DYNAMICS OF DISCHARGE-EXCITED CO₂ LASERS

BY

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ABSTRACT

A tunable diode laser (TDL) operating in the region of 2150 to 2350 cm\(^{-1}\) wavenumber is used in this work to investigate the dynamics of level populations in CO\(_2\) lasers. The wide tunability of the TDL is exploited in determining the populations in any level of the CO\(_2\) molecule. Thus, the vibrational population distributions in a CW CO\(_2\) laser discharge under both lasing and non-lasing conditions are measured and compared with the mode temperature model.

The relaxation processes associated with the upper and lower levels of CO\(_2\) lasers are also investigated. In particular, the electron excitation and de-excitation rates of the upper laser level in typical CO\(_2\) discharges are determined directly from the experiment, and it is shown that electron de-excitation is responsible for the saturation of the \(v_3\) mode temperature in electrically excited CO\(_2\) lasers at high discharge currents, and imposes a fundamental limitation on the gain attainable in CO\(_2\) lasers.

The relaxation of the lower laser level is complicated by the occurrence of several competitive vibration-vibration (V-V) processes. The TDL measurements enable us, for the first time, to monitor separately the population in all levels of concern to the relaxation of the lower laser level and to determine the rate constant of each of the available decay channels. It is shown that the O\(_2\)\(^{20}\) level plays an important role in the relaxation of the lower laser level.
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CHAPTER 1

INTRODUCTION

The CO₂ laser is one of the most powerful and efficient laser systems ever developed. Its economic operation and excellent output characteristics have led to an ever-increasing range of applications in industry, medicine, environmental studies and military hardware. CO₂ lasers with continuous output powers in excess of ten kilowatts are available commercially, and large laser systems with single pulse energies over ten kilojoules are used for the studies of inertial confinement fusion. In addition, the CO₂ laser has gained widespread use in producing mid-infrared and far-infrared lasers. Due to this wide range of application, the dynamics of CO₂ lasers have been the subject of extensive research since the first report of laser action in CO₂ was made by Patel in 1964 [1]. In general, the basic mechanisms governing the operation of the various types of CO₂ laser systems are now fairly well understood, but several major aspects of CO₂ laser dynamics remain uncertain; a situation which reflects the experimental difficulties associated with the techniques used prior to this work. In the present work, we describe new techniques of probing CO₂ discharges which enable us to obtain, for the first time, detailed quantitative information on all relevant CO₂ level populations. These measurements provide us with an unique and effective tool to examine the previously unresolved dynamical processes controlling CO₂ laser dynamics.
Conventional techniques for investigating the dynamics of CO₂ lasers and amplifiers generally rely upon the use of line-tunable CO₂ laser oscillators as a probe or as an excitation source. A good deal of information on laser gain characteristics [2,3] and energy transfer processes [4,5] has been obtained with these techniques and has provided an overall basis for understanding the physics of the CO₂ laser. In general, a CW low pressure CO₂ laser was used to probe a CO₂ discharge. As a result, only the levels directly associated with the laser transitions are probed and only the difference of population between the laser levels is monitored; little can be experimentally determined about the population of the non-laser levels. Hence, the CO₂ laser probe technique is unable to elucidate many important mechanisms, such as the reduction of the small-signal gain in CO₂ laser amplifiers at high excitation current [2,3]. Another commonly used technique to investigate relaxation processes in CO₂ lasers is the laser-induced fluorescence technique. In this case, a pulsed CO₂ laser is used to excite a CO₂ gas medium, and then the properties of the medium are determined from the resulting fluorescence [4]. As the induced fluorescence originates from a great number of strongly coupled levels, the complications caused by the reabsorption and the overlap of the radiation render the interpretation of these measurements uncertain and ambiguous in spite of the use of optical filters or spectrometers [6,7].

The present experimental approach utilizes a PbSnSe tunable diode laser operating in the 2150 to 2350 cm⁻¹ region to probe the vibrational
populations in a CW CO₂ discharge. The great advantage of the TDL lies in its wide tunability. That is, it can be tuned to monitor any vibrational transition in CO₂; one is no longer limited to transitions which can be made to lase in a separate CO₂ oscillator. Highly excited vibrational levels of CO₂ in all three normal vibrational modes can be monitored, and one can determine the absolute population of the levels. Moreover, the TDL can be used to study the relaxation processes of each level under a variety of experimental conditions.

The aim of the present work is to examine experimentally the validity of the mode temperature model which is widely used in the modelling of CO₂ lasers, and to identify and determine quantitatively those processes which limit the extraction of optical energy from and the energy storage in the CO₂ laser system. The verification of the mode temperature model is made by direct measurements of absolute level populations in CO₂ discharges. Then, the relaxation rates of all relevant levels are measured. These latter measurements allow us to evaluate the effects of various excitation and de-excitation processes affecting the laser levels, and thereby determine the laser efficiency. The content of each chapter is briefly outlined below.

Chapter 2 discusses the energy transfer processes in the molecule-molecule and electron-molecule collisions in CO₂ laser discharges. Particular attention is given to the experimental methods which have been employed previously in the investigation of these processes.

Chapter 3 describes the measurements of vibrational population distributions in CO₂ discharges. Measurements on more than 25 vibrational levels are used to ascertain the validity of the mode temperature model.
In Chapter 4, the relaxation rate of the $\nu_3$ mode levels is investigated. In particular, the effects of electrons in the discharge, including both excitation and de-excitation processes, are examined and analysed in detail. The implications of the results for the operation of CO$_2$ lasers are discussed.

Chapter 5 concerns the processes involved in the relaxation of the lower laser level. A 6-level kinetic model is developed to assess the importance of each of the available decay channels.

Chapter 6 summarizes the major results of this thesis. Several suggestions for future work using the present experimental technique are also discussed.
CHAPTER 2

ENERGY TRANSFER PROCESSES IN $\text{CO}_2$ LASERS

2.1 **Introduction**

This chapter is intended to review the current status on the molecular excitation and de-excitation rates of processes involved in electrically excited $\text{CO}_2$ lasers. It begins with a brief description of the relevant $\text{CO}_2$ laser transitions in the 9 $\mu$m and 10 $\mu$m regions. Then, a detailed description of the principal physical processes in the electron-molecule and molecule-molecule collisions follows, with special emphasis on the techniques used for experimental determination of the rates involved. Finally, the importance of radiation and diffusion relaxation processes is discussed.

2.2 **$\text{CO}_2$ Laser Transitions**

The $\text{CO}_2$ molecule is a linear symmetric molecule belonging to the point group $D_{\infty h}$ which has three normal modes of vibration, i.e., symmetric stretching $v_1$, bending $v_2$, and asymmetric stretching $v_3$; the bending mode is doubly degenerate. Each vibrational level of the $\text{CO}_2$ molecule is identified by a set of four quantum numbers $(i, j, k, \ell)$ where $i, j, k$ denote the vibrational quantum numbers associated with the $v_1, v_2$ and $v_3$ modes respectively, and $\ell$ is an angular quantum number describing the degeneracy of the bending mode. For every vibrational level there exists a set of rotational sublevels with quantum number $J$, corresponding to the rotational
movement of the molecule. In addition, the $10^0_0$ and $02^0_0$ levels (and similar levels of higher vibrational energy) have almost the same vibrational frequencies, i.e., $\nu_1 = 2\nu_2$, which leads to a perturbation of their energies as first recognized by Fermi [8]. This, so called "Fermi resonance", causes a strong mixing of the individual mode vibrational eigenfunctions (this has an important consequence in the relaxation of the lower laser levels [9]). Consequently, these levels are more correctly represented as $[10^0_0, 02^0_0]_I$ and $[10^0_0, 02^0_0]_II$. However, this nomenclature will not be adopted in this thesis. For convenience, $10^0_0$ is used to represent the $[10^0_0, 02^0_0]_I$ level, $02^0_0$ for the $[10^0_0, 02^0_0]_II$ level, and similar notation for other higher lying Fermi levels (e.g., $10^0_1$ for the $[10^0_1, 02^0_1]_I$ level). Laser oscillation has been obtained from both the P-branch ($\Delta J = -1$) and R-branch ($\Delta J = +1$) of the $10.4 \mu m \; 00^0_1 \rightarrow 10^0_0$ and $9.4 \mu m \; 00^0_1 \rightarrow 02^0_0$ transitions. Figure 2.1 shows a detailed transition diagram for laser oscillations in both the P and R branches of the $10.4 \mu m$ regular bands. Note that all the regular transitions are denoted by even quantum numbers. This is because identical spinless oxygen nuclei are on either side of the carbon nucleus in the $^{12}_2O_2$ molecule [10]. These regular laser transitions were the main working $CO_2$ laser transitions up to 1976. In that year, Reid and Siemens succeeded in producing lasing from higher $\nu_3$ mode levels in a $CO_2$ laser by using an in-cavity hot cell to suppress the strong regular laser transitions [11]. These new laser transitions, named sequence bands, are the $10.4 \mu m \; 00^0_2 \rightarrow 10^0_1$, $9.3 \mu m \; 00^0_2 \rightarrow 02^0_1$, $10.4 \mu m \; 00^0_3 \rightarrow 10^0_2$, and $9.3 \mu m \; 00^0_3 \rightarrow 02^0_2$ bands which play an important role in the understanding of $CO_2$ laser dynamics [2,3].
FIGURE 2.1 Detailed transition diagram of laser oscillation in the 10.4 \( \mu \text{m} \) and 9.4 \( \mu \text{m} \) regular laser bands of \( \text{CO}_2 \).
2.3 Electron-Molecule Collisional processes

