing sufficiently high gain coefficients for accurate measurements in a 33-cm amplifier cell. Thus, for most conditions the pump intensity is essentially uniform over the volume probed by the NH₃ laser which facilitates the comparison between theory and experiment.

A typical single-mode R(30) pump pulse is shown in Fig. 6.2 and consists of an initial spike of ~250 ns FWHM with a peak intensity about 3-4 times that in the tail. The pump intensity is practically constant for the duration 0.3 to 1.2 μs after the peak of the pump pulse. Gain measurements are taken during this period of nearly steady-state pumping. The exact timing of the various measurements depends on the NH₃ probe signal. Reliable measurements can only be made if the probe intensity is slowly varying relative to the 50 ns risetime of the HgCdTe detector. Most of the NH₃ laser emissions appear near the time of the peak of the pump pulse. Thus, gain coefficients can usually be evaluated throughout the "steady-state" pumping regime.

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*For most of the pumping conditions that we examine, the relaxation rates are fast enough that the vibrational populations follow the variations in pump intensity after the peak of the pulse.
Fig. 6.2: Typical pulse shape of the 9R(30) pump. Note that the intensity only varies by \( \pm 10\% \) in the time between 0.3 and 1.2 \( \mu s \) after the peak of the pulse. Most of the gain measurements are taken during this time period.
6.3 Small-Signal Gain as a Function of Transition

There are three aspects of the variation in gain with transition to be examined here. The first two, the dependence on the rotational quantum number J and the effect of inversion doubling, are a consequence of the thermalization of the rotational level populations. The experimental results confirm that the entire distribution of relative gain coefficients can be characterized by the single parameter $N_1/N_0$, under the assumption of thermalized rotational populations. The measurements show that thermalization also produces much higher gain coefficients on a-transitions than s-transitions due to the inversion doubling which splits the $v_2\alpha$ and $v_2\beta$ levels by 36 cm$^{-1}$. The third aspect of the gain variation with transition concerns the distinction between the two species of NH$_3$, ortho and para. We observe gain on transitions from both species only if both species are pumped, i.e. 9R(30) must pump both sR(5,0) and sR(5,1). All three aspects of the gain distribution are important in selecting transitions to optimize NH$_3$ lasers.

6.3.1 Gain Variation with J

Before examining the experimental results let us briefly review the predicted variation of gain with J as the population inversion is increased. Figure 6.3 illustrates the pressure-broadened gain coefficients for a range of transitions calculated as a function of $N_1/N_0$, the population inversion parameter. Recall from Chapter 5 that $N_1/N_0$ determines the distribution of the gain, i.e. the relative gain coefficients on all the transitions, whereas $(N_0+N_1)/N$ scales the gain magnitude. For $N_1/N_0$ less than 0.9, gain occurs only in the P branch.
Fig. 6.3: Calculated small-signal gain coefficients for selected transitions as a function of the vibrational inversion parameter \( N_1/N_0 \), with \( (N_0 + N_1)/N = 0.9 \). The dashed line illustrates that the gain coefficients on s-transitions are significantly lower than on the corresponding a-transitions.
1% NH$_3$ in N$_2$

SMALL-SIGNAL GAIN COEFFICIENT (% cm$^{-1}$)

1) aP(7,3)
2) sP(7,3)
3) aP(6,0)
4) aP(4,0)
5) aP(2,0)
6) aR(0,0)
7) aQ(3,3)

N$_1$ / N$_0$
and is peaked towards high-J transitions \((J=6,7)\). As \(N_1/N_0\) increases gain appears in the Q and R branches and the peak gain shifts to low-J transitions \((J=3,4)\). (Slight discrepancies between Fig. 6.3 and the similar figure in Chapter 5, Fig. 5.2, are a result of incorporating the difference between s-type and a-type transitions in the gain calculation program for Fig. 6.3. This aspect of the gain distribution is pursued in greater detail in the next section.)

Experimentally measured gain coefficients for a range of transitions are shown in Fig. 6.4, and compared to model calculations. The distribution of the gain coefficients and their relative values are well described by \(N_1/N_0=1.40\), which is the value predicted by the model. This value of \(N_1/N_0\) is close to the maximum value of 1.78 for the \(sR(5,0)\) transition (see Table 5.1) and is a much higher \(N_1/N_0\) than was obtained in Chapter 5 by pumping \(aR(6,0)\) with \(9R(16)\). To calculate \(N_1/N_0\) the rate equations were solved for the experimentally determined conditions of pump pulse shape, pump intensity, gas mixture and pressure. Only one of the model parameters was changed from the values used in Chapter 5. The variable parameter \(t\), which controls the vibration-vibration relaxation rate, was set to its maximum value \(t=1.0\). This change in \(t\) was found necessary to obtain from the model calculations the high values of \(N_1/N_0\) which fit the measured gain distributions reported throughout this chapter. The new value of \(t\) is in keeping with the investigations of Chapter 5 and is used consistently in the rest of this thesis. The predicted gain coefficients in Fig. 6.4 were evaluated using \(N_1/N_0=1.40\) and an \(NH_3\) concentration of 0.91%, which is in reasonable agreement with the nominal concentration of 1% \(NH_3\). Indeed, a fit to the measured
Fig. 6.4: Comparison between theory and experiment for small-signal gain coefficients of several NH$_3$ transitions. The solid lines are the measured coefficients evaluated for a pump intensity of $\sim$130 kW/cm$^2$, 0.6 $\mu$s after the peak of the pump pulse. The model predicts $N_1/N_0 = 1.40$ and gives the gain coefficients indicated by the dashed lines. The estimated error for the experimental measurements is $\pm$0.2 %cm$^{-1}$. 
NOMINAL
1% NH$_3$ in N$_2$
76 Torr

GAIN COEFFICIENT (% cm$^{-1}$)

EXPERIMENT
- - -

CALCULATION
- - -

NH$_3$ TRANSITIONS
aR(0,0) sP(1,0) aP(2,0) aQ(3,3) aP(4,0) aP(4,3) aP(6,3) aP(7,3) aP(9,3)
gain coefficients may be regarded as a more accurate technique for measuring the NH$_3$ concentration. The pressure-broadening coefficient of N$_2$ was again maintained at 3.2 MHz/Torr for all transitions on which gain coefficients are calculated. Slight discrepancies between the calculated and measured gain coefficients may be due to minor variations in the N$_2$ broadening coefficients with transition (see Chapter 5 and Appendix A). However, the good agreement between theory and experiment in Fig. 6.4 conclusively shows that rotational thermalization, and its associated parameter N$_1$/N$_0$, is the most important concept required to describe the gain distribution. In particular, there is no need to invoke rotational resonance between NH$_3$ and N$_2$ [11] to explain the observed gain.

6.3.2 Effect of Inversion Doubling

Previous studies of the R(30)-pumped NH$_3$ lasers have reported that a-transitions are more easily produced than s-transitions [9, 17]. In Chapter 5, higher gains were observed for a-transitions than s-transitions and the difference was attributed to the inversion doubling of the v$_2$ level. The rate-equation calculation of N$_1$/N$_0$ neglects the inversion doubling of the vibrational levels. However, the inversion doubling is easily incorporated into the calculation of gain coefficients from the vibrational populations specified by N$_1$/N$_0$. Figure 6.3 illustrates that a higher gain coefficient is calculated for aP(7,3) than for sP(7,3) at all values of N$_1$/N$_0$. If the 36 cm$^{-1}$ splitting of the v$_2$ level were neglected then there would be no difference in the calculated gain coefficients for these two lines. The results of
a detailed experimental comparison of gain coefficients between a- and s-transitions are shown in Fig. 6.5 for aP(7,6) and sP(7,6). These two transitions were chosen for this comparison because they are easily produced in the NH$_3$ probe laser and they provide sufficient discrimination in the monochromator, especially for the s-transition, to be measured separately from neighbouring transitions. In general, sP-transitions are much more closely grouped in frequency than are aP-transitions, but the separation increases with J and K. The maximum value of K is 6 in this case. As Fig. 6.5 illustrates, the measured gain coefficients for aP(7,6) are significantly higher than for sP(7,6) over a wide range of pump intensities. The curves in Fig. 6.5 are obtained from a "sectioned-cell" calculation to allow for pump attenuation along the length of the amplifier cell. A more complete explanation of this approach is provided in Section 6.5 where its use is more important. For the conditions depicted in Fig. 6.5, it is sufficient to note that pump intensities greater than 20 kW/cm$^2$ suffer negligible attenuation. Thus, most of the calculated results shown in Fig. 6.5 could be obtained by assuming uniform pumping throughout the cell. The NH$_3$ concentration employed in the calculation was determined from the absorption measurements with no pump present. The agreement between theory and experiment validates the model and confirms that thermalization occurs between a- and s-levels within the vibrational states.

A further confirmation of the effect of the inversion doubling is given by the gain coefficients, calculated and experimental, for the sP(1,0) transition shown in Fig. 6.4. The measured gain coefficient for sP(1,0) fits in well with the thermalized distribution of gain. If
Fig. 6.5: Comparison between theory and experiment for small-signal gain coefficients of one pair of a- and s-transitions as a function of pump intensity. The experimental values were measured 0.9 μs after the peak of the pump pulse. The gas mixture is 0.87% NH₃ in N₂ at a total pressure of 35 Torr.
inversion doubling is neglected then the model calculates a gain coefficient \(\sim 50\%\) larger than the calculated value shown in Fig. 6.4. The discrepancy between this larger value and the observed value for \(sP(1,0)\) is much larger than the difference between theory and experiment for any of the other lines. Thus, we conclude that inversion doubling must be incorporated into the gain calculation to obtain satisfactory agreement with experiment for all lines. The absence of gain measurements on other \(s\)-transitions from Fig. 6.4 is due to the difficulty in resolving these lines in the detection system.

6.3.3 Effect of \(NH_3\) Species

All of the gain measurements discussed so far in this chapter are for ortho-\(NH_3\) transitions. To demonstrate that gain is produced in para-\(NH_3\) and to illustrate the differences in gain between ortho-\(NH_3\) and para-\(NH_3\) transitions, we measured gain coefficients as a function of pump intensity for all the \(aP(7,K)\) lines. The results are displayed in Fig. 6.6. A gas pressure of 35 Torr was used to enhance the difference in pump absorption for the \(sR(5,0)\) and \(sR(5,1)\) lines. The larger pump offset for the \(sR(5,1)\) line implies that the pump absorption is \(\sim 1/3\) of that for \(sR(5,0)\) at this gas pressure. At very low pump intensities, there is gain on the two ortho-transitions, \(K=3\) and 6, but all the para-transitions are still absorbing, as shown in Fig. 6.6(a) and (b). Thus, there is no evidence of thermalization of rotational populations between ortho and para. To create significant gain in para-\(NH_3\) requires intense pumping of \(sR(5,1)\), as illustrated in Fig. 6.6(c). At this high
Fig. 6.6: Experimental measurements of the small-signal gain coefficients for the $aP(7,K)$ transitions for three different pump intensities, $I_p$. The values are an average of measurements made at 0.6 and 0.9 μs after the peak of the pump pulse, and the estimated error is ±0.2 %cm$^{-1}$. The gas mixture is 1% NH$_3$ in N$_2$ at 35 Torr.
(a) $I_p = 2.8 \text{ kW/cm}^2$

(b) $I_p = 5.9 \text{ kW/cm}^2$

(c) $I_p = 112 \text{ kW/cm}^2$

Gain coefficient (% cm$^{-1}$)

$NH_3$ transitions $\alpha P(7,K)$
pump intensity, the pump absorption is completely saturated on both the sR(5,0) and sR(5,1) transitions and the population inversions for ortho and para-NH$_3$ are nearly equal. The use of high pump intensities in practical R(30)-pumped NH$_3$ lasers is undoubtedly the reason that the distinction between ortho-NH$_3$ and para-NH$_3$ has not been noticed previously. The remaining differences in gain coefficients illustrated in Fig. 6.6(c) are mainly due to differences in statistical weights; recall that ortho levels have twice the weight of para levels. The much lower gain coefficient for K=6 relative to that for K=3 is a consequence of the K-dependence of the transition dipole moment (see Appendix A).