The most common method of exciting a gas medium is the use of an electrical discharge. The high efficiency of CO₂ laser systems results from the efficient coupling of the electron energy into the vibrational energy of the CO₂ and N₂ molecules, and the favorable molecular relaxation processes involved. This section deals with the electron-molecule collisional processes; whereas the molecule-molecule collisional processes will be discussed in the next section.

Electron energy is transferred to the rotational, vibrational, and electronic energies of the atoms and molecules, and can also be lost through ionisation and dissociation. In a discharge, all these processes occur simultaneously with rates critically dependent on the collisional cross sections and electron energy. Therefore, a determination of the distribution of the input power transferred to the various vibrational modes requires a knowledge of electron density, electron energy distribution, mean electron energy, and elastic and inelastic collision cross sections between electrons and all gas components in the discharge. Because some of these parameters are difficult to measure experimentally, calculations are heavily relied upon for quantitative predictions of laser performance. Using Holstein's formulation of the Boltzmann transport equation [12] and available electron cross sections, Nighan has numerically calculated the electron distribution function and determined the fractional power transferred to vibrational excitation, electronic excitation, and ionization of CO₂ and N₂ molecules, as a function of the ratio of applied electric field to total particle density, E/N [13]. These calculations were extended
to a wider range of experimental conditions by Lowke et al. [14] and Judd [15]. Later work by Sakai et al. [16] have also included the effects of attachment, dissociation and dissociative ionisation by electrons. Finally, the validity of the Boltzmann equation method was examined by Taniguchi et al. [17] with Monte Carlo simulations, and by Pitchford et al. [18] with high order terms in the solution of the Boltzmann equation. It appears from these works that the two-term expansion solution used by Nighan and others is valid for \( E/N < 5 \times 10^{-16} \text{V-cm}^{-2} \).

Typical values of \( E/N \) found in self-sustained CO\(_2\) laser discharge are of \( 2-8 \times 10^{-16} \text{V-cm}^{-2} \) [19] resulting in average electron energies in the range of 0.5 - 3 eV. A number of authors have measured electron cross sections for vibrational and electronic excitation of CO\(_2\) in this energy range using a monoenergetic electron beam and an electron spectrometer. Boness and Schulz [20] have reported large cross sections for vibrational excitation of the \( 00^1 \), \( 10^0 \) and \( 20^0 \) levels of CO\(_2\), and have attributed the resonance effects to the formation of negative ions with vibrationally excited CO\(_2\) as final product, i.e., \( e + \text{CO}_2 \rightarrow \text{CO}_2^- \rightarrow \text{CO}_2^* + e \).

However, later work by Andrick et al. suggested that dipole interaction with slow electrons was responsible for the strong vibrational excitation of the optically active \( 00^1 \) and \( 01^1 \) levels [21]. This assumption was supported by the theoretical calculations of Itikawa [22] who also suggested that the optically non-active \( 10^0 \) level could be excited through polarisation interaction. Further work by Boness et al. [23] identified the oscillatory structure in the excitation of the \( n0^0 \) and \( n1^1 \) levels. This is analogous to the characteristic signature of the formation of temporary negative ions in diatomic molecules as was found in the e-N\(_2\).
excitations [24]. In the electron beam measurements, the determination of the absolute magnitude of electron cross sections is difficult and is subject to many instrumental corrections. Although the detailed structure and physical mechanisms involved are well understood, the absolute magnitude of electron-molecule collisional cross sections is not known with good accuracy. Hake and Phelps [25] have taken another approach to derive the electron-molecule collisional cross sections. They used an initial set of elastic and inelastic cross sections in the solution of the Boltzmann transport equation to calculate the transport coefficients, i.e., electron drift velocity, characteristic energy, attachment coefficient, and ionisation coefficient. Then, they adjusted the initial set of cross sections successively in order to obtain a good agreement between the calculated and measured transport coefficients over a large range of E/N values. The set of cross sections, thus determined has allowed the prediction of CO₂ laser performance which is in general agreement with experiments [3,26]. Recently, Bulos et al. have measured rate coefficients for the excitation of the 4.3 μm bands of CO₂ by low energy electrons using a drift tube technique [27]. They deduced a set of electron cross sections for CO₂ significantly different from that of Hake et al. [25]. At the present moment, it is not clear which set of cross sections is more reliable. In Fig. 2.2, we show a simplified energy diagram for CO₂ and N₂ where several important energy transfer rates relevant to the operation of CO₂ lasers are indicated. In the figure, the dashed arrowed lines denote the electron excitation processes; whereas the solid arrowed lines are for the molecular collision processes. The values of electron excitation rates shown in
FIGURE 2.2  Summary of collisional relaxation rates in a laser discharge of 10% CO₂:10% N₂:80% He mixture at 20 Torr with an electron density of $10^{10}$ cm⁻³. The solid arrowed lines indicate molecule-molecule collisional processes whereas the dashed arrowed lines represent the electron-molecule collisional processes. Also shown are the regular and sequence 10 μm laser transitions.
Fig. 2.2 are obtained from the calculations of Sakai et al. [16] who have used the electron cross sections compiled by Lowke et al. [14] (which is a modified set of Häke et al.).

As is true in all reversible thermodynamic processes, there exists electron de-excitation process of the excited levels. The rate of the latter process can, in principle, be deduced from the rate of excitation process by using the principle of detailed balance. There is, however, some doubt about the applicability of detailed balance in a non-equilibrium situation found in discharges [28]. The experimental measurements of electron de-excitation rate are scarce and often ambiguous [29,30]; no reliable data exists at present. In Section 4.4, an experimental determination of the electron excitation and de-excitation rates in typical CO₂ laser discharges will be given. The results are consistent with the power density measurements and the calculated excitation rates.

2.4 Molecule-Molecule Collisional Processes

Data on molecular collision processes in CO₂ are much more reliable and more accurate than those on electron collision processes discussed previously. With the exception of the vibration-vibration relaxation processes of the lower laser levels, the rates of many molecular collision processes in CO₂ are known to good accuracy (∼ 5-10%) and good agreement is found between measurements obtained by different experimental techniques. Three techniques have been widely used in the measurements of molecular collision relaxation rates: shock tube [31], photo-acoustic [32], and laser fluorescence [7]. The laser fluorescence technique is the most
A laser pulse of a frequency chosen to selectively populate a particular excited level of interest irradiates a gas medium containing the molecules or/and atoms to be studied, then the fluorescence decay of various excited levels is monitored separately through the use of optical filters or a spectrometer. Frequently, the fluorescence decay can be described by a simple exponential decay with a time constant directly related to the relaxation rate of the process investigated. On the contrary, for the shock tube and photo-acoustic techniques, a rather complex expression is usually required to relate the observable parameters to the relaxation rate [31,32]. As both these methods work on the change of the gas pressure or density caused by the gas temperature increase, near-resonant processes with small energy loss to the translational degree of freedom cannot be studied by these methods. Moreover, the slow mechanical response in both methods prevents them from measuring fast relaxation rates.

Molecular collision processes can be categorized into rotational relaxation processes, vibration-vibration (V-V) relaxation processes, and vibration to rotation/translation (V-R/T - this is often indistinguishable from V-T) relaxation processes. The rotational relaxation has the fastest rate. Its value is near the kinetic collision rate and is quite independent of the collision partner. The rotational rate constant of CO₂ is: \(1.3 \times 10^7 \text{ s}^{-1}\text{Torr}^{-1}\) in CO₂, \(1.2 \times 10^7 \text{ s}^{-1}\text{Torr}^{-1}\) in N₂, and \(0.6 \times 10^7 \text{ s}^{-1}\text{Torr}^{-1}\) in He [33]. These fast rates ensure the thermalisation of the rotational sublevels within each vibrational level. The V-V relaxation processes play an important role in the CO₂ laser system. Nitrogen
is an important gas component in CO₂ lasers and provides a major vibrational excitation source for the upper laser level of CO₂ through the near-resonant V-V energy transfer process

\[
\text{CO}_2(00^01) + \text{N}_2(0) \rightarrow \text{CO}_2(00^00) + \text{N}_2(1) + 18 \text{ cm}^{-1}
\]  

(2-1)

with a rate constant of \(1.9 \times 10^4\ \text{s}^{-1} \text{ Torr}^{-1}\) [4]. An even faster V-V transfer rate is observed for the processes:

\[
\text{CO}_2(01^10) + \text{CO}_2(00^01) \rightarrow \text{CO}_2(00^00) + \text{CO}_2(01^11) + 12 \text{ cm}^{-1}
\]  

(2-2)

with a rate constant of \(3.7 \times 10^6\ \text{s}^{-1} \text{ Torr}^{-1}\) [34] and

\[
\text{CO}_2(10^01) + \text{CO}_2(00^00) \rightarrow \text{CO}_2(00^01) + \text{CO}_2(10^00) - 22 \text{ cm}^{-1}
\]  

(2-3)

with a rate constant of \(4.2 \times 10^6\ \text{s}^{-1} \text{ Torr}^{-1}\) [35]. The intramode V-V processes such as:

\[
\text{CO}_2(00^02) + \text{CO}_2(00^00) \rightarrow 2\text{CO}_2(00^01) - 25 \text{ cm}^{-1}
\]  

(2-4)

are believed to be very fast. A rate constant of \(1.8 \times 10^7\ \text{s}^{-1} \text{ Torr}^{-1}\) is calculated for the process (2-4)[36]. These fast near-resonant V-V processes, i.e., Eqs. (2-1)-(2-4) promote a rapid energy redistribution within the CO₂ ν₃ mode and between the CO₂ ν₃ mode and the N₂ vibrational mode, and hence enable a more efficient energy extraction from the upper laser level. The near-resonant V-V processes are shown theoretically to be due to the long range interaction forces, e.g., the dipole-dipole interaction is dominant in CO₂-CO₂ exchange and the dipole-quadrupole interaction in CO₂-N₂ exchange [36,37]. Furthermore, the CO₂ laser system benefits from the relatively slow intermode coupling between the ν₃ mode and the ν₁ (or ν₂) mode, that is:
\[
\text{CO}_2(00^{0}1) + \text{M} \rightarrow \text{CO}_2(i, j^{\pm}, 0) + \text{M} \quad (2-5)
\]

where M is any gas molecule. Measured rate constants for this process are 350 s\(^{-1}\) Torr\(^{-1}\) for M = CO\(_2\), 106 s\(^{-1}\) Torr\(^{-1}\) for M = N\(_2\) and 85 s\(^{-1}\) Torr\(^{-1}\) for M = He [4].

In addition to the favorable relaxation processes of the upper laser level, the relaxation of the lower laser level is also sufficiently fast to minimize the effect of bottle-necking such as is found in the He-Ne laser system [38]. The relaxation of the first \(v_2\) level (01\(^1\)0) becomes relatively fast due to the addition of He. The rate constant measured for this V-\(\bar{T}\) process,

\[
\text{CO}_2(01^{1}0) + \text{M} \rightarrow \text{CO}_2(00^{0}0) + \text{M} \quad (2-6)
\]

is 196 s\(^{-1}\) Torr\(^{-1}\) for M = CO\(_2\) [39], 100 s\(^{-1}\) Torr\(^{-1}\) for M = N\(_2\) [40], and 3.7 \times 10^3 s\(^{-1}\) Torr\(^{-1}\) for M = He [41]. However, it is the relaxation of the lower laser level, 10\(^0\)\(_0\), to its nearby vibrational levels, i.e., 02\(^0\)\(_0\), 02\(^2\)\(_0\), and 01\(^1\)\(_0\) through the V-V processes

\[
\begin{align*}
\text{CO}_2(10^{0}0) + \text{M} & \rightarrow \text{CO}_2(02^{0}0) + \text{M} \quad (2-7) \\
\text{CO}_2(10^{0}0) + \text{M} & \rightarrow \text{CO}_2(02^{2}0) + \text{M} \quad (2-8) \\
\text{CO}_2(10^{0}0) + \text{CO}_2(00^{0}0) & \rightarrow 2 \text{CO}_2(01^{1}0) \quad (2-9)
\end{align*}
\]

that generally controls the relaxation behavior of the lower laser levels. Numerous experimental determinations of the rate constants for these processes have been made using various techniques. However, the precise values are still in dispute; values for process (2-7) ranging from \(\sim 10^5\) to \(\sim 10^6\) s\(^{-1}\) Torr\(^{-1}\) are reported [42-45], and values for process (2-9) vary from \(\sim 10^3\) to \(\sim 10^5\) s\(^{-1}\) Torr\(^{-1}\) [46-48]. The cause for this apparent
inconsistency in the reported values is not entirely clear, but the interpretation of the measurements is ambiguous in many cases. There are two theoretical formulations used to calculate the V-V coupling rate constant of processes (2-7) – (2-9). Seeber [49] applied the short range interaction formulation of Schwartz-Slawsky-Herzfeld (SSH) in his calculations, while Sharma [50] proposed a long range interaction formulation for the calculations. Although the results obtained from both theories are similar for process (2-9), they differ significantly for processes (2-7) and (2-8). Unfortunately, the previously available experimental measurements are far too scattered to distinguish between the theories. In Chapter 5, the rate constant of these V-V processes will be discussed in light of the tunable diode laser measurements, and the results will show that the SSH formulation is more appropriate for the V-V coupling processes of the lower laser level. Hence, the calculated values of Seeber are used to produce the rate indicated in Fig. 2.2 where the rates of the aforementioned processes are also shown for a 10% CO$_2$:10% N$_2$:80%He laser mixture at 20 torr in an electron density of 10$^{10}$ cm$^{-3}$ [51].

2.5 Radiation and Diffusion Relaxation Processes

In a comprehensive study, Statz et al. [52] have calculated the Einstein A-coefficients in CO$_2$ for all relevant CO$_2$ transitions. All spontaneous emission rates are very slow (≈ 0.5 – 200 s$^{-1}$), and some are further reduced by the effect of self-trapping; hence, in the absence of lasing, collisionally-induced vibrational relaxation (see Section 2.4) dominates the energy relaxation processes in CO$_2$ lasers. However, in a
laser oscillator and in a saturated laser amplifier, the stimulated emission rate can become dominant.

In high pressure transversely excited CO₂ lasers, diffusion relaxation is negligible. But, as the diffusion rate is inversely proportional to the gas pressure, diffusion relaxation can be significant in low pressure CW CO₂ lasers. In a series of measurements on the relaxation rate of the upper laser level in different tube materials, Kovacs et al. [53] concluded that the excited molecules diffuse towards the wall and are subsequently de-excited at the wall surface by the adsorbed ground-state CO₂ molecules. Also Christensen et al. found that the saturation parameter of low pressure CW CO₂ lasers is strongly affected by the diffusion. The vibrational relaxation rate measurements of the upper laser level reported in Chapter 4 indicate that the diffusion relaxation is quite significant for the upper laser level, and dominates the relaxation rate in low pressure gas mixtures. Consequently, diffusion can play an important role in low pressure CW CO₂ lasers.

2.6 Summary

This chapter has presented a comprehensive discussion of the state of knowledge on processes affecting the CO₂ laser levels prior to the work reported in this thesis. The issue of electron excitation cross-sections for the CO₂ molecule remained unresolved; in particular, the effect of electron de-excitation was not established with satisfaction prior to this work. Furthermore, the important V-V coupling processes of the lower laser levels were not well understood, and the rate constants remained to be determined for accurate modelling of CO₂ lasers.
CHAPTER 3

VIBRATIONAL POPULATION DISTRIBUTIONS IN CO₂ GLOW DISCHARGES

3.1 Introduction

This chapter describes in detail the use of a tunable diode laser (TDL) to probe the vibrational populations in a CW CO₂ discharge. The advantages of the technique are demonstrated through measurements of vibrational population distributions in CO₂ glow discharges with and without the presence of an intense 10 μm laser field. The significance of the results is discussed, with emphasis on their implications for CO₂ laser dynamics.