6.4 Small-Signal Gain as a Function of NH$_3$ Concentration

Most of the line-tunable NH$_3$ lasers reported in the literature have worked best for concentrations of 1 to 2% NH$_3$ in mixtures with N$_2$. To develop an understanding of the factors which determine the optimum concentration, let us first examine the theoretical basis for the dependence of gain on NH$_3$ concentration. Given sufficient pump intensity the gain coefficients will scale linearly with the concentration of NH$_3$ if all other parameters can be held constant. However, the interplay between rotational relaxation and vibration-translation (V-T) relaxation reduces the maximum possible gain at concentrations higher than 1% NH$_3$. To sustain a population inversion in any mixture, the rate of pumping must compensate for the loss of inversion due to V-T relaxation. In mixtures of NH$_3$ and N$_2$, the individual contributions
of \( \text{NH}_3 \) and \( \text{N}_2 \) to the total \( V-T \) rate are equal for a 0.9% concentration of \( \text{NH}_3 \), and the \( V-T \) rate is dominated by \( \text{NH}_3 \) at higher concentrations. The pumping rate is limited by the rotational relaxation rate (the so-called "bottle-neck" effect [61]), which is dominated by \( \text{N}_2 \) pressure-broadening up to concentrations of 28% \( \text{NH}_3 \). Thus, as the concentration increases from 1% \( \text{NH}_3 \) (with the total pressure fixed) the \( V-T \) rate increases much faster than the rotational relaxation rate. This effect results in a reduction of the maximum possible value of \( N_f/N_0 \) and hence a slower than linear increase in the gain coefficients with increasing concentration. These rate considerations can be placed in perspective if we compare the \( V-T \) relaxation time \( (\tau_{VT}) \) to the rotational relaxation time of the lower pumped level \( (\tau_0) \), for a 1% \( \text{NH}_3 \) and a 10% \( \text{NH}_3 \) mixture in a total pressure of 76 Torr (recall that relaxation rates are the inverse of relaxation times). In the 1% \( \text{NH}_3 \) mixture, \( \tau_{VT}=529 \) ns and \( \tau_0=0.358 \) ns, and in the 10% mixture, \( \tau_{VT}=93.5 \) ns and \( \tau_0=0.317 \) ns. Hence, increasing the concentration by a factor of 10 to 10% \( \text{NH}_3 \) is accompanied by more than a five-fold increase in the \( V-T \) rate, while the rotational relaxation rate increases by less than 13%. The differential change in these rates reduces the predicted maximum value of \( N_f/N_0 \) from 1.47 in the 1% \( \text{NH}_3 \) mixture to 0.86 in the 10% \( \text{NH}_3 \) mixture.

To determine the actual gain dependence, gain coefficients for \( aP(4,0) \) were measured as a function of \( \text{NH}_3 \) concentration in a total pressure of 76 Torr, and the results are displayed in Fig. 6.7. The \( aP(4,0) \) transition was selected for this study because it generally has the highest gain coefficient and is easily produced in the \( \text{NH}_3 \) probe laser. The experiment was performed by tightly focusing the pump
Fig. 6.7: Comparison between theory and experiment for small-signal gain coefficients of $aP(4,0)$ as a function of $NH_3$ concentration in $N_2$. The experimental points, shown with appropriate error bars, were evaluated for a pump intensity of $\sim 950$ kW/cm$^2$, 0.3 $\mu$s after the peak of the pump pulse. The upper curve is calculated assuming the gas temperature remains constant at 300 K. The lower curve is calculated with the gas temperature allowed to rise due to the energy absorbed from the pump.
beam in an 11-cm cell and evaluating the gain coefficients 0.3 μs after the peak of the pump pulse. At that time the pump intensity was ~950 kW/cm², more than enough to completely saturate the pump absorption for all the mixtures examined. The gain coefficients peak for a 4% NH₃ mixture, and linear scaling of the gain with concentration only occurs for mixtures containing 2% NH₃ or less. To compare experiment with theory, an initial calculation was performed by assuming a steady-state pump intensity of 950 kW/cm², and a constant gas temperature of 300 K. The calculated results, shown as the upper curve in Fig. 6.7, lie significantly higher than the measured gain coefficients for NH₃ concentrations greater than 2%. This discrepancy is due to increases in the gas temperature at the higher NH₃ concentrations. A rise to 400 K from 300 K in the ambient gas temperature is predicted to reduce the gain coefficients by a factor of ~0.6, assuming constant number density and constant N₁/N₀. The lower curve in Fig. 6.7 was calculated with the rate-equation model modified to allow for increases in gas temperature due to pump absorption. The calculation assumes constant number density as the gas cannot expand significantly in the first 0.5 μs of the pump pulse. The revised model accounts for heating due to pump absorption by ortho-NH₃ and para-NH₂, for the temperature dependence of the pressure-broadening coefficients [24], and for the temperature dependence of the V-T relaxation rates. Linear interpolation between

*As the pump absorption is saturated at intensities well below 950 kW/cm² (see Section 6.5), changes in the intensity by as much as a factor of 2 have negligible effect on the gain calculation.
rate coefficients provided by Hovis and Moore [52] was employed to evaluate the V-T rates up to 398 K, the maximum temperature reported. For temperatures greater than 398 K the V-T rates were maintained equal to the values for 398 K. Considerably better agreement with the experimental measurements is obtained with the variable-temperature calculation. The model predicts a temperature rise of 30 K in 4% NH₃, a rise of 125 K in 10% NH₃, and an increase of less than 10 K for concentrations less than 2% NH₃.

Further experimental confirmation of the rise in gas temperature was obtained from the measured time-dependence of the gain coefficients. In a 1% NH₃ mixture the gain coefficients follow the variation in pump intensity, which is fairly constant for \( \sim 1.0 \) \( \mu s \). In a 10% NH₃ mixture the gain coefficient is halved \( 0.3 \) \( \mu s \) after the time of measurement for the points shown in Fig. 6.7. Measurements of the gain coefficient near the peak of the pump pulse revealed values as high as 30 \( \% \) cm\(^{-1}\) for the 10% NH₃ mixture, but the measurements are not easily quantified because of the rapid variation in pump and probe intensity at that time. Thus, the optimum concentration appears to be \( \sim 4\% \) NH₃, limited chiefly by thermal heating due to pump absorption. If thermal heating is a serious problem in a particular device then lower NH₃ concentrations can be employed while maintaining relatively high gain coefficients.

No scaling or fitting has been applied to the calculations for Fig. 6.7, other than setting the parameter \( t=1.0 \) to adjust the V-V relaxation rate, as mentioned in Section 6.3.1. The effect of increasing \( t \) (from 0.23 in Chapter 5) is to reduce the transfer of population to the \( 2v₂ \) level, and thus predict higher gain-coefficients.
A problem arises if we leave $t=0.23$, as the model then predicts gain on the $2v_2$ transitions, which is contrary to our observations (see Chapters 7 and 8). The $2v_2$ level could be completely removed from the model with negligible effect on the calculated results if the V-T relaxation rate were adjusted appropriately. A brief investigation reveals that removing the $2v_2$ level could be accommodated by doubling the V-T rate. However, the estimated errors in the V-T rate coefficients are at most 20% [52]. Thus, it is appropriate to leave the $2v_2$ level in the model, and adjust the V-V rate to limit the population that is transferred to that level. These results indicate that there is no significant V-V pumping in NH$_3$ beyond the $1v_2$ level for the range of experimental conditions examined.

6.5 Small-Signal Gain as a Function of Pump Intensity

The dependence of small-signal gain on pump intensity is a prime criterion in the optimization of optically pumped lasers. Measurements of gain coefficients for $aP(4,0)$ and $aQ(3,3)$, the two highest gain transitions for large $N_1/N_0$, as a function of pump intensity are displayed in Fig. 6.8. The curves in Fig. 6.8 are calculated by a "sectioned-cell" method to allow for the pump attenuation along the 33-cm length of the amplifier cell. In the calculation the cell is divided into several sections, so that the maximum pump absorption in each section is 20% or less. In each section, the pump intensity is considered to be spatially uniform (but still varying with time) and the calculated pump absorption is used to reduce the pump intensity for the next section. The incident pump intensity is only employed in the first section. The net gain coefficient for the cell is the simple average of the gain coefficients from each section. The net gain
coefficients, calculated and experimental, are plotted in Fig. 6.8 as a function of the pump intensity at the entrance of the cell. The pump intensities measured in the experiment are scaled down by a factor of 0.77 to obtain the fit shown in the figure. In addition, the nominal 1% NH₃ concentration of the experiment was reduced to 0.85% in the calculation. These two scaling factors are quite reasonable in view of the uncertainties involved in absolute measurements of intensity and NH₃ concentrations (see Fig. 6.4 and 6.5 for other nominal 1% NH₃ mixtures). The calculated curves are in good agreement with the experiment results over the entire range of pump intensity.

At low pump intensities in Fig. 6.8, the gain coefficient for aP(4,0) is much greater than that for aQ(3,3) as expected from Fig. 6.3. The gain coefficients on both transitions saturate at a pump intensity of ~50 kW/cm², which corresponds very well with the calculated pump saturation intensity of 58 kW/cm² for the conditions shown. Thus, pump intensities greater than 50 kW/cm² are a waste of pump energy in terms of increasing the small-signal gain in a mixture of 76 Torr. The saturation intensity \( I_s \) is given by

\[
I_s = \frac{h \nu_p}{2 \sigma \tau}
\]  
(6.1)

where \( \nu_p \) and \( \sigma \) are defined in Eq. 5.5, and \( 1/\tau \) is the effective rotational relaxation rate. From Eq. 5.11, \( 1/\tau \) can be replaced by \( 2\pi \Delta \nu \). Figure 6.5 illustrates that a lower pump intensity of ~20 kW/cm² is required to saturate the gain coefficients in a mixture at 35 Torr. Calculation gives \( I_s = 25 \) kW/cm² under those conditions. Hence, the optimum pump intensity for creating gain is comparable to the intensity
Fig. 6.8: Comparison between theory and experiment for small-signal gain coefficients of $aP(4,0)$ and $aQ(3,3)$ as a function of pump intensity. The values are an average of measurements made at 0.6 and 0.9 µs after the peak of the pump pulse. The curves are calculated for a mixture of 0.85% $NH_3$ in $N_2$, and the measured pump intensities are scaled down by a factor of 0.77 (see text for details).
required to saturate the pump absorption. The saturation intensity scales with the square of the pressure in the pressure-broadened regime for resonant pumping. However, it is nearly constant for a wide range of NH$_3$ concentrations at fixed pressure, as the absorption linewidth is dominated by N$_2$ pressure-broadening up to concentrations of 28% NH$_3$.

It appears, then, that the small-signal gain coefficients can be increased by increasing the NH$_3$ concentration without changing the pump intensity. This would be true except that the pump absorption scales almost linearly with the NH$_3$ concentration. Saturation of the pump absorption does not necessarily imply that the pump absorption is negligible. Thus shorter cell lengths may be necessary for higher concentrations to ensure that the entire length is adequately pumped. The occurrence of very high gain coefficients suggests that very compact devices can be built. On the other hand, longer cells are generally required to maximize the power output. The exact pump intensity requirements for a specific device will depend on the details of construction. However, it should be noted that the gain coefficients depend on pump intensity and not on pump power. Thus, laser cells of different diameters can be employed to obtain the optimum pump intensity for a given pump power.

6.6 Summary

In this chapter, a detailed study of inversion gain is carried out employing the sR(5,0) transition pumped on resonance by the 9R(30) CO$_2$ line. This pump transition has produced the most successful line-tunable NH$_3$ lasers. The study reveals that the dependence of gain on transition is well described by a thermalized distribution of
rotational populations. Thermalization within a vibrational state occurs for all J values, and between a- and s-levels, but does not occur between the two species ortho and para. To obtain gain on the para-NH$_3$ transitions requires that a para-NH$_3$ transition be pumped. We also examine the small-signal gain as a function of NH$_3$ concentration and pump intensity. Calculations with an extended rate-equation model are used to show that thermal heating is a major problem in mixtures of high NH$_3$ concentrations. The pump saturation intensity, defined with parameters in the model, is shown to be a useful gauge for estimating the optimum pump intensity in the production of gain. All of the experimental results are in good agreement with the predictions of the model. Thus, calculations with the model can be employed in conjunction with the experimental results presented in this chapter to aid in the optimization of inversion gain in pulsed line-tunable NH$_3$ lasers.
CHAPTER 7
HIGH PRESSURE NH₃ LASER OPERATION

7.1 Introduction
For many mid-infrared applications it is desirable to have a high-power laser source which is continuously-tunable and/or can produce pulses of sub-nanosecond duration. The general requirement for developing these characteristics is a broad gain bandwidth, which is accomplished in gas lasers by operating at high pressure. In this chapter, we investigate the effects of pressures up to ~13 atmospheres (1 atm equals 760 Torr) on the small-signal gain in optically-pumped, line-tunable NH₃ lasers. Consequently, we only consider NH₃ lasers which employ dilute mixtures of NH₃ in N₂, a typical buffer gas.

Increasing the pressure in any gas laser can increase the tuning range in two ways. First, the linewidth of each transition broadens, and second, the broadened profiles of adjacent lines can overlap. Unlike the evenly distributed CO₂ laser lines, NH₃ laser transitions are spaced rather irregularly. Furthermore, there is a large variation in the maximum gain coefficient even for adjacent NH₃ lines, chiefly due to the difference in statistical weight between ortho-NH₃ and para-NH₃.

To evaluate the possible overlaps of NH₃ lines, consider a dilute mixture of NH₃ in N₂ at a pressure of 10 atm, which would give a pressure-broadened linewidth of ~25 GHz HWHM. This width is sufficient to merge all the transitions within each aP(J,K) multiplet from J=3 to 8. However, the spacings between aP(J,K) transitions are much larger:
~25 GHz, ~40 GHz, and ~58 GHz between K=1 and 2, K=2 and 3, and K=3 and 4, respectively. Thus, at a pressure of 10 atm, continuous tuning would likely be possible only up to K=3 within each aP(J,K) multiplet, which would provide a maximum tuning range of ~120 GHz. The separation between successive values of J is generally greater than 100 GHz, which is much too large to allow continuous tuning between multiplets at 10 atm.

As mentioned above, the possibility of generating short pulses is another reason for having a broad gain bandwidth. An estimate of the minimum pulse duration Δt that can be supported by a gain bandwidth Δν (full-width) is given approximately by ΔνΔt ~1. Thus, from the previous example, a tuning range of 120 GHz is a sufficient bandwidth to support pulses of ~8 ps duration. Techniques for creating short pulses are well developed. Passive mode-locking of an NH₃ laser has produced pulses as short as 7 ns in pressures less than 100 Torr [56]. Synchronous pumping with a mode-locked source has generated pulses ~1 ns in duration [62,63]. Applications of these techniques to NH₃ lasers operating at pressures of a few atmospheres should yield frequency-tunable pulses of sub-nanosecond duration.

Most of the line-tunable NH₃ lasers described in the literature have generally worked best at pressures of ~100 Torr (e.g. Ref. 11).

These studies report results on directly-pumped transitions in pressures of 5-30 Torr of pure NH₃. Thus, the gain bandwidth due to ac Stark shifts and the bandwidth of the pump source through the Raman process (see Ref. 63), and not due to pressure broadening. This result does not detract from the general applicability of synchronous pumping to the conditions examined in this chapter.
More recent studies have discussed an NH$_3$ laser which can operate at pressures up to 3.2 atm [57], and which has been tuned continuously over a range of ~0.25 cm$^{-1}$ (7.5 GHz) at a pressure of 1.1 atm [64]. In this chapter, experimental and theoretical results are presented to determine the factors which limit high-pressure operation. Experimental measurements of small-signal gain are obtained by pumping NH$_3$-N$_2$ mixtures at pressures up to 760 Torr with the 9R(30) CO$_2$ line. Theoretical calculations with the rate-equation model extend the investigations of small-signal gain to higher pressures, up to 10$^4$ Torr. Section 7.2 shows that the concentration of NH$_3$ strongly affects the maximum pressure attainable. As the pressure is increased, gas heating due to pump absorption reduces the gain coefficients. The change in temperature increases with increasing concentration for any given pressure. Section 7.3 examines the problem of absorption lines in the 2$\nu_2$ bands, which broaden and overlap the $\nu_2$ laser transitions as the pressure is increased. The absorption on the 2$\nu_2$ transitions is enhanced by optical pumping of the $\nu_2$ band, and thus can strongly interfere with the gain on adjacent $\nu_2$ transitions.

7.2 Small-Signal Gain as a Function of Pressure

The pressure of a gas mixture does not directly affect the small-signal gain at line center on a transition, as long as the transition lineshape is pressure-broadened. For NH$_3$-N$_2$ mixtures, the NH$_3$ transitions are pressure-broadened at pressures greater than 50 Torr. The gas pressure does affect the small-signal gain indirectly through the relaxation rates and their magnitudes relative to the pumping rate. The rotational relaxation rate, which is associated with
the pressure-broadened linewidth, determines the pump saturation intensity (see Eq. 6.1). In Chapter 6, we found that gain was relatively independent of pump intensity for intensities greater than the pump saturation intensity. Thus, for a given concentration, the small-signal gain is independent of pressure, provided that the pump intensity is sufficiently high. The minimum intensity to maintain this condition increases as the square of the pressure, the scaling law for the pump saturation intensity. A practical upper limit to the pump intensity is defined by the optical breakdown threshold of the gases and materials used in an NH$_3$ laser. In NH$_3$-N$_2$ mixtures that limit is 1 GW/cm$^2$ [57], and a similar value holds for crystals of NaCl [65], a common window material. Several manufacturers of high-power reflective optics quote optical damage thresholds of between 0.1 and 1 GW/cm$^2$. For this study, we will take 100 MW/cm$^2$ as a conservative upper limit for the pump intensity.

We carried out measurements of small-signal gain coefficients as a function of pressure to test our model of the gain dynamics. The experimental apparatus and technique is identical to that discussed in Chapter 6, particularly with respect to the study of gain as a function of concentration. The NH$_3$ oscillator and amplifier are pumped by the 9R(30) CO$_2$ line. In the 11-cm long amplifier cell, the pump beam is tightly focused to produce pump intensities of 1 MW/cm$^2$ in the tail of the pump pulse immediately after the peak (see Fig. 6.2). The aP(4,0) transition was chosen for the gain measurements as it generally has the highest gain coefficients and is easily produced in the NH$_3$ probe.
laser. In Chapter 6, a concentration of 4% NH$_3$ in N$_2$ was shown to be the optimum mixture for small-signal gain. Thus, a 4% NH$_3$ mixture was employed for the initial measurements of gain as a function of pressure, and the results are shown in Fig. 7.1. The experimental points were evaluated for a pump intensity of $\sim$1 MW/cm$^2$, 0.6 $\mu$s after the peak of the pump pulse. The gain coefficients are greater than 15 cm$^{-1}$ for pressures up to 80 Torr, but fall rapidly with increasing pressure to $\sim$4 cm$^{-1}$ at $\sim$250 Torr. It was noted in Chapter 6 that the gain was reduced in high concentration mixtures by increases in the gas temperature due to pump absorption. Accordingly, the solid curve in Fig. 7.1 is the pressure dependence calculated with the rate-equation model modified to allow temperature increases during the pump pulse, as described in Chapter 6. The dotted curve shows the predicted gain coefficients for a constant gas temperature of 300 K. The pump pulse shape used in these calculations was determined from the experiment (see Fig. 6.2). Clearly, the solid curve is in much better agreement with the experimental measurements. At 300 Torr the variable-temperature calculation predicts a temperature rise of $\sim$180 K at 0.6 $\mu$s after the peak of the pump pulse. The more important point is that with a 4% NH$_3$ concentration the maximum useful pressure is $\sim$300 Torr for a pump intensity of $\sim$1 MW/cm$^2$. To obtain useful gain coefficients in higher pressures of this mixture will require much higher pumping intensities. A shorter pump pulse of 100 ns duration, rather than the 1 $\mu$s pulse used for the experimental measurements, will also help to limit the rise in temperature. The dashed curve in Fig. 7.1 is a calculation of gain coefficients for a Gaussian-shaped pulse of 100 ns FWHM and peak
Fig. 7.1: Comparison between theory and experiment for small-signal gain coefficients of \( aP(4,0) \) as a function of pressure in a mixture of 4\% NH\(_3\) in N\(_2\). The experimental points were measured for a pump intensity of \( \sim 1 \text{ MW/cm}^2 \), 0.6 \( \mu \text{s} \) after the peak of the pump pulse. The solid curve is calculated with the gas temperature allowed to rise due to the energy absorbed from the pump. The dotted curve is calculated assuming that the gas temperature remains constant at 300 K. Both curves are calculated for the pump pulse shape used in the experiment. The dashed curve is a variable-temperature calculation for a peak pump intensity of 100 MW/cm\(^2\) in a Gaussian-shaped pulse of duration 100 ns FWHM.
intensity of 100 MW/cm². In the absence of temperature increases, the factor of 100 increase in pump intensity provides a factor of 10 increase in the maximum useful pressure. The calculation for the dashed curve includes temperature changes. Gain coefficients >5 cm⁻¹ are predicted up to 5000 Torr, but only at the expense of very high gas temperatures. At 5000 Torr the calculated temperature at the peak of the pump pulse is 570 K, a rise of 270 K. Besides the reduction in the gain coefficients, the major problem with such a large and rapid temperature increase is distortion of the optical beam if the entire gas is not heated uniformly. Furthermore, significant gas heating necessitates an efficient cooling mechanism to remove the heat if high repetition rates are desired.