3.2 Experimental Approach

Previous investigations of CO₂ laser dynamics were generally made using line-tunable CO₂ laser oscillators as a probe. This CO₂ laser probe technique has shown considerable success in the studies of laser gain characteristics [2,3] and relaxation processes [4,5] in CO₂ lasers, but is somewhat limited in versatility and is unable to reveal the details of many important mechanisms. Advances in the development of tunable semiconductor lasers led Blum et al. [54] in 1972 to utilize a CW tunable PbSnSe diode laser operating near 5.3 μm to measure the full gain and loss lineshape of several vibration-rotation lines of a CO gas laser amplifier. These authors have also pointed out the great usefulness of the technique in studying the physics of gas lasers. Since then, however,
no further work was reported in the literature, prior to the present research.

In a series of experiments, a tunable diode laser (TDL) operating in the 2150-2350 cm\(^{-1}\) wavenumber region has been used to probe the vibrational populations in a CW CO\(_2\) discharge. The TDL possesses the great advantage that it can be tuned to monitor any vibrational transition in CO\(_2\); one is no longer limited to transitions which can be made to lase in a separate CO\(_2\) oscillator. Hence, highly excited vibrational levels of CO\(_2\) in all three normal vibrational modes can be monitored. In the \(v_3\) mode, all the levels up to 000\(^9\) (i.e. 20,000 cm\(^{-1}\) above the ground state) are studied, while in the \(v_1\) and \(v_2\) modes, populations in all levels between 01\(^1\)0 and 11\(^1\)0 are measured. Phase sensitive detection techniques are used and these enable quantitative measurements of vibrational populations as low as 10\(^{-6}\) of the ground state CO\(_2\) population.

In this chapter, the new experimental approach is applied to check the validity of the mode temperature concept which is widely used in the modelling of CO\(_2\) lasers. This is done by direct measurements of the absolute population of all levels in a conventional, flowing gas, CW CO\(_2\) laser discharge. The details of the analysis are given in Sections 3.4 and 3.5, while the next section discusses two theoretical models and relates the vibrational level populations to the absorption coefficients measured with the TDL.

3.3 Theoretical Models

The usual theoretical model for predicting CO\(_2\) laser performance involves separate vibrational temperatures for the different vibrational
modes of CO\textsubscript{2}, and was first introduced by Gordietz et al. [55] and Moore et al. [4]. Experimental confirmation of this model was generally limited to probing a CO\textsubscript{2} amplifier with a regular CO\textsubscript{2} laser beam. Recently, Siemsen et al. [2] also used sequence CO\textsubscript{2} lasers as probes, and were able to monitor the populations in several vibrational levels in addition to the regular laser levels. However, in all cases, the mode temperature model is assumed a priori and then used to deduce the vibrational temperatures which, in turn, are employed in the gain calculations. The good agreement between calculated and measured gain coefficients gives confidence in the model. This is a rather indirect confirmation and is limited to a few vibrational levels. In contrast, the experiments described here determine the absolute vibrational populations in more than 25 different vibrational levels and enable a more detailed comparison between experiment and theory to be made as discussed in Sections 3.4 and 3.5.

3.3.1 Boltzmann Distribution

Figure 3.1 shows some of the relevant energy levels in CO\textsubscript{2}. According to the mode temperature model [4,55], the vibrational level populations of each normal mode of CO\textsubscript{2} can be characterized by a Boltzmann distribution. Thus, in a discharge, vibrational temperatures $T_1$, $T_2$ and $T_3$ are associated with $\nu_1$, $\nu_2$ and $\nu_3$ modes, respectively. For convenience, exponential factors $x_1$, $x_2$ and $x_3$ are introduced, defined by

$$x_n = \exp(-\hbar \nu_n / k_B T_n)$$  \hspace{1cm} (3-1)

where $\hbar \nu_n$ is the mode spacing of the $n^{th}$ mode. This mode temperature model has been successfully applied to both CW and pulsed CO\textsubscript{2} lasers [2,3], and
FIGURE 3.1 Simplified vibrational energy level diagram of CO$_2$ showing the three fundamental modes with their associated mode temperatures. Also shown are some typical transition bands in the 2300 cm$^{-1}$ region which are probed with the tunable diode laser.
its use is justified by the very fast intramode relaxation rates which have been measured in CO$_2$ [36]. A fourth temperature required in the kinetic model is the rotational temperature $T_r$ which is generally equal to the translational temperature due to the extremely fast rotational relaxation rates in CO$_2$ [33].

In the experiment, measurements of the absorption coefficient are made in the fundamental $v_3$ band of CO$_2$ and all its associated "hot" bands, i.e., transitions between levels $ij^k$ and $ij^{k+1}$. Typical transitions are shown in Fig. 3.1. By measuring the absorption coefficients of such transitions, one can determine the population difference $(N_{ij^k} - N_{ij^{k+1}})$. The relationship between such population differences and the absorption coefficients has been derived by many authors and is given in Appendix A. For computational purposes, the vibrational matrix elements of the fundamental 00$^0$-00$^0$ band as measured by Fridovich et al. [56] and the values of the linewidths for the same band as calculated by Yamamoto et al. [57] are used. Moreover, the relative vibrational matrix elements of the various bands are assumed to be given by the simple harmonic oscillator approximation [58], and the linewidths are assumed to be the same for all bands [59]. As the lineshape is influenced by both Doppler and Lorentz broadening, a Voigt profile is used for the lineshape factor.

Once the population difference $(N_{ij^k} - N_{ij^{k+1}})$ has been determined from the absorption coefficients, one can determine the absolute vibrational population by noting that

$$N_{ij^k} = \sum_{k' \geq k} (N_{ij^{k'}} - N_{ij^{k'+1}})$$

(3-2)
Where the summation is over all high lying vibrational bands. In practice, only a few levels contribute to the sum, and the relevant absorption coefficients are easily measured with the TDL. As the absolute vibrational populations are known, they can be compared with the populations given by the mode temperature model [60], i.e.,

$$N_{ij,k} = N x_1^i x_2^j x_3^k g_v/Q_v$$  \hspace{1cm} (3-3)

where $N$ is the total number density of CO$_2$ molecules, $g_v$ is the degeneracy of the vibrational level and $Q_v$ is the vibrational partition function given by [60]

$$Q_v = (1 - x_1)^{-1}(1 - x_2)^{-2}(1 - x_3)^{-1}$$  \hspace{1cm} (3-4)

### 3.3.2 Treañor Distribution

The Boltzmann distribution results from the fact that the vibrational levels of each mode are assumed to follow those of an harmonic oscillator. This is a good approximation for the low-lying vibrational levels, but is not valid for highly excited levels where the anharmonicity of the molecule becomes significant. Treañor et al. [61] have examined the effects of anharmonicity on vibrational population distributions. They found that the vibrational distribution becomes non-Boltzmann upon the introduction of anharmonicity. This new distribution (hereafter referred to as Treañor distribution) has the following form

$$N_v = N_0 \exp \left\{ -hc[vG_1/\nu T]_v^* - \nu(v-1)\omega e^2 / 2k_B \right\}$$  \hspace{1cm} (3-5)

where $N_0$, $N_v$ are the population densities of the ground and excited vibrational levels, $G_1$ is the energy spacing between the first and ground
vibrational levels, \( w_e X_e \) is the anharmonicity, \( h \), \( c \) and \( k_B \) are the Planck constant, the speed of light and the Boltzmann constant, respectively. \( T \) is the translational temperature, and \( T^* \) is the Treanor vibrational temperature, defined by the relation:

\[
N_1/N_0 = \exp(-hcG_1/k_B T^*)
\]  

(3-6)

Note that if the anharmonicity is very small (i.e. \( w_e X_e \approx 0 \)), the relation (3.5) gives the familiar Boltzmann distribution with a vibrational temperature \( T_v = T^* \) - In the presence of significant anharmonicity, the additional term in the exponential of the relation (3-5) has a substantial effect on the populations of the high vibrational levels. In the case of CO molecules in a discharge, this mechanism of anharmonic pumping creates a partial population inversion and is responsible for the operation of the CO laser [62]. We will show that the Treanor distribution also provides a good description of the vibrational populations in the \( v_3 \) mode of the \( \text{CO}_2 \) molecule.

3.4 Measurements in a CW CO\(_2\) Laser Amplifier

The initial measurements of population distributions are carried out in a CW CO\(_2\) laser amplifier with no 10 \( \mu \)m CO\(_2\) laser field present. The effects of lasing on the level populations are considered in the next section.