In mixtures of lower NH₃ concentration there is less pump absorption and consequently less heating. Figure 7.2 shows the experimental and predicted results for a mixture of 0.5% NH₃ in N₂. In this case there is very little difference between the constant-temperature and variable-temperature calculations for the pump intensity of 1 MW/cm². Both calculations predict gain coefficients in good agreement with the experimental measurements. Although the gain coefficients are generally lower than for the 4% NH₃ mixture, it is possible to maintain significant gains up to much higher pressures. The predicted temperature rise is less than 30 K for all pressures and the gain coefficient remains above 3 cm⁻¹ out to 1000 Torr. Higher pump intensities are required to achieve similar gain coefficients at higher pressures. The dashed curve is a variable-temperature calculation with the Gaussian-shaped 100-ns pulse and a peak intensity of 100 MW/cm². At 10⁴ Torr the calculated
Fig. 7.2: Comparison between theory and experiment for small-signal gain coefficients of aP(4,0) as a function of pressure in a mixture of 0.5% NH₃ in N₂. See caption of Fig. 7.1 for full details.
temperature rise at the peak of the pulse is less than 30 K. This temperature rise is insignificant while the gain coefficient is higher than that predicted at $10^4$ Torr from a 4\% NH$_3$ mixture. There should be no need to use mixtures of less than 0.5\% NH$_3$ in real lasers, unless the rise in temperature must be limited still further. The study by Akhrarov et al. [57] reported that a 0.15\% concentration was necessary to have the laser operate at 3.2 atm ($\sim$2400 Torr) for a pump intensity of 11.5 MW/cm$^2$. If we scale this pump intensity to 100 MW/cm$^2$ (factor of 9 increase), then their device should operate up to $\sim$10 atm (7500 Torr, factor of $9^{1/2}$ increase), in accord with the predicted gain coefficients in Fig. 7.2. Thus, a 10-atm NH$_3$ laser appears to be feasible. From the calculations in Section 7.1, we can predict the fractional tuning range covered by such a laser operating on the $P$-branch transitions. We estimate that emission from a tunable 10-atm NH$_3$ laser will cover $\sim$36\% of the wavelength range from 10.5 to 13.8 $\mu$m.

Synchronous-pumping with a train of short mode-locked pulses is another technique which may be successful in achieving laser operation at pressures greater than 1 atm. As the vibration-translation relaxation rate is very fast at such high pressures it is necessary to have sufficient pump intensity in each pulse to produce gain; there can be no buildup of gain by a succession of pulses. Very high gain coefficients would be necessary to achieve a rapid buildup of an NH$_3$ laser pulse and minimize the number of pump pulses required. Calculations for a 4\% mixture at 5000 Torr and a Gaussian-shaped pump pulse of 1 ns FWHM in duration indicate that a peak intensity of 100 MW/cm$^2$ is insufficient to create
gain. For a peak intensity of 1 GW/cm² the model predicts a peak gain coefficient of 22 %cm⁻¹ with positive gain lasting for more than 2 ns. The model also predicts a temperature rise of ~12 K. The temperature rise is still a problem as the heat could not be extracted during a train of mode-locked pump pulses, typically 10-20 in number.

One partial solution to the problem of excessive gas heating is to begin with a gas temperature lower than 300 K. Previous studies have shown that NH₃ laser operation is enhanced for gas temperatures as low as 200 K [48,55,66]. However, this only moves the regime of operating temperatures to a lower range, and does not solve the problem of a rapid rise in temperature which may produce distortion in the optical path. The only real solution is to limit the change in temperature either by reducing the NH₃ concentration, or by utilizing a buffer gas which has better thermal properties (i.e. higher heat capacity, and higher heat conductance) than N₂, yet which retains the properties of a good buffer gas as defined in Chapter 5.

7.3 Overlapping Absorptions

A situation that occurs in many applications of molecular gases is an overlap in frequency of transitions in one band by transitions in another band, usually in the same mode. In CO₂ lasers this situation resulted in the development of sequence band lasing [67]. Many of the sequence transitions in CO₂ contribute to gain on the regular band transitions, but that is only because all of the vibrational modes are pumped by an electric discharge. In most optically-pumped NH₃ lasers, only one vibrational level is excited, the v₂ level. Thus, the
selective pumping increases the absorption on all transitions whose lower level is the \( \nu_2 \) level, such as the \( 2\nu_2 \) band transitions which overlap the \( \nu_2 \) band transitions. Thus, any \( 2\nu_2 \) transitions which lie close in frequency to \( \nu_2 \) transitions will tend to reduce the gain on those \( \nu_2 \) transitions. Pressure broadening will increase the interference, and tend to reduce tunability of the laser emission rather than increase it. High-resolution spectroscopy is a valuable aid for revealing transitions where overlaps occur. Figure 7.3 displays frequency scans taken with a tunable-diode-laser (TDL) in the region near the \( aP(7,3) \) transition. A sweep-integration technique was employed \([68,69]\), and the scans shown are an average of four sweeps. The TDL was used to probe a cell containing an \( \text{NH}_3 \) mixture which could be pumped by a cw \( \text{CO}_2 \) laser. With the \( \text{CO}_2 \) laser off there is only absorption on the \( aP(7,3) \) transition. Turning the \( \text{CO}_2 \) laser on creates gain on \( aP(7,3) \) and simultaneously creates absorption on \( 2sP(7,1) \), 460 MHz away from \( aP(7,3) \). These scans were taken at a pressure of 5 Torr in a 1% mixture. At pressures over 100 Torr, absorption on the \( 2sP(7,1) \) transition would significantly reduce the gain coefficient at the line center of \( aP(7,3) \).

The available spectroscopic data are not sufficiently accurate to evaluate the overlapping absorptions for all the \( \nu_2 \) transitions. A more direct method is to measure the gain coefficients as a function of pressure for the \( \nu_2 \) transitions of interest. Measurements of gain coefficients at 76 Torr and 500 Torr are displayed in Fig. 7.4 for a range of \( \nu_2 \) transitions. As predicted from Fig. 7.3, the \( aP(7,3) \) gain coefficient is much reduced at the higher pressure. The gain coefficient for one other transition, \( aP(8,2) \), changes from a small positive value
Fig. 7.3: High-resolution frequency scan of the region near \(\Delta P(7,3)\) taken with a tunable-diode-laser probing a \(\text{CO}_2\) laser-pumped sample cell containing 1% \(\text{NH}_3\) in \(\text{N}_2\) at a total pressure of 5 Torr. The middle trace shows that there is only absorption on \(\Delta P(7,3)\) when the \(\text{CO}_2\) laser is off. The upper trace shows that gain is produced on \(\Delta P(7,3)\) when the \(\text{CO}_2\) laser is on, and simultaneously an absorption feature, identified as \(2s\Delta P(7,1)\), appears 460 MHz away. The bottom trace is a frequency calibration of the TDL with an etalon; 1 fringe is 0.01627 cm\(^{-1}\).
Fig. 7.4: Comparison between measured and calculated small-signal gain coefficients for a range of transitions in a mixture of 0.46% NH₃ with N₂ at 76 Torr and 500 Torr. The experimental values were obtained at a pump intensity of ~1 MW/cm², 0.6 μs after the peak of the pump pulse. Two sets of calculations are displayed. The thick cross bars indicate the calculations which include all the known overlapping gain and absorption contributions due to ν₂ and 2ν₂ NH₃ transitions within ±30 GHz (1.0 cm⁻¹) of each transition listed. (At 500 Torr, 30 GHz corresponds to ~18 half-widths.) Thin cross bars, where they appear, indicate the gain coefficients calculated by excluding all overlapping gain contributions.
NH₃ TRANSITIONS

(a) 76 Torr
(b) 500 Torr

GAIN COEFFICIENT (\% cm⁻¹)

- Experiment
- Calculation
at 76 Torr to a large negative value at 500 Torr. This dramatic change is due to interference by $2aR(6,3)$, a very strong absorption ~1.7 GHz away. This result is particularly interesting as the unpumped absorption on $aP(8,2)$ in 500 Torr was one-third of the absorption in the presence of the pump. The large increase in absorption with pumping supports the contention that a $2\nu_2$ absorption is the source of interference. Most of the other transitions show much less change in their gain coefficients. There is an overall decrease in the gain coefficients at the higher pressure due to the increase in the relaxation rates relative to the pumping rate which reduces the population inversion. Less effective pumping is more noticeable on the Q and R transitions, as they are more sensitive to changes in the population inversion. The calculated gain coefficients in Fig. 7.4 were obtained by including all the known overlapping transitions from the $\nu_2$ and $2\nu_2$ bands within ±30 GHz of the $\nu_2$ transitions of interest. Of course, the contributions due to overlapping inverted $\nu_2$ transitions increase the gain coefficients. The overall agreement between theory and experiment is very good for both pressures despite the uncertainties of frequency and linestrength for the $2\nu_2$ transitions. All other overlapping bands, such as $\nu_4+\nu_2$ to $\nu_2$, were neglected. The final arbiter of useful laser transitions at high pressure is experiment. In the study by Akhrarov et al. [57] the only emissions observed at the highest pressures (>2.5 atm) were due to the $sP(5,K)$ transitions. However, their results were obtained in a non-selective cavity. Laser operation in a line-tunable cavity would certainly produce many other emissions at high pressures. The experimental results in Fig. 7.4 illustrate several transitions which would probably
remain useful up to a few atmospheres of pressure.

7.4 Summary

In this chapter we have examined the potential for operating line-tunable NH$_3$ lasers at pressures of several atmospheres. The motivation for developing high-pressure NH$_3$ laser operation is to increase the tunability of the emission and produce sub-nanosecond pulses. Experimental measurements of small-signal gain coefficients illustrate that NH$_3$ concentrations of 0.5% or less must be employed to minimize the problem of gas heating. Theoretical calculations indicate that a pump intensity of 100 MW/cm$^2$, a reasonable upper limit for preventing optical breakdown in the laser, creates sufficient gain for laser action in a 0.5% NH$_3$ in N$_2$ mixture up to 10 atm (7600 Torr). The maximum continuous tuning range at a pressure of 10 atm is estimated to be $\sim$120 GHz (4 cm$^{-1}$), which is sufficient gain bandwidth to support pulses less than 10 ps in duration. Most transitions will give 30-50 GHz tunability at 10 atm. Obvious exceptions are the aP(7,3) and aP(8,2) transitions, which have their gain coefficients drastically reduced due to overlapping absorption from $2\nu_2$ band transitions. Measurements indicate that several interference-free transitions do exist, but there remains a need for high-resolution spectroscopy to help identify such transitions. If we neglect overlapping absorption, then our calculations predict that a 10-atm NH$_3$ laser operating on the P-branch transitions will be tunable across $\sim$36% of the wavelength range from 10.5 to 13.8 $\mu$m.
CHAPTER 8
LINE-TUNABLE NH₃ LASER OPERATING ON THE 2ν₂ - ν₂ TRANSITIONS

8.1 Introduction

Previous chapters have examined optically-pumped NH₃ lasers which are efficient line-tunable sources in the 11- to 13-μm wavelength region. In this chapter we describe a novel technique using two TEA CO₂ lasers to extend line-tunable NH₃ laser operation to the 16- to 21-μm region. Lasing at these longer wavelengths is obtained by inverting transitions in the 2ν₂ band with a two-step optical-pumping process.

For the first step a TEA CO₂ laser operating on the R(30) 9-μm line is used to pump the NH₃ sR(5,0) transition in a dilute mixture of NH₃ with N₂, and to transfer a significant fraction of the ground state population to the ν₂ vibrational level. For the second step, another TEA CO₂ laser operating on the 9P(24) line pumps the 2sR(4,3) NH₃ transition and transfers population to the 2ν₂ level. During each pulse rapid rotational thermalization occurs in all vibrational levels due to the presence of N₂ as a buffer gas. This rapid thermalization allows the utilization of two of the best available coincidences between CO₂ laser lines and R-branch lines in NH₃ (pumping in the R-branch allows both P- and Q-branches to be inverted [53,54], and good line-tunability obtained). The small size of the pump offsets, 190 MHz for R(30) [31] and 475 MHz for P(24) [30], ensures good absorption of the pump energy, which provides the potential for high conversion efficiency.
Previous studies of two-step [70,71] and two-photon [10,72-74] optical pumping of NH$_3$ have also reported lasing on 2v$_2$ transitions, but only in pure NH$_3$ at low pressures. In contrast to our pumping scheme, these other techniques rely either on a radiative cascade in the v$_2$ level to couple the two pumping transitions [70,71], or on direct two-photon absorptions which are sensitive to the overall pump offset [10,72-74]. Consequently, both methods generally have low pump absorption which results in poor efficiency. In addition, line tuning is limited to those transitions connected by radiative cascade to the upper pumped level.

Section 8.2 describes the two pump lasers and examines the results of a preliminary experiment performed to demonstrate the feasibility of two-step pumping. Section 8.3 discusses the laser cavities employed to produce lasing on the 2v$_2$ transitions. A careful examination of the two-step pumping process accounts for the transitions observed and the behaviour of their emissions. Typical values of lasing efficiency and energy output are reported. Section 8.4 is a brief study of possible extensions to the two-step pumping technique, including cw line-tunable operation and the use of different isotopes to extend the wavelength tuning range.

8.2 The Two Pump Lasers and Pump Absorption Measurements

A basic requirement for two-step pumping is two CO$_2$ lasers. One of the lasers is the hybrid single-mode device described in Chapter 3. This laser was tuned to the 9P(24) CO$_2$ line. The second laser is a single TEA discharge module (Lumonics K-901-L), 60 cm long, in a grating-
tunable cavity. The second laser, tuned to the 9R(30) CO$_2$ line, produces pulses consisting of a single transverse mode (TEM$_{00}$) and many longitudinal modes. Thus, the R(30) and P(24) pump pulses are both spatially uniform but differ in frequency content. Broadband radiation is acceptable for the first pumping step with R(30), as many NH$_3$ lasers have been successfully created with such a pump [9,11,17]. The single-mode P(24) pulse enables better characterization of the P(24) absorption in the gas mixtures. Typical pulse shapes of the two lasers are shown later in Section 8.3.

An examination of the feasibility of two-step pumping in a buffered gas mixture was carried out by measuring the small-signal absorption of the P(24) pump. A 42-cm cell containing a dilute mixture of NH$_3$ in N$_2$ was pumped collinearly by the R(30) pulse from the reflection of a dielectric-coated mirror of 90% reflectivity. The attenuated P(24) pulse was made orthogonally polarized to the R(30) pulse and entered the cell at the other end from the internal reflection off a KRS-5 Brewster window. The orthogonal linear polarization of the two beams eliminated interference between the two lasers without adversely affecting the absorption measurements. Apertures were placed at either end of the cell to ensure that the two beams overlapped in space. The firing of the laser discharges was arranged so that the pump and probe pulses coincided in time. The fraction of the P(24) pulse transmitted by the 90% reflectivity mirror was focused onto a fast HgCdTe detector (risetime <50 ns). Absorption measurements were performed at a fixed time delay after the peak of the R(30) pulse. The absorption coefficients were evaluated from the ratio of the P(24)
Fig. 8.1: Small-signal absorption coefficients of the $9R(24)$ CO$_2$ line in mixtures of NH$_3$ with N$_2$ pumped by the $9R(30)$ CO$_2$ line. The measurements were taken for a pump intensity of $\sim 140$ kW/cm$^2$, at 0.6 $\mu$s after the peak of the $9R(30)$ pump pulse.
signal with and without gas in the cell. The results are displayed in Fig. 8.1. The high values of the absorption coefficients illustrated in Fig. 8.1 should be contrasted with the low thermal absorption observed when no R(30) pump was present in the cell. In the absence of pumping, the absorption coefficient for P(24) was always less than 1.2 cm\(^{-1}\). Thus, pumping sR(5,0) with R(30) creates significant absorption for P(24) on the 2sR(4,3) transition. The absorption coefficients scale with the NH\(_3\) concentration at low pressures but decrease at higher pressures. The drop in absorption is due to attenuation of the R(30) pump, which results in non-uniform pumping of the cell. The measurements provide an excellent guide to the selection of NH\(_3\) concentrations and total pressures for potential 2\(v_2\) laser operation. Mixtures containing 1\% NH\(_3\) or less in pressures up to \(\approx\)150 Torr should be the most useful. Higher NH\(_3\) concentrations do not provide any increase in population inversion as the absorption scales with NH\(_3\) concentration. Pressures greater than \(\approx\)150 Torr will merely increase the relaxation rates without increasing the absorption coefficient proportionately.

The most important point illustrated by the results in Fig. 8.1 is that, as expected from our earlier results, sufficient rotational thermalization does occur in the \(v_2\) level to make two-step pumping a feasible process.

8.3 The 2\(v_2\) NH\(_3\) Laser

Two different pumping configurations were used in our next set of experiments, as shown schematically in Fig. 8.2. The R(30) and P(24)
pump beams were combined on a grating, $G_1$. The initial experiments to produce lasing were carried out by rotating the linear polarization of the combined $\text{CO}_2$ radiation and longitudinally pumping a 42-cm long cell from the internal reflection off a KRS-5 Brewster window (Fig. 8.2(a)). A high-Q non-selective cavity was formed for the $\text{NH}_3$ laser with concave metal mirrors. The $\text{NH}_3$ radiation reflected from the second KRS-5 Brewster window was focused through a 1/2-m monochromator onto a HgCdTe detector. In the second pumping scheme, Fig. 8.2(b), the $\text{NH}_3$ cavity contained the $\text{CO}_2$ beam-combining grating, which totally reflects wavelengths greater than 14.8 $\mu$m into zeroth order. The combined $\text{CO}_2$ radiation collinearly pumped a 110-cm long cell sealed with KBr Brewster windows. A second grating, $G_2$, provided line-tunable $\text{NH}_3$ laser operation, and restricted the pump beams to a single pass. Thus, only $\text{NH}_3$ radiation was present in the second arm of the cavity, which was terminated by a partially transmitting dielectric-coated ZnSe mirror. An energy meter and a HgCdTe detector were used to monitor the $\text{NH}_3$ laser emission.

Lasing on several $2\nu_2$ transitions was observed on the first attempt with the non-selective cavity. Table 8.1 lists the observed wavelengths together with the transition identifications and the calculated frequencies. The measurements were made on the ndn-selective cavity with a gas mixture of 0.5% $\text{NH}_3$ in $\text{N}_2$ at a total pressure of 50 Torr (the last two lines in Table 8.1 were only observed in a 0.25% $\text{NH}_3$ in $\text{N}_2$ mixture). To account for the particular transitions observed requires a more detailed examination of the two-step pumping process. A fundamental requirement for the occurrence of multi-line operation is that rapid rotational thermalization occurs within each vibrational
Fig. 8.2: Schematic diagrams of the two pumping configurations. The CO$_2$ pump beams are combined on grating $G_1$ (135 lines/mm, blazed for 10.6 $\mu$m). (a) High-Q non-selective cavity collinearly pumped from the internal reflection off a KRS-5 Brewster window. (b) Grating $G_2$ (40 lines/mm, blazed for 22.5 $\mu$m), provides line-tunable operation while $G_1$ totally reflects wavelengths greater than 14.8 $\mu$m into zeroth order. Mirror $M$ transmits ~30% at 18 $\mu$m. The Freon cell contains Freon 12 and Freon 114, and absorbs both 9-$\mu$m pump beams.
Table 8.1

Observed $2\nu_2-\nu_2$ NH$_3$ laser lines.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency$^a$ Calculated [cm$^{-1}$]</th>
<th>Frequency Observed [±0.04 cm$^{-1}$]</th>
<th>Wavelength Observed [±0.001 μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2aP(8,6)</td>
<td>468.866(3)</td>
<td>468.75</td>
<td>21.333</td>
</tr>
<tr>
<td>2aP(8,3)</td>
<td>484.971(4)</td>
<td>484.92</td>
<td>20.622</td>
</tr>
<tr>
<td>2aP(7,6)</td>
<td>485.386(4)</td>
<td>485.34</td>
<td>20.604</td>
</tr>
<tr>
<td>2aP(8,0)</td>
<td>491.204(9)</td>
<td>491.20</td>
<td>20.358</td>
</tr>
<tr>
<td>2aP(7,3)$^c$</td>
<td>499.763(3)</td>
<td>499.80</td>
<td>20.008</td>
</tr>
<tr>
<td>2aP(6,3)$^c$</td>
<td>515.426(4)</td>
<td>515.43</td>
<td>19.401</td>
</tr>
<tr>
<td>2aP(6,0)$^d$</td>
<td>520.884(5)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>2aP(5,3)$^c$</td>
<td>531.967(3)</td>
<td>531.97</td>
<td>18.798</td>
</tr>
<tr>
<td>2aP(4,3)</td>
<td>549.320(4)</td>
<td>549.37</td>
<td>18.203</td>
</tr>
<tr>
<td>2aP(4,0)</td>
<td>554.106(5)</td>
<td>554.14</td>
<td>18.046</td>
</tr>
<tr>
<td>2aP(2,0)</td>
<td>590.409(6)</td>
<td>590.45(21)$^e$</td>
<td>16.936(6)</td>
</tr>
<tr>
<td>2aq(3,3)</td>
<td>628.348(4)</td>
<td>628.40(12)$^e$</td>
<td>15.913(3)</td>
</tr>
</tbody>
</table>

$^a$Calculated by combining $\nu_2$ and inversion-rotation frequencies from Ref. 75 with Ga-$2\nu_2$s frequencies from Ref. 76. Numbers in parentheses are estimated uncertainties from Ref. 76.

$^b$Vacuum wavelength.

$^c$Also observed by Pinson et al., Ref. 71.

$^d$Does not lase because R(30) directly populates the lower level.

$^e$Larger errors due to unstable laser emission on these lines.
level, induced by collisions between NH$_3$ and N$_2$ molecules. Recall that each vibrational level in the $\nu_2$ mode is split into a lower symmetric (s) and an upper anti-symmetric (a) level; the separation increasing with vibrational quantum number. The R(30) pump transfers population from the ground state to the $\nu_2$s level which then populates the $\nu_2$a level by thermalizing collisions as illustrated in Fig. 8.3. This effectively creates a new "ground state" from which to populate the $\nu_2$a level by pumping with P(24). The $\nu_2$s level is then populated by thermalization with the $\nu_2$a level. At room temperature the 36 cm$^{-1}$ splitting of the $\nu_2$ level produces 16% less population in $\nu_2$a than in $\nu_2$s. Similarly, the 285 cm$^{-1}$ splitting of the $\nu_2$ level means that $\nu_2$s contains 4 times the population of the $\nu_2$a level. Thus, 2a-transitions ($\nu_2$s-$\nu_2$a) are much more likely to lase than 2s-transitions ($\nu_2$a-$\nu_2$s).

As expected, we have only observed the 2a-transitions listed in Table 8.1 and shown in Fig. 8.3. Furthermore, only ortho-NH$_3$ (K=3n) transitions were seen, consistent with the facts that P(24) pumps only ortho-NH$_3$, and that there is no interconversion between ortho- and para-NH$_3$ (K=3n±1).