3.4.1 Experimental Technique

A PbSnSe tunable diode laser (as supplied by Laser Analytics Inc.) operating in the 2150-2350 cm\(^{-1}\) region is used for all measurements. The diode laser is mounted on a cold finger tip inside a vacuum chamber as.
shown in Fig. 3.2. The finger is cooled by a helium refrigerator as supplied by CTI Cryogenics. Coarse tuning of the wavelength emitted from the diode laser is controlled by the temperature of the cold finger which can be set anywhere in the 10-70 K range and be stabilized by a feedback loop to within a few millidegrees. The fine tuning of the laser emission is obtained by varying the drive current supplied to the diode. The present diode laser has a typical output power of \( \sim 200 \text{ mW} \) distributed over 2-3 longitudinal modes. The beam from the TDL is focussed into a short \( \text{CO}_2 \) discharge tube, and then imaged onto the entrance slit of a 0.5 m spectrometer to select a single mode, as shown in Fig. 3.3. The output from the spectrometer is focussed onto a HgCdTe detector. The signal at the detector is fed into the input of a lock-in amplifier (PAR model 128A) whose output goes to the Y-axis of a recorder. The X-axis of the recorder is driven by a voltage from the laser control module which is proportional to the drive current. For direct detection of strong absorption lines, a chopper is used to interrupt periodically the probe beam and to provide a reference signal to the lock-in. For very weak absorption lines, second harmonic detection is used; in this case, the chopper is removed and a sinewave generator is used to modulate the drive current and to provide a reference signal to the lock-in. The \( \text{CO}_2 \) discharge tube has a bore of 1 cm and an active length of \( \sim 10 \text{ cm} \). It is operated with a fast gas flow rate of \( \sim 840 \text{ ml/min NTP} \) to minimize dissociation, and the cooling jacket temperature is maintained at 260K. An iris is placed in front of the discharge tube to restrict the probe beam to a small beam diameter of 2 mm for probing the center of the discharge. Quoted pressures
FIGURE 3.2 Photograph of the mounting of the tunable diode laser inside the cold head chamber.
FIGURE 3.3 Schematic diagram of the apparatus.
are averages of both inlet and outlet pressures.

Figure 3.4 shows two typical TDL scans taken with the laser beam passing through the discharge tube. The spectrometer selects a mode near 2284.4 cm\(^{-1}\), and the lower and upper traces are taken with and without a discharge current. Fortunately, the spectroscopy of CO\(_2\) in the 4.3 µm region has been studied in great detail [63], and line identification is not a problem. In general, to facilitate the task of line identification, computer generated spectra using available molecular constants were used, and line positions are predicted to be accurate to ±0.005 cm\(^{-1}\).

The more important absorption lines in Fig. 3.4 are labelled beneath the traces. Clearly, the TDL technique can supply a wealth of information on the population distribution in a discharge. The appearance of very strong absorption lines in the 00\(^0\)2 and 00\(^0\)3 bands demonstrates the efficiency of the discharge in populating the \(v_3\) mode of CO\(_2\), while absorption in bands such as 01\(^1\)0 and 10\(^0\)0 can be used to monitor vibrational populations in \(v_1\) and \(v_2\) modes.

As a first step in analyzing TDL scans such as those in Fig. 3.4, let us consider the upper trace. In the absence of a discharge, the CO\(_2\) molecules are in thermal equilibrium at a known temperature and pressure. As the gas mixture and absorption pathlength are also accurately known, one can compare the measured absorption coefficients to those predicted by the model of Section 3.3. This provides an experimental check on the matrix elements and linewidths for the various bands, and also ensures that no systematic errors are present in our measurements of gas mixture and pressure. In general, experiment and calculation agree to better than
FIGURE 3.4  Typical TDL scans taken with the laser beam focussed through the discharge tube. The upper scan is taken with no discharge current, while the lower scan corresponds to a current of 10 mA in a 10% CO$_2$:38% N$_2$:52% He mixture at 15 Torr. The more important absorption lines are labelled beneath the traces.
10% for lines with \( J \approx 20 \); one then normalises the calculation to agree with experiment. This step removes any errors which may arise due to inaccurate literature values of matrix elements or linewidths for the various bands. Of course, this "self-consistency" procedure can only be used for absorption bands which have a measurable room temperature absorption, and is therefore limited to bands with lower levels below \( \sim 2000 \text{ cm}^{-1} \). For higher lying bands we must rely entirely on the assumptions made for the linewidths and the linestrengths as discussed in Section 3.3.

The next step in the analysis is to select suitable absorption lines for each vibrational band under investigation. One ensures that the chosen lines are free from interference (i.e., no nearby lines), and where possible uses lines with \( J \) values near 20 to minimize the effects of the varying gas temperature. As can be seen in Fig. 3.4, this is not possible for the lower levels of the \( v_3 \) mode as the absorption under discharge conditions is far too strong near the center of the P and R branches. For these bands, one measures the absorption on weaker lines with high \( J \) values, i.e., \( J \approx 50-70 \) for \( 00^00 \) and \( 00^01 \) bands and \( J \approx 30-40 \) for \( 01^10 \) and \( 00^02 \) bands. Fortunately, the TDL used in these investigations gives almost complete coverage from 2140 to 2310 cm\(^{-1}\), and we were able to select suitable lines in \( \sim 25 \) different bands to determine the population distribution in the discharge.

### 3.4.2 Vibrational Distributions

The experimental measurements are made on individual vibration-rotation transitions, and can therefore only be used directly to determine
the population difference between the upper and lower vibro-rotational levels, $n_{\text{h}} - n_{\text{u}}$. Before $n_{\text{h}} - n_{\text{u}}$ can be calculated, one must know the rotational/ translational temperature, $T$, under discharge conditions. $T$ is easily evaluated by measuring the absorption coefficients of several lines in the same vibrational band [64]. In practice, the relative absorption coefficients of pairs of lines with a large difference in $J$ number are used. Each pair of lines gives a direct measure of $T$. Within experimental error ($\pm 10$ K), the temperatures deduced from different pairs of lines in the same band are in good agreement. By repeating these measurements for several different vibrational bands, we confirmed that all bands have the same rotational temperature. Once $T$ is known accurately, the measured absorption coefficient on any vibro-rotational transition can be converted to $n_{\text{h}} - n_{\text{u}}$, and then to a vibrational population difference $N_{\text{h}} - N_{\text{u}}$. Finally, from the population differences of the various bands, one can deduce the absolute population of each vibrational level using the summing relation (3.12).

The vibrational populations for a variety of gas mixtures under a wide range of discharge currents have been monitored. The vibrational distribution in the $\nu_3$ mode of CO$_2$ is of primary importance in the dynamics of CO$_2$ lasers. Figure 3.5 shows results obtained for the $\nu_3$ mode distribution at two discharge currents for a typical cw laser gas mixture (10% CO$_2$:10% N$_2$:80% He) and pressure (15.5 Torr). The solid curves are the calculated Treanor distributions in which the gas temperature $T$ is measured experimentally and the temperature $T_3^*$ is determined from a best fit to the data points. There is a very good agreement between the Treanor distribution
FIGURE 3.5 Vibrational population distributions in the $v_3$ mode of CO$_2$ at discharge currents of 5 and 25 mA. Data points are experimental measurements made with the TDL, while the solid lines are calculated Treanor distributions. The dashed line represents a Boltzmann distribution at 1600 K, and appears as a straight line in this semi-log plot.
\[ \log \left( \frac{N_{00}^{00}k}{N_{00}^{00}} \right) \]

VIBRATIONAL ENERGY (cm\(^{-1}\))

BOLTZMANN

\[ T_3 = 1600K \]

15.5 Torr

10% CO\(_2\) : 10% N\(_2\) : 80% He
and the measured populations. In Fig. 3.5, a Boltzmann distribution with \( T_3 = 1600 \) K is also shown. The deviation from the straight-line Boltzmann distribution can be clearly seen in the higher vibrational levels. Nevertheless, more than 98% of the excited \( v_3 \) molecules are in the first 3 vibrational levels where the distribution is well described by a Boltzmann. Thus, the use of the Boltzmann distribution (i.e., the mode temperature model) gives good agreement with experiment measurements of small-signal gain for both regular and sequence lasers [2]. The results shown in Fig. 3.5 demonstrate that \( T_3^* \) only increases by 40% as the discharge current is increased by a factor of 5. This behavior agrees with previous measurements [2], where it was shown that the most effective method to increase \( T_3^* \) is to have a large \( N_2 \) to \( CO_2 \) ratio in the gas mixture. Therefore, measurements on a 2% \( CO_2 \):20%\( N_2 \):78% He mixture at 15.5 Torr were also carried out. The results for the population distribution of the \( v_3 \) levels are plotted in Fig. 3.6. A significant increase of \( T_3^* \) is observed at all currents as compared to the 10% mixture, and once again the population distributions are well fitted by a Treanor distribution. These two factors result in a very dramatic increase of population in the highly excited \( v_3 \) levels. For example, the absolute population of the 00010 level in the 2% mixture is \( \sim 100 \) times that of the 10% mixture at identical current of 25 mA. The high values of \( T_3^* \) attained in the 2% mixture suggest that a partial inversion between two adjacent vibrational levels may occur at higher 000k level [62]. Our TDL could not be tuned beyond \( k = 10 \), and even with the aid of liquid nitrogen cooling of the discharge we were unable to observe gain on the P-lines of the 0009-0008 transition.
FIGURE 3.6 Repeat of Fig. 3.5 for a 2% CO₂: 20% N₂: 78% He mixture. Note the increase in $T^*$ which occurs as the CO₂ content is decreased from 10% in Fig. 3.5.
Nevertheless, it may be possible to operate CO$_2$ lasers at $\sim$ 5$\mu$m using the anharmonic pumping mechanism that is so efficient in the CO laser [62].