To examine the relative strength of the $\nu_2$a transitions in the NH$_3$ laser the cavity shown in Fig. 8.2(a) was converted to single-line tunable operation by replacing one mirror with grating G$_2$. Lasing was obtained on all of the transitions observed previously. The optimum conditions were 0.5% NH$_3$ at a total pressure of 80 Torr. The largest gain coefficients were obtained on the 2aP(4,0) and 2aP(5,3) lines, as estimated from the build-up time of the radiation from the onset of the P(24) pulse. All transitions other than those with J=6 behaved as
Fig. 8.3: Left: The two pump transitions and the lasing transitions are illustrated together with the appropriate vibrational energy levels. The wavy lines indicate rotational thermalization. Right: An enlargement of the dashed box on the left showing the rotational energy levels of most of the lasing transitions observed.
expected for a thermalized distribution of rotational populations. The 2aP(6,0) transition was absent, undoubtedly due to the fact that its lower level is the upper level of sR(5,0), which is pumped by R(30). Pulses from 2aP(6,3) were delayed with respect to those from 2aP(7,3), indicating a lower gain coefficient for 2aP(6,3), although the reverse is expected in a thermalized rotational distribution. The lower level of 2aP(6,3) is the upper level of sR(5,3), which is also pumped by R(30) but not as effectively as is sR(5,0). The non-thermalized populations on the upper levels of sR(5,0) and sR(5,3) are created by pumping with R(30), and are sufficient to eliminate the gain on 2aP(6,0) and reduce the gain on 2aP(6,3).

The typical time dependence of the pump pulses and NH₃ radiation is shown in Fig. 8.4 for the case of 2aP(4,0). The P(24) pulse was deliberately delayed with respect to the R(30) pulse. The 2aP(4,0) signal did not begin until after the onset of the P(24) radiation; no 2v₂ transitions were observed by pumping with R(30) alone. Due to the long tail in the R(30) pump pulse the relative timing of the two pump pulses was not very critical. Delaying the onset of the P(24) pulse by up to 2.5 μs only reduced the 2aP(4,0) signal to half its peak value. The duration of the NH₃ pulse decreased with increasing NH₃ concentration and total pressure, roughly corresponding to increases in the vibration-translation relaxation rate [52].

The pumping configuration shown in Fig. 8.2(b) with the longer NH₃ cell was used to investigate energy conversion. Maximum energy
Fig. 8.4: Oscilloscope traces of the CO$_2$ pump pulses and the $2aP(4,0)$ NH$_3$ pulse produced from 0.25% NH$_3$ in N$_2$ at 60 Torr. All traces are four-shot averages, detection-limited by the 25 MHz sampling rate of the digital storage oscilloscope.
output of 0.38 mJ was obtained on the 2aP(4,0) transition*. This energy was obtained from a 0.5% NH₃ mixture at 80 Torr, with a conversion efficiency (energy emitted/pump energy absorbed) of 0.26%. The fraction of total energy absorbed from the combined pump beams was 33%, of which two thirds was from the P(24) beam. For a wide range of R(30) pump energies the 2aP(4,0) output energy was directly proportional to the P(24) energy absorbed. This supports the idea that the ν₂ level acts as a new "ground state" for the 2ν₂ transitions. The overall conversion efficiency obtained is comparable to previously reported values for 2ν₂ lasing [10,71-73], and considerable improvements in efficiency can be expected with better optics.

8.4 Prospects for Other Line-Tunable 2ν₂ Lasers

The 2ν₂ NH₃ laser described in the previous section can only emit on ortho-NH₃ transitions. To extend the line-tuning capability of this NH₃ laser to the para-NH₃ transitions a different pump line is required for the second pumping step. Only possible pump coincidences with 2sR-transitions are considered since it is well known that pumping in the R-branch is significantly better than pumping in the P- or Q-branch [53,54]. Table 8.2 lists three possibilities for pulsed pumping with 12C¹⁶O₂ laser lines. One 12C¹⁸O₂ line lies within the Doppler width, and opens the possibility for cw lasing by pumping on resonance.

*Measurements show that the ZnSe mirror absorbs ~40% of the laser emission on 2aP(4,0).
Table 8.2
Pump coincidences with $^{14}$NH$_3$ for two-step pumping.

<table>
<thead>
<tr>
<th>Transitions $^{NH_3}$</th>
<th>Pump$^a$</th>
<th>Offset$^b$ [MHz]</th>
<th>Transitions $^{NH_3}$</th>
<th>Pump$^a$</th>
<th>Offset$^b$ [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>sR(5,0)</td>
<td>626r 9R(30)</td>
<td>-190$^c$</td>
<td>2sR(4,3)</td>
<td>626r 9P(24)</td>
<td>-475$^e$</td>
</tr>
<tr>
<td>aR(3,3)</td>
<td>636r 9P(8)</td>
<td>77</td>
<td>2sR(3,1)</td>
<td>626r 9P(44)</td>
<td>472</td>
</tr>
<tr>
<td>sR(5,1)</td>
<td>626r 9R(30)</td>
<td>-345$^d$</td>
<td>2sR(4,2)</td>
<td>626s 9P(23)</td>
<td>720</td>
</tr>
<tr>
<td>aR(5,1)</td>
<td>626s 9P(7)</td>
<td>-86$^c$</td>
<td>2sR(6,2)</td>
<td>828r 9P(16)</td>
<td>-56</td>
</tr>
<tr>
<td>aQ(8,7)</td>
<td>N$_2$O P(13)</td>
<td>10</td>
<td>2sR(7,2)</td>
<td>626r 9R(34)</td>
<td>545</td>
</tr>
<tr>
<td>aQ(8,7)</td>
<td>636s 10R(23)</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Three digits represent CO$_2$ isotopes, e.g. 626=^{12}$^{16}$O$_2$: r, regular bands; s, sequence bands.

$^b$(NH$_3$-Pump). NH$_3$ frequencies from Ref. 77 for $\nu_2$ transitions, and calculated from Refs. 75 and 78 for $2\nu_2$ transitions, except for offsets noted. Pump frequencies from Refs. 79-82.

$^c$Ref. 31. $^d$Ref. 60. $^e$Ref. 30.
with both pumping steps. Recently Rolland et al. [27] have obtained cw line-tunable operation on the ortho-$^{14}$NH$_3$ $v_2$ transitions by pumping on resonance with $R(30)$, downshifted 180 MHz in two acousto-optic modulators. This technique can be readily applied to any pump line, and Table 8.2 lists two $v_2$ coincidences which would require only one modulator, and a third line which is already resonant. Two-step pumping can be applied to other NH$_3$ isotopes such as $^{15}$NH$_3$ and $^{14}$ND$_3$ if appropriate pump coincidences can be found, thereby augmenting the wavelength tuning range in the pulsed, and possibly the cw, regime.

8.5 Summary

In this chapter we report the first demonstration of line-tunable lasing on $2v_2$ NH$_3$ transitions. A two-step pumping technique, employing two of the best CO$_2$ laser coincidences, one for each of the $v_2$ and $2v_2$ bands, is applied to mixtures of NH$_3$ buffered with N$_2$. The technique relies on rapid thermalization of the rotational populations in all vibrational levels. The thermalization concept is validated by absorption measurements and by laser emission on many $2v_2$ ortho-NH$_3$ transitions. The $2v_2$ laser operation is explained in detail, and typical values of efficiency and energy output are presented. Methods for creating cw operation and extending the wavelength tuning range are also discussed.
CHAPTER 9

CONCLUSIONS

In this final chapter, the conclusions that can be derived from the work are presented. The intent of the research was to elucidate the principles of operation of optically-pumped pulsed mid-infrared NH$_3$ lasers, and we have, to a great extent, succeeded. Prior to this work, there was little known about the gain dynamics of NH$_3$ lasers. Now, there are two models, one for each of the two gain mechanisms in optically-pumped NH$_3$. Both models have been validated by an extensive series of experiments. The purpose of this chapter is to relate the significance of these theoretical and experimental results to the future development of NH$_3$ lasers, and of optically-pumped molecular lasers in general.

The two gain mechanisms in optically-pumped NH$_3$ lasers are the Raman process and population inversion. Both processes are always present, but one or the other generally dominates the gain dynamics, depending upon the pumping conditions. As discussed in Chapter 2, the size of the pump offset frequency, relative to the NH$_3$ transition linewidth and to the Rabi frequency associated with the pump radiation field, plays a major role in the gain dynamics. In general, Raman gain dominates at large pump offsets, and inversion gain dominates at small pump offsets. Consequently, a range of pump transitions was selected for the experiments so that the two gain mechanisms could be investigated independently. The most important factor in facilitating the comparison between theory and experiment throughout this work was
the use of a single-mode line-tunable $\text{CO}_2$ laser as the pump source. This pump laser provided a well-characterized pump intensity at a fixed pump offset.

All of the experiments on Raman gain are discussed in Chapter 4 and in Refs. 83 and 84. Raman gain is a coherent process which involves the simultaneous interaction of two radiation fields with three molecular levels. An appropriate theory for this process is a quantum-mechanical density-matrix model. At low pump intensities in pure $\text{NH}_3$, the laser gain spectrum is characterized by a strong absorption at line center, and by Raman gain at a frequency which is offset from the emitting transition by an amount comparable to the pump offset. At higher pump intensities, the Raman gain and the absorption feature at line center are shifted away from each other by the ac Stark effect. Experiments show that the ac Stark shift affects both of the mid-infrared transitions which are directly connected to the pumped transition employed. The density-matrix model predicts the appearance of Raman gain and ac Stark shifts for all transitions which have one level in common with the pumped transition. However, in pure $\text{NH}_3$ we have obtained Raman emission only on the directly pumped transition; the one whose upper level is in common with the pumped transition. To produce Raman emission from the second connected transition (lower level in common with the pumped transition) requires pumping of mixtures of $\text{NH}_3$ with a buffer gas. At high pump intensities in these mixtures, the pump laser induces significant population transfer, which creates gain near the line center of both connected transitions in addition to the Raman emission. Small-signal gain measurements on both the inversion
and Raman components of the connected transitions are in good agreement
with calculations of the density-matrix model. Accurate predictions
with this model require a detailed knowledge of the pump intensity and
level populations. Under conditions of significant population transfer,
we find that a rate-equation calculation can be employed to calculate
the level populations, as the density-matrix model treats the three
rotational levels in isolation from the total vibrational populations.
The overall conclusions from Chapter 4 are that the Raman process and ac
Stark shifts affect the gain dynamics of all transitions which form a
three-level system with the pumped transition and that a density-matrix
model describes these effects properly and accurately.

Inversion gain dominates the gain dynamics of NH₃ lasers under
conditions of significant population transfer. These conditions are
obtained with high pump intensities in buffered gas mixtures. In
Chapter 5 and Ref. 84, we show that a simple rate-equation model
accounts for all the major features of inversion gain dynamics in pulsed
NH₃ lasers. The entire distribution of gain and absolute gain
coefficients are accurately predicted by the model which is based on two
major concepts: (1) the distribution of rotational level populations is
completely thermalized, except for the levels of the pumped transition,
and (2) there is no vibrational energy transfer between ortho-NH₃ and
para-NH₃. The concept of rotational thermalization permits the relative
gain coefficients for all transitions to be characterized by a single
parameter, N₁/N₀, which is the ratio of the vibrational population in
the first excited state to that in the ground state of the ν₂ mode.
Prior to this work, there was no adequate explanation for the distribution of emitting transitions in line-tunable NH$_3$ lasers. Rotational thermalization also occurs between the a- and s-levels of each vibrational state. Consequently, the 36 cm$^{-1}$ splitting of these levels in the 1$_2^+$ state accounts for the observation of higher gain coefficients on the a-transitions than on the corresponding s-transitions. This conclusion resolves the issue noted by previous researchers that lasers operate differently on a-transitions than on s-transitions [9,17]. Recognition of the distinction between ortho-NH$_3$ and para-NH$_3$ is essential to an understanding of NH$_3$ laser operation, as there is no thermalization between the two species of NH$_3$. To obtain gain on ortho-NH$_3$ transitions requires that an ortho-NH$_3$ transition be pumped, and similarly for para-NH$_3$. The work described in Chapter 5 also identifies the parameters which determine the effectiveness of a buffer gas in pulsed NH$_3$ lasers. The ratio of the pressure-broadening coefficient to the vibration-translation relaxation rate is much higher for N$_2$ than for He. This ratio corresponds to the relative efficiency of these two gases as buffers for NH$_3$, and thus it is a useful figure of merit to evaluate buffer gas effectiveness.

In the past, the most successful line-tunable NH$_3$ lasers have been produced by resonantly pumping NH$_3$-N$_2$ mixtures with the 9R(30) CO$_2$ line. In Chapter 6, we apply the results obtained in Chapter 5 to explain the operation of R(30)-pumped NH$_3$ lasers. The two major concepts of the rate-equation model are re-examined and validated by comparing model calculations at high values of N$_1$/N$_0$ to detailed measurements of small-signal gain coefficients. Methods of optimizing
the inversion gain, by varying the NH$_3$ concentration and the pump intensity, are examined in Chapter 6 by comparing gain measurements to calculations with an extended rate-equation model. Thermal gas heating due to pump absorption is shown to be a major problem in mixtures of greater than 4% NH$_3$. A useful estimate of the optimum pump intensity is given by the saturation intensity of the pumped transition. Good agreement is obtained between theory and experiment for all the studies of inversion gain in Chapters 5 and 6. Thus, we are confident that the rate-equation model can be applied to predict scalability and optimum operating conditions for a variety of optically pumped NH$_3$ lasers.

Two applications of the rate-equation model are discussed in Chapter 7 and 8. Chapter 7 examines the potential for scaling the operating pressure of the R(30)-pumped NH$_3$ laser to several atmospheres. The aim of high-pressure operation is to permit continuous frequency tuning and the generation of sub-nanosecond pulses. Our calculations indicate that operation of an NH$_3$ laser at a pressure of 10 atm (7600 Torr) is feasible by employing a pump intensity of $\sim$100 MW/cm$^2$. At this pressure, the predicted maximum continuous tuning range is $\sim$120 GHz, which is sufficient gain bandwidth to support pulses less than 10 ps in duration. A 10-atm NH$_3$ laser operating on the P-branch transitions is predicted to be tunable across 36% of the wavelength range from 10.5 to 13.8 $\mu$m. This tuning range will be reduced by the presence of absorption on $2\nu_2$ transitions which overlap the gain on $\nu_2$ transitions. However, overlapping absorptions are expected to be a minor problem, as only a few transitions are affected. Future work should be directed at actually building a 10-atm NH$_3$ laser to exploit
the potential tuning range.

The concept of rotational thermalization in buffered NH₃ mixtures is applied to create a new type of NH₃ laser, as discussed in Chapter 8 and Ref. 85. A two-step pumping process is used to generate line-tunable lasing on many 2ν₂ transitions in the 16- to 21-μm wavelength range. Two of the best CO₂ laser coincidences, one for each of the ν₂ and 2ν₂ bands, are employed on two unconnected transitions. Rapid thermalization in all vibrational levels permits a significant transfer of population on both pumping steps and then distributes the gain over many 2ν₂ ortho-NH₃ transitions. The first goal of subsequent experiments on the 2ν₂ laser should be to improve its efficiency from the present value of 0.25%. Efficiencies of a few percent, perhaps even exceeding 10% (about half the value for several ν₂ NH₃ lasers), should be possible by optimizing the laser optics and the pumping conditions (i.e. cell construction, gas mixture, and pump intensities).

An understanding of the maximum possible efficiency may require a better knowledge of the relaxation rates of the 2ν₂ population. For example, there may be significant population transfer to the ν₄ level, which is close to resonance with the 2ν₂ level. One obvious extension of the 2ν₂ laser is to produce lasing on the 2ν₂ para-NH₃ transitions by using a para-NH₃ pump transition for the second step; the pump for the first step is the 9R(30) line which pumps both ortho and para-NH₃. Another possibility for extending the tuning range is to pump a different isotope, such as ¹⁵NH₃ or ¹⁴ND₃, if appropriate pump coincidences can be found.
In this thesis, we have characterized, with theory and experiment, the operation of optically-pumped NH₃ lasers which cover the wavelength range from 10 to 21 µm. Further optimization of these lasers will be considerably aided by the theoretical models. As the models can easily be adapted to other molecules, we expect that improvements in the characterization and optimization of many other optically-pumped molecular lasers will be possible.
APPENDIX A

CALCULATION OF GAIN COEFFICIENTS FOR NH₃

The formula for calculating the gain coefficients due to population inversion between a lower level 1 and an upper level 2 can be written

\[ \alpha(v) = \frac{8\pi^3}{h\lambda_0} |\mu_{12}|^2 \left( \frac{g_1}{g_2} n_2 - n_1 \right) g(v) \]  \hspace{1cm} (A.1)

In this formula, \( h \) is Planck's constant, \( \lambda_0 \) is the wavelength at line center, \( \mu_{12} \) is the transition dipole moment, \( n_1 \) and \( n_2 \) are the population densities of the lower and upper levels respectively, \( g_1 \) and \( g_2 \) are the statistical weights of those levels, and \( g(v) \) is the normalized lineshape function evaluated at frequency \( v \).

The transition dipole moment is given by

\[ |\mu_{12}|^2 = \frac{\mu^2}{3} A_{JK} \]

where \( \mu \) is the vibrational transition dipole moment. Note that \( \mu_{12} \) is the dipole moment required in the calculation of the Rabi frequency associated with a pump field (see Section 2.4). The values of \( \mu \) are listed in Section 2.2 for the four vibrational bands considered in this thesis. The factor \( A_{JK} \) depends on the branch of the transition as follows [24]

\[ R(J,K): \]

\[ A_{JK} = \frac{(J+1)^2 - K^2}{(J+1)(2J+1)} \]
Q(J,K):

\[ A_{JK} = \frac{K^2}{J(J+1)} \]

P(J,K):

\[ A_{JK} = \frac{J^2 - K^2}{J(2J+1)} \]

where J and K refer to the lower level. The statistical weights in (A.1) are the \( g_J \) factors defined in Section 2.3.

The normalized lineshape function can be expressed as

\[ g(\nu) = \frac{\nu^2}{\pi^{3/2} \Delta \nu_L \Delta \nu_D} \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{y^2 + (x-t)^2} \, dt \quad (A.2) \]

which is a Voigt profile where \( x = (\ln 2)^{1/2} (\nu - \nu_0) / \Delta \nu_D \), \( (\nu_0 = c/\lambda_0, c \) is the speed of light), \( y = (\ln 2)^{1/2} \Delta \nu_L / \Delta \nu_D \), \( \Delta \nu_L \) is the pressure broadened half-width at half maximum, and \( \Delta \nu_D \) is the Doppler broadened half-width at half maximum. A fast and accurate computer program to evaluate the integral in (A.2) is listed in Ref. 86. If \( y \gg 1 \) then \( g(\nu) \) can be more simply expressed by the Lorentzian lineshape

\[ g(\nu) = \frac{1}{\pi} \frac{\Delta \nu_L}{(\Delta \nu_L)^2 + (\nu - \nu_0)^2} \]

At line center \( (\nu = \nu_0) \) the integral in (A.2) can be evaluated analytically for any value of \( y \) to give

\[ g(\nu) = \frac{1}{\pi \Delta \nu_L} y \exp(y^2) \text{erfc}(y) \]

where \( \text{erfc} \) is the complementary error function. The Doppler broadened half-width is given by

\[ \Delta \nu_D = \frac{1}{\lambda_0} \left( \frac{2k_B T}{M} \ln 2 \right)^{1/2} \]
where $k_B$ is Boltzmann's constant, $T$ is the ambient gas temperature, and $M$ is the mass of the NH$_3$ molecule. At 300 K, $\Delta v_0$ is equal to 38 MHz for $\lambda_0=12$ \textmu m, and 50 MHz for $\lambda_0=9$ \textmu m. The pressure-broadening coefficients for NH$_3$-NH$_3$ collisions are given in Appendix C. The pressure-broadening coefficients for NH$_3$-N$_2$ collisions on the pump transitions listed in Table 2.1 (except for $aR(4,2)$) were determined from absorption measurements performed with a cw CO$_2$ laser.

\[
\begin{array}{ll}
  aR(1,1) & \Delta v_L/\rho = 4.34\pm0.28 \text{ MHz/Torr} \\
aR(6,0) & 2.88\pm0.10 \\
sR(5,0) & 3.62\pm0.20 \\
2sR(4,3) & 3.67\pm0.15 \\
\end{array}
\]

The quoted errors are estimated from the calculated fits to the absorption coefficients as a function of pressure. On all the transitions for which gain is calculated, a value of 3.2 MHz/Torr was used as the N$_2$ broadening coefficient. The temperature dependence of the NH$_3$ and N$_2$ broadening coefficients are [24]

\[(\Delta v_L/\rho)_{\text{NH}_3} \propto T^{-1}\]

\[(\Delta v_L/\rho)_{\text{N}_2} \propto T^{-5/6}\]

All of the above data for calculating gain coefficients are included in a computer program. The program accepts, as input, values of $N_1/N_0$, $(N_0+N_1)/N$, gas temperature, and gas mixture to evaluate the gain coefficients for any number of NH$_3$ transitions in the $\nu_2$ and $2\nu_2$ bands.
APPENDIX B

DENSITY-MATRIX EQUATIONS AND SOLUTION

The density-matrix equations and solution presented here closely follow the treatment given by Heppner et al. [16], and employ the level numbering of Fig. 2.1. The CGS system of units is used throughout. The development of the equations treats a single molecule in its rest frame, and the elements of the density matrix are averages over the ensemble of possible histories of the molecule. Thus, the density matrix represents a statistical average over all the molecules. The equation of motion for the elements of the density matrix can be written for the off-diagonal elements as

\[ \dot{\rho}_{mn}(r,t) = \frac{i}{\hbar} [\rho, H]_{mn} + \rho_{mn} \gamma_{mn} \]  \hspace{1cm} (B.1a)

and for the diagonal elements

\[ \dot{\rho}_{nn}(r,t) = \frac{i}{\hbar} [\rho, H]_{nn} + (\rho - \rho^0)_{nn} \gamma_{nn} \]  \hspace{1cm} (B.1b)

The diagonal elements represent the population densities of the levels and the \( \rho^0 \) are their values for the steady state in the absence of fields. The \( \gamma \)'s are relaxation rates; the \( \gamma_{nn} \) are population relaxation "\( T_1 \)-type" rates, and the \( \gamma_{mn} \) are coherence relaxation "\( T_2 \)-type" rates. The matrix elements of the Hamiltonian are

\[ H_{nn} = W_n \delta_{nn} - \mu_{nn} E'(r,t) \]  \hspace{1cm} (B.2)

where \( W_n \) is the energy of a molecule in level \( n \), \( \mu_{nn} \) is the transition dipole moment between levels \( m \) and \( n \), and \( E'(r,t) \) is the total radiation
field in the molecular rest frame. We assume \( \nu_{12} \) is zero, which is true for the transitions considered in Chapter 4. Thus, \( E'(r,t) \) can be written as the sum of two travelling plane waves, \( E_1'(z,t) \) for the probe wave (NH\(_3\) emission) and \( E_2'(z,\varepsilon,t) \) for the pump wave (CO\(_2\) laser), and \( \varepsilon \) denotes their relative direction; \( \varepsilon = +1 \) for co-propagating and \( \varepsilon = -1 \) for counter-propagating fields. The two fields can be expressed as

\[
E_1'(z,t) = A_1(z)\exp[i(\Omega_1 - k_1v)t] + \text{complex conjugate}
\]

\[
E_2'(z,\varepsilon,t) = A_2(z,\varepsilon)\exp[i(\Omega_2 - \varepsilon k_2v)t] + \text{c.c.} \tag{B.3}
\]

where \( v \) is the axial velocity of the molecule, and \( k_1v \) and \( k_2v \) are the Doppler shifts of the field frequencies in the moving frame, \( \Omega_1 \) and \( \Omega_2 \). We define \( \Omega_1' = \Omega_1 - k_1v \) and \( \Omega_2' = \Omega_2 - \varepsilon k_2v \).