After investigating the $v_3$ mode, we turned our attention to the $v_1$ and $v_2$ modes. It is known that Fermi resonance causes strong coupling between these two modes, and it has often been assumed that the two modes are in equilibrium at the same vibrational temperature, i.e., $T_1 = T_2$.

The TDL provides the ideal probe to check this assumption. The populations in levels such as 01$^1$0, 02$^0$0, 03$^3$0, and the Fermi pairs 10$^0$0/02$^0$0 and 03$^3$0/01$^1$0 were measured. The results are given in Fig. 3.7, where, all the $v_1$ and $v_2$ mode populations are seen to lie on the same straight line, i.e., $T_1 = T_2$. A common vibrational temperature is observed under all discharge conditions, confirming the strong coupling between the two modes. As a final check on the consistency of the results, the populations in combination levels such as 01$^1$k, 02$^0$k and 10$^0$k (where k varies from 0 to 3) are measured as shown in Fig. 3.8. In all cases, the mode temperatures deduced from the combination levels agree well with $T_3^*$ in Fig. 3.5 and $T_1$ and $T_2$ in Fig. 3.7.

Figure 3.9 displays the variation of the rotational and vibrational temperatures in CO$_2$ as a function of current for a typical laser mixture. For each current, the value of $T$ is calculated from several pairs of vibro-rotational transitions, as described in the beginning of Section 3.4.2. The results shown in Fig. 3.9 are similar to those obtained by Siemsen et al. [2], but are now based on much more detailed TDL measurements. Once again, clear evidence is seen of a saturation of $T_3^*$ with increasing current, while no such saturation is observed in $T_1$ and $T_2$. 
FIGURE 3.7 Vibrational population distributions in the $v_1$ and $v_2$ modes of CO$_2$ at discharge currents of 5 and 25 mA. Data points are experimental measurements for the levels indicated in the figure while the solid lines represent Boltzmann distributions for given $T_1 = T_2$ temperatures.
FIGURE 3.8 Vibrational population distributions in the combination levels $01^1k$, $02^0k$ and $10^0k$ with $k = 0$ to $3$ at 25 mA. The mode temperatures as indicated in the figure are deduced from the combination levels shown. A good agreement with $T_3^* = 2250$ K in Fig. 3.5 is clearly seen.
FIGURE 3.9 Experimental values of $T_3$, $T_2 (=T_1)$ and $T$ as a function of discharge current. The various measurements of $T$ represent results calculated from different pairs of vibrational-rotational transitions in two different vibrational bands.
As it will be discussed in the next chapter, this saturation of $T_3^*$ is shown conclusively to be caused by electron de-excitation in the discharge.

3.4.3 CO$_2$ Dissociation

As the TDL enables one to monitor all vibrational levels in CO$_2$ containing significant populations, one can carry out a final check by summing all measured populations and comparing with the known CO$_2$ content of the gas mixture. However, before this check can be carried out one must know the degree of dissociation of CO$_2$ into CO in the discharge. This dissociation can be measured by determining the absorption coefficients on a few CO lines in the 1-0 and 2-1 bands which were within the tuning range of the TDL. A linear increase in CO concentration along the axis of the discharge is assumed [65], and Table 3.1 reports the observed fractional CO concentration averaged over the discharge length. As expected, in a short 10 cm discharge with fast flow rates, the degree of dissociation is minimal - only 2.4% dissociation at the maximum current. The rest of Table 3.1 summarizes the distribution of the CO$_2$ molecules through the various vibrational levels as a function of discharge current for a 10% CO$_2$ : 10% N$_2$ : 80% He mixture at 15.5 Torr. All values in Table 3.1 are averaged along the discharge length. From the Table, one can see that approximately half of the CO$_2$ molecules are found in excited levels at 25 mA. The populations of the 00$^0K_l$ levels initially increases sharply with current, but levels off for currents higher than 10 mA. In contrast, the populations of the 1$^2K_0$ levels show a steady increase with discharge current. The total observed CO$_2$ and CO molecules is given in
TABLE 3.1 Summary of the distribution of CO$_2$ molecules through the various vibrational levels as a function of discharge current.

<table>
<thead>
<tr>
<th>Group</th>
<th>0mA (a)</th>
<th>5mA</th>
<th>10mA</th>
<th>15mA</th>
<th>20mA</th>
<th>25mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>00$^0$0</td>
<td>0.95(b)</td>
<td>0.83</td>
<td>0.68</td>
<td>0.58</td>
<td>0.52</td>
<td>0.48</td>
</tr>
<tr>
<td>$\Sigma_{k \neq 0} (00^0k)$</td>
<td>0</td>
<td>0.10</td>
<td>0.13</td>
<td>0.14</td>
<td>0.14</td>
<td>0.13</td>
</tr>
<tr>
<td>$\Sigma_{i \neq 0} (ij^k0)$</td>
<td>0.05</td>
<td>0.09</td>
<td>0.11</td>
<td>0.13</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>$\Sigma (ij^k)c$</td>
<td>0</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>CO$_2$ (d)</td>
<td>1.00</td>
<td>1.03</td>
<td>0.94</td>
<td>0.88</td>
<td>0.83</td>
<td>0.80</td>
</tr>
<tr>
<td>CO</td>
<td>0.00</td>
<td>0.008</td>
<td>0.014</td>
<td>0.017</td>
<td>0.021</td>
<td>0.024</td>
</tr>
<tr>
<td>Total (e)</td>
<td>1.00</td>
<td>1.04</td>
<td>0.95</td>
<td>0.90</td>
<td>0.85</td>
<td>0.82</td>
</tr>
</tbody>
</table>

(a) Calculated using $T_1 = T_2 = T_3 = 260$K.
(b) All populations are normalized to the total number density of $^{12}$C$^{16}$O$_2$ molecules entering the discharge at the measured temperature T.
(c) Summation for $k \neq 0$ and $i$ or $j \neq 0$.
(d) Sum of the first 4 rows.
(e) Sum of CO$_2$ and CO.
the last row of Table 3.1. At 0 mA, this total is normalized to unity by the procedure described in Section 3.4.1. At higher currents, a slight discrepancy is seen, with only 82% of the calculated CO₂ molecules being directly observed with the TDL at 25 mA. However, any measurement of absolute population at 25 mA requires substantial corrections for the increased value of T, and also relies on the accuracy of matrix elements and linewidths of the highly excited transitions. In addition, any CO₂ molecules which are present in excited electronic states or as ions will not be detected by the TDL measurements. Consequently, it is felt that the discrepancy observed in the final column of Table 3.1 is within experimental errors, and that the TDL measurements give a very detailed and accurate picture of the population distributions in a CO₂ discharge.

3.4.4 Conclusion

The TDL measurements confirm the validity of the mode temperature model for the low vibrational levels in CO₂, but indicate that the populations of the high v₃ mode levels are best described by a Treonor distribution. Moreover, it is shown that the v₁ and v₂ modes in CO₂ are very strongly coupled, and that the v₃ mode excitation saturates at high input energies. Although the present series of measurements have been confined to small-signal effects in CO₂ discharges, the versatility of the TDL enables the measurement technique to be used to examine saturation dynamics in the presence of intense 10 μm laser fields. Such a situation encountered in CW CO₂ laser oscillators is studied in detail in the next section.
3.5 Measurements in a CW CO₂ Laser Oscillator

This section deals with the effects of CW lasing on the vibrational population distributions; this is of primary importance in the modelling of high power CW CO₂ lasers.

3.5.1 Experimental Apparatus

The same TDL and experimental technique as described in Section 3.4.1 are used. However, the short discharge tube is now placed inside a V-shaped laser cavity as shown in Fig. 3.10. The V-shaped cavity employed possesses several advantages: By utilizing the dichroic mirrors M₁ and M₂, the TDL beam only probes a discharge length of 10 cm. This short pathlength is essential as many of the probed transitions have very large absorption coefficients. However, the majority of the in-cavity 10 μm radiation is provided by the longer 1.0 m discharge tube in the second arm of the V-cavity. Thus, one is able to achieve a laser intensity of ~ 600 W/cm² in the center of the short discharge tube. As the discharge current, gas pressure and mixture in the short tube are varied over a wide range, minor adjustments in the operating conditions of the 1.0 m discharge are sufficient to maintain the in-cavity 10 μm intensity at a constant value. The CW 10 μm field is several times larger than the saturation parameter in the short tube, and hence one is able to produce very large steady state perturbations of the vibrational populations. In addition, a small absorber cell situated behind the chopper absorbs the CO₂ laser beam and prevents it from reaching the laser.
FIGURE 3.10 Schematic diagram of the apparatus used to study vibrational populations in the presence of a strong laser field. The solid line indicates the path of the tunable diode laser beam, whereas the dashed line represents the CO$_2$ laser beam. The CO$_2$ laser cavity is formed by the grating G, and two highly reflecting 10 µm mirrors, M$_1$ and M$_2$. The small absorber cell selectively absorbs the 10 µm radiation and prevents it from reaching the diode laser.
3.5.2 Vibrational Distributions

In Section 3.4, it was shown experimentally that the concept of a mode temperature provides a very good representation of populations in a CO$_2$ discharge. One is now concerned with the change in these populations induced by intense CW 10 $\mu$m radiation.

The TDL scans shown in Fig. 3.11 illustrate the substantial population changes which are induced by the 10 $\mu$m P (22) line with an in-cavity intensity of 560 W/cm$^2$. A removable screen near the mirror $M_1$ allows one to take TDL scans with and without lasing. Note the dramatic reduction in absorption on lines A and B in the presence of 10 $\mu$m lasing. This can be contrasted with the small change in line C. Using techniques described in Section 3.4.2, the measured absorption coefficients are converted into vibrational populations which are plotted in Figs. 3.12 and 3.13. We can see that the population distributions agree well with the mode temperature model for both lasing and no lasing cases. The significant cooling of the $v_3$ mode temperature is clearly displayed, whereas there is only a minimal heating of the $v_1$ and $v_2$ modes. These observations are typical of our measurements on conventional CW CO$_2$ laser discharges; under lasing conditions the upper laser level is emptied while the lower laser level does not show a substantial increase in population. This type of behavior clearly contributes to the high efficiency of the CO$_2$ laser. The results in Figs. 3.12 and 3.13 are obtained for a gas pressure of 19.4 Torr which is typical of CW CO$_2$ lasers. As the pressure is reduced, so are the collisional relaxation rates, and one expects to see anomalous populations in the directly pumped levels. The anomalies in
FIGURE 3.11 Typical TDL laser scans showing the effect of 10 μm laser radiation on the vibrational populations. Lasing and no lasing refer to the presence or absence of a saturating 10 μm P(22) field with intensity of 560 W/cm². Most of the absorption lines are identified at the bottom of the figure. Lines A and B are associated with the $v_3$ mode (upper 10 μm laser level), while line C is coupled to the lower laser level. The short discharge tube contained a 9.2% CO₂:11% N₂:79.8% He mixture at 19.4 Torr total pressure. The discharge current was 10 mA.
FIGURE 3.12 Vibrational population distributions in the $v_3$ mode of CO$_2$ for a discharge current of 25 mA. Lasing and no lasing refer to the presence or absence of a saturating 10 $\mu$m P(22) field with intensity of 560 W/cm$^2$. The dramatic reduction of the $v_3$ mode level populations with lasing is clearly displayed.
FIGURE 3.13  Vibrational population distributions in the $v_1$ and $v_2$ modes of $\text{CO}_2$ at a discharge current of 25 mA. Again, lasing and no lasing refer to the presence or absence of a saturating 10 $\mu\text{m}$ P(22) field with intensity of 560 W/cm$^2$. Only a small increase of level populations is observed upon lasing.
19.4 Torr
92% CO₂ : 11% N₂ : 79.8% He

$N_{ij}/g_0 N_{000}$

Lasing

No Lasing

VIBRATIONAL ENERGY ($10^8$ cm⁻¹)
the vibrational distributions are illustrated in Figs. 3.14 and 3.15 for a 2.4 Torr gas mixture. One can see from the curve (b) of Fig. 3.14 that the 00^01 level has a vibrational population smaller than that expected from the mode temperature model. Concurrently, the population of the 10^00 level in the 10 μm laser (curve b of Fig. 3.15) and that of 02^00 level in the 9 μm laser (curve c of Fig. 3.15) are both significantly higher than the predictions of the mode temperature model. The anomalies in the vibrational populations of the upper and lower laser levels are the result of competition between the stimulated emission process and the equilibration processes of the levels. Details of these processes are discussed in Chapter 4 and Chapter 5.

3.5.3 Small-signal Gain and Saturated Gain

From the above discussion, the concept of a mode temperature is generally valid in the presence of the intense CW 10 μm laser field. Therefore, the vibrational population distributions of the 19.4 Torr gas mixture are presented in terms of vibrational and rotational temperatures plotted in Figs. 3.16 and 3.17 for both lasing and no lasing cases. The most significant difference between the two sets of temperatures is the reduction in T_3 with lasing. A useful parameter to represent the two sets of temperatures is the saturated and small-signal gain as shown in Fig. 3.18. The small-signal gain γ_0 rises very rapidly at low currents, then levels off, and finally drops at large currents. In contrast, the saturated gain γ_s increases steadily with current. Also shown in Fig. 3.18 is the stimulated emission power density, P_s, which is evaluated from the product of the in-cavity laser intensity and the saturated gain. One can
FIGURE 3.14  Repeat of Fig. 3.12 with a much lower gas pressure for two cases: (a) no laser field is present; (b) a 10 $\mu$m P(22) field with intensity of 500 W/cm$^2$ is present. Note that the upper laser level, 00$^01$, has a population smaller than that expected from a Boltzmann distribution.
2.4 Torr
9.2% CO₂: 11% N₂: 79.8% He

VIBRATIONAL ENERGY (10³ cm⁻¹)

(a) No Lasing

(b) Lasing
FIGURE 3.15 Repeat of Fig. 3.13 with a much lower gas pressure for three cases: (a) no laser field is present; (b) a 10 μm P(22) field with intensity of 500 W/cm² is present; (c) a 9 μm P(22) field with intensity of 108 W/cm² is present. Note that the lower laser levels, 10°0 and 02°0, have anomalously high populations under the 10 μm and 9 μm lasings respectively.
2.4 Torr
92% CO₂ : 11% N₂ : 79.8% He

(a) No Lasing

(b) 10 μm Lasing

(c) 9 μm Lasing

$N_{ij}/k/g_{ij}N_{ij}$

VIBRATIONAL ENERGY (10^6 cm⁻¹)
FIGURE 3.16  Vibrational and rotational temperatures as a function of discharge current in the presence of an intense 10 μm field with intensity of 560 W/cm².
Lasing
19.4 Torr
9.2% CO₂, 11% N₂, 79.8% He

\[ T_1 = T_2 \]

\[ T \]

\[ T_3 \]
FIGURE 3.17 Vibrational and rotational temperatures as a function of discharge current in the absence of a laser field. Note the saturation of $T_3$ at high discharge currents.
FIGURE 3.18 Calculated small signal gain, $\gamma_0$, and saturated gain, $\gamma_s$, as a function of discharge current using the measured temperatures displayed in Figs. 3.16 and 3.17. Also shown is the power density, $P_s$, extracted from the short discharge due to stimulated emission at 10 $\mu$m.
19.4 Torr
9.2% CO₂ : 11% N₂ : 79.8% He

GAIN (% cm⁻¹)

CURRENT (mA)

P_s W/cm³

γ₀

γ_s
see that $P_s$ also increases steadily with current, indicating a steady increase of the electron excitation rate to the upper laser level. The values of $P_s$ will be used in Chapter 4 to determine the electron excitation and de-excitation rates.