The polarization induced by the fields is given by

\[
P = \text{tr}[\mu_0]
\]

and can be separated into two parts, one for each field.

\[
P_j = 2\text{Re}\{\mu_{0j} \rho_{j0}\} = \text{Re}\{x_j(v)2A_j(z)\exp(i\omega_j't)\} \tag{B.5}
\]

The second line in (B.5) derives from \( P = \mu E \) and defines \( \chi(v) \), the complex susceptibility as a function of velocity. The expression for the gain coefficient of each field, due to the molecules in one velocity class, is derived from the time-averaged power emitted per unit volume.
\[ \frac{d}{dz} I_v(\tilde{\alpha}_j) = -\langle \rho_j E_j' \rangle \text{ time} \]
\[ = \frac{1}{2} \tilde{\alpha}_j |2a_j|^2 \operatorname{Im}(\chi_j(v,c)) \]
\[ = \alpha_j(v) I_v(\tilde{\alpha}_j) \] (B.6)

This completes the connection between the elements of the density matrix and the gain coefficients.

Equation (B.1) may be solved in the steady state, by setting the time derivatives to zero, if population fluctuations are negligible. This requires \( \Omega_j \gg \mu |E_j| \), i.e. that the Rabi frequencies associated with the fields must be much less than the field frequencies. (This requirement is met, for all the conditions that we investigate as \( \Omega_j = 1000 \text{ cm}^{-1} = 3 \times 10^4 \text{ GHz} \) and the maximum pump intensity employed is \( \sim 1 \text{ MW/cm}^2 \) which is associated with a Rabi frequency of \( \sim 1 \text{ GHz} \).) As the induced polarizations are resonant with the fields, a nearly exact solution of (B.1) may be found by assuming resonant forms for the off-diagonal density-matrix elements.

\[ \rho_{01} = \Lambda \exp(-i\Omega_1 t) \]
\[ \rho_{20} = \lambda \exp(+i\Omega_2 t) \]
\[ \rho_{21} = D \exp[i(\Omega_2 - \Omega_1)t] \] (B.7)

where \( \Lambda, \lambda, \) and \( D \) are constants. Substituting (B.7) into (B.1) yields five linear equations.

\[ (r_{10} - r_{10}^0) = i[(\frac{1}{Y_0} + \frac{1}{Y_1})\alpha \Lambda - \frac{\beta \Lambda}{Y_0}] + \text{c.c.} \]
\[ (r_{20} - r_{20}^0) = i[-(\frac{1}{Y_0} + \frac{1}{Y_2})\beta \Lambda + \frac{\alpha \Lambda}{Y_0}] + \text{c.c.} \]
\[ -L_1 \Lambda = 8D + \alpha^* r_{10} \] (B.8)
\[ L_2 \lambda = \beta^* r_{20} + \alpha \delta \]
\[ RD = \alpha^* \lambda - \beta^* \lambda \]

The new symbols in (B.8) have the following meanings

\[ r_{ij} = \rho_{ii} - \rho_{jj}, \quad r_{ij}^0 = \rho_{ii}^0 - \rho_{jj}^0 \]
\[ \alpha = \mu_1 A_1/N, \quad \beta = \mu_2 A_2/N \]
\[ L_1 = \Omega_1 - \omega_1 + i \gamma_{10} \]
\[ L_2 = -\Omega_2 + \omega_2 + i \gamma_{20} \]
\[ R = (\Omega_1 - \omega_1) - (\Omega_2 - \omega_2) + i \gamma_{12} \]

and \( \omega_j \) is the frequency of the molecular transition \( j \). Solving (B.8) provides expressions for the complex susceptibilities and the population differences.

\[ x_1(v) = \frac{[\nu_1^2]}{4N} \left[ |\beta|^2 r_{20} + (L_2 R - |\alpha|^2) r_{10} \right] \]
\[ x_2(v) = \frac{[\nu_2^2]}{4N} \left[ |\alpha|^2 r_{10} + (L_1 R - |\beta|^2) r_{20} \right] \]
\[ r_{10} = (J_{22} r_{10}^0 + J_{12} r_{20}^0)/(J_{11} J_{22} - J_{12} J_{21}) \]
\[ r_{20} = (J_{21} r_{10}^0 + J_{11} r_{20}^0)/(J_{11} J_{22} - J_{12} J_{21}) \]

with

\[ N = L_1 L_2 R - L_1 |\alpha|^2 - L_2 |\beta|^2 \]
\[ J_{11} = 1 - \frac{2|\alpha|^2}{\gamma_0} \text{Im}\left[ \left( \frac{\gamma_1 + \gamma_0}{\gamma_1} \right) \left( L_2 R - |\alpha|^2 \right) + |\beta|^2 / N \right] \]
\[ J_{12} = \frac{2|\beta|^2}{\gamma_0} \text{Im}\left[ \left( L_1 R - |\beta|^2 \right) + \left( \frac{\gamma_1 + \gamma_0}{\gamma_1} \right) |\alpha|^2 / N \right] \]
\[ J_{21} = \frac{2|\alpha|^2}{\gamma_0} \text{Im}\left[ \left( L_2 R - |\alpha|^2 \right) + \left( \frac{\gamma_1 + \gamma_0}{\gamma_2} \right) |\beta|^2 / N \right] \]
\[ J_{22} = I_{\omega} - \frac{2|\beta|^2}{\gamma_0} \text{Im}[\left(\frac{L_{1R} - |\beta|^2}{\gamma_2}\right) + |a|^2]/\text{N} \]

The M-degeneracy of the molecular levels can be removed by treating the populations as the populations of the individual M-levels, and allowing for the M-dependence of the transition dipole moments as follows:

\[ R(J,K) : |v_{mn}'|^2 = \mu^2 \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(J+1)^2(2J+1)(2J+3)} \]

\[ Q(J,K) : |v_{mn}'|^2 = \mu^2 \frac{K^2 M^2}{J^2(J+1)^2} \]

\[ P(J,K) : |v_{mn}'|^2 = \mu^2 \frac{(J^2 - K^2)(J^2 - M^2)}{J^2(2J-1)(2J+1)} \]

The final expression for the gain coefficients is obtained from (8.10) by an integration over the molecular velocity distribution and a sum over M.

\[ \alpha(J,v) = 4\pi \frac{\Omega_v}{c} \sum_N \int_{-\infty}^{\infty} \text{Im} (\chi_{jN}(M,v,\epsilon)) f(v) dv \]

The function \( f(v) \) is the Maxwell-Boltzmann velocity distribution which can be written

\[ f(v) = \frac{1}{\pi^{1/2} a} \exp(-v/a^2) \]

with

\[ a = (M/2k_B T)^{1/2} \]

and here \( M \) is the mass of the \( \text{NH}_3 \) molecule, \( k_B \) is Boltzmann's constant, and \( T \) is the ambient gas temperature (see also \( \Delta \nu_0 \) in Appendix A).
APPENDIX C

NH₃ PRESSURE-BROADENING COEFFICIENTS

The tables listed by Taylor [45] contain the pressure-broadening coefficients, $\Delta \nu / p$, for NH₃-NH₃ collisions. As mentioned by Taylor, these coefficients can be expressed by a polynomial in terms of J and K. An analysis of Taylor's values provides the following expression for $(\Delta \nu / p)_{JK}$ in units of cm⁻¹ atm⁻¹:

$$(\Delta \nu / p)_{JK} = a_0 + a_1 J + a_2 K + a_3 J^2 + a_4 J K + a_5 J^3 + a_6 J^2 K + a_7 J^3 K$$

with

\[
\begin{align*}
    a_0 &= 0.4008 \\
    a_1 &= -0.08274 \\
    a_2 &= 0.2103 \\
    a_3 &= 0.01310 \\
    a_4 &= -0.04021 \\
    a_5 &= -6.967 \times 10^{-4} \\
    a_6 &= 3.182 \times 10^{-3} \\
    a_7 &= -8.859 \times 10^{-5}
\end{align*}
\]

The value of $\Delta \nu / p$ for the transition $(J',K') \rightarrow (J'',K'')$ is obtained with $J=(J'+J'')/2$ and $K=(K'+K'')/2$. The factor to convert $\Delta \nu / p$ from units of cm⁻¹ atm⁻¹ to units of MHz/Torr is 39.45 ($=2.998 \times 10^4/760$). Equation (C.1) is accurate to 0.5% in reproducing Taylor's values up to $J=11.5$ and $K=11$. 

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APPENDIX D

NUMERICAL SOLUTION TO THE RATE EQUATIONS

The rate equations (Eq. 5.6) for the model of inversion gain are solved by using a predictor-corrector numerical scheme, given in general form by Hamming [87]. The predictor-corrector technique solves the problem \( y' = \frac{dy}{dt} = f(t, y) \), with \( y'_n = f(t_n, y_n) \) for each equation and \( h = t_n - t_{n-1} \), by predicting the new \( y \)'s at the point \( t_{n+1} \) in terms of previous values and then correcting the predicted values for estimated numerical errors. The scheme that was chosen employs a "2/3" Adams-Bashforth predictor and corrector. This scheme is a sixth-order method, as it integrates a fifth-order polynomial exactly. The "2/3" predictor-corrector algorithm is as follows:

Predict:
\[
    p_{n+1} = \left( \frac{2y_{n-1} + y_{n-2}}{3} \right) + \\
    \left( \frac{h}{72} \right) \left( 191y'_n - 107y'_{n-1} + 109y'_{n-2} - 25y'_{n-3} \right)
\]

Modify:
\[
    m_{n+1} = p_{n+1} - (707/750)(p_{n-1} - c_{n-1})
\]

Correct:
\[
    c_{n+1} = \left( \frac{2y_{n-1} + y_{n-2}}{3} \right) + \\
    \left( \frac{h}{72} \right) \left( 25m_{n+1} + 91y'_n + 43y'_{n-1} + 9y'_{n-2} \right)
\]

Final value:
\[
    y_{n+1} = c_{n+1} + \left( \frac{43}{750} \right)(p_{n+1} - c_{n+1})
\]

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The algorithm is not self-starting, and hence a fourth-order Runge-Kutta method is used to evaluate the first three steps from the initial values. The entire process is applied to the four rate equations simultaneously. As the solution progresses, the time step \( h \) is allowed to vary by doubling or halving. A decision to change the time step is based on estimates of stability and truncation error generated by the solution. The truncation error is the difference between the "real" and computed solutions. It is estimated from the difference between the predicted and corrected values. The criterion for numerical stability, suggested by Hamming, is that \( |Ah| < 0.4 \) where \( A = \frac{\partial f}{\partial y} \). The allowed variation in the step size makes the predictor-corrector method very efficient of computer time, given a proper choice of limits. The numerical solution was implemented in a FORTRAN program on a PDP 11/44 computer.
REFERENCES

2. C.R. Jones, Laser Focus 14, August (1978), pp. 68.


70. A.N. Bobrovskiǐ, A.A. Vedenov, A.V. Kozhevnikov, and D.N. Sobolenko, JETP Lett. 29, 536 (1979).