3.5.4 Vibrational Temperature of CO

It has been shown by Treanor et al. and others [61,62] that, in a system of oscillators where the intramode vibration-vibration exchange dominates the energy transfer processes, the populations of the vibrational mode follow a quasi-equilibrium distribution: a Boltzmann distribution for harmonic oscillators and a Treanor distribution for anharmonic oscillators (see Section 3.3). Moreover, in a mixture of vibrational oscillators where the vibration-vibration exchange dominates the energy transfer processes, the vibrational mode with smallest vibrational quantum energy possesses the highest vibrational temperature. This situation is very common in the CO$_2$ laser where N$_2$ and CO molecules are often added to the discharge. For convenience, we define the $v_4$ mode as the vibrational mode of N$_2$ and the $v_5$ mode as the vibrational mode of CO. The V-V energy transfer from the CO$_2$ $v_3$ mode to the N$_2$ $v_4$ mode (with $h\nu_3 - h\nu_4 = 18$ cm$^{-1}$) and from the CO$_2$ $v_3$ mode to the CO $v_5$ mode (with $h\nu_3 - h\nu_5 = 206$ cm$^{-1}$) are $\sim 1.9 \times 10^4$ s$^{-1}$ Torr$^{-1}$ and $5.7 \times 10^3$ s$^{-1}$ Torr$^{-1}$, respectively [4,66].

These V-V rates are much faster than the deactivation rate of the $v_3$ mode by N$_2$ which is $\sim 106$ s$^{-1}$ Torr$^{-1}$ [4] and by CO which is $\sim 250$ s$^{-1}$ Torr$^{-1}$ [66], and are also much faster than their self-deactivation rates. As the vibrational temperature $T_4$ is not accessible in the present experiment, only $T_3$ and $T_5$ are measured. For simplicity, the vibrational temperature
$T_3$ is determined from the ratio of absorption coefficients measured in the $00^04 \leftrightarrow 00^03$, $00^03 \leftrightarrow 00^02$ and $00^02 \leftrightarrow 00^01$ bands; similarly, $T_5$ is determined from measurements made in the $3 \leftrightarrow 2$ and $2 \leftrightarrow 1$ bands of CO. The measurements are shown in Fig. 3.19 for a mixture of 4.9% CO$_2$:3.8% CO:91.3% He at 15.4 Torr in both lasing and no lasing conditions using the apparatus described previously. As expected, a much higher $T_5$ temperature is observed. In the no lasing case, the $T_3$ and $T_5$ temperatures agree reasonably well with the relation [61]:

$$\frac{h\nu_3}{k_B T_3} - \frac{h\nu_5}{k_B T_5} = \frac{h(\nu_3 - \nu_5)}{k_B T}$$

(3-7)

where $T$ is measured experimentally. However when the intense 10 $\mu$m field is present, the very large stimulated emission rate requires that corrections must be made to the relation (3-7) as discussed by Caledonia et al. [62]. One can see from Fig. 3.19 that in the lasing case, $T_3$ is dramatically reduced as observed previously, while $T_5$ only decreases by a small amount. Similar behavior is expected for CO$_2$:N$_2$:He mixtures, since the V-V exchange rate for CO$_2$:N$_2$ is only a few times larger than that for CO$_2$:CO. This very large difference in the vibrational temperatures $T_3$, $T_4$, and $T_5$ must be taken into account for accurate modelling of CO$_2$ lasers.

One can also compare the attainable $T_3$ temperature in a CO$_2$:CO:He mixture to that attainable in a CO$_2$:N$_2$:He mixture. The results of such a comparison are shown in Fig. 3.20. Note that the $T_3$ temperatures in a CO$_2$:N$_2$:He mixture are clearly higher than those in a CO$_2$:CO:He mixture for both lasing and no lasing conditions. Although a detailed comparison would require measurements of all vibrational and rotational temperatures,
FIGURE 3.19 Measured values of $T_3$ and $T_5$ as a function of discharge current with and without the presence of a 10 $\mu$m laser field. Note the substantial change in $T_3$ with lasing; whereas $T_5$ is only reduced by a small amount.
FIGURE 3.20  Comparison between $T_3$ in a $\text{CO}_2:\text{N}_2:\text{He}$ mixture and $T_3$ in a $\text{CO}_2:\text{CO}:\text{He}$ mixture. Note that the $T_3$ temperatures in a $\text{CO}_2:\text{N}_2:\text{He}$ mixture are clearly higher than those in a $\text{CO}_2:\text{CO}:\text{He}$ mixture for both lasing and no lasing conditions.
the general behavior agrees with that expected from the better energy matching between CO$_2$ and N$_2$ and a larger electron excitation rate for N$_2$.

3.6 Summary

This chapter has presented detailed measurements of vibrational population distributions, and vibrational and rotational temperatures in typical CO$_2$ discharges for both lasing and no lasing conditions. The anharmonicity of the CO$_2$ molecule has a great effect on the populations of the highly excited CO$_2$ v$_3$ mode levels, and requires a Treanor distribution for proper description of the population of these levels. In general, the results support the use of the mode temperature model in the modelling of CO$_2$ lasers.
CHAPTER 4

VIBRATIONAL RELAXATION OF THE CO₂ UPPER LASER LEVEL

4.1 Introduction

The previous chapter dealt with steady state population distributions in a CW CO₂ laser discharge. These populations are maintained by a delicate balance between excitation and de-excitation processes. It was shown in Chapter 3 that the T₃ vibrational temperature saturates at high discharge currents (see Fig. 3.9), indicating the existence of some de-excitation processes which prevent the continuous build-up of the ν₃ mode population. The increase of de-excitation rate with current may be caused by both thermal and electron effects [2,29]. Experimentally, the de-excitation rate of any level can be conveniently determined from the relaxation rate of the level, i.e., the rate of return to equilibrium after a perturbation of the level population. From measurements of the vibrational relaxation rate of the upper laser level in CO₂ mixtures both with and without a discharge, we are able to separate thermal effects from electron effects; in particular, we can determine the electron de-excitation rate in typical CO₂ laser discharges. These measurements are described in Sections 4.5 and 4.6. The next section presents a theoretical model for the relaxation of the upper laser level, and in Section 4.3 the relations between relaxation rates and electron excitation and de-excitation rates are discussed. It will be shown that electron de-excitation is responsible for the saturation of the ν₃ mode temperature at high discharge currents.
This chapter is concerned mainly with the behavior of the upper laser level, the next chapter will discuss the relaxation mechanisms of the lower laser level.

4.2 Relaxation Model for the Upper Laser Level

To describe the relaxation of the CO\(_2\) (00\(^0\)1) level in CO\(_2\):N\(_2\):He mixtures, a modified version of the model developed by Gower and Carswell [30] is used. Due to the fast intramode energy transfer processes, and the fact that a Boltzmann population distribution is observed in the \(v_3\) mode under all experimental conditions, one can treat the coupled \(\sum_{ij} (i j ^2 1)\) levels in CO\(_2\) as a single level with population \(C_1\). Thus, referring to the energy level diagram in Fig. 4.1, the changes in level population are as follows:

\[
\frac{dC_1}{dt} = -(k_{CN} N + k_{1M} + \delta_c + n_{e'C_c} C_1) + k_{NC} C_0 N_1 + n_{e'C_c} C_0 \quad (4-1)
\]

\[
\frac{dN_1}{dt} = + k_{CN} N O C_1 - (k_{NC} + \delta_N + n_{e'N_c} N_1) + n_{e'N_0} N_0 \quad (4-2)
\]

where \(C\) and \(N\) are the total number density of CO\(_2\) and N\(_2\) molecules respectively; \(C_0\) and \(C_1\) are the single-level representation of the coupled levels \((i j ^0 0)\) and \((i j ^2 1)\) respectively; \(N_0\) and \(N_1\) are the number density in the ground and first excited levels of the N\(_2\) vibrational mode; \(k_{CN}\) and \(k_{NC}\) are the rate constants of the vibrational energy transfer between CO\(_2\)\((v_3)\) and N\(_2\)\((v_4)\) modes; \(k_{1M}\) is the collisional de-excitation rate of the level \(C_1\) due to all molecules \(M\); \(\delta_c\) and \(\delta_N\) are the diffusion relaxation rate of the levels \(C_1\) and \(N_1\) respectively; \(n_{e'C_c}\) and \(n_{e'N_c}\) are the effective electron excitation and de-excitation rates of the level \(C_1\);
FIGURE 4.1 Simplified vibrational energy level diagram showing the three normal modes of CO$_2$ and the vibrational mode of N$_2$ with their associated mode temperatures $T_1$, $T_2$, $T_3$ and $T_4$. The dashed lines indicate typical vibrational bands in the 4.3 $\mu$m region which are probed by the TDL. The solid lines show some important energy transfer processes between the $\nu_3$, $\nu_4$ modes and electrons.
$n_e N$ and $n_e r'$ are the effective electron excitation and de-excitation rates of the level $N_1$. The collisional de-excitation of excited $N_2$ molecules is neglected.

The equations (4-1) and (4-2) can be rewritten as:

$$\frac{dC_1}{dt} = -\alpha_1 C_1 + \alpha_2 N_1 + \alpha_0 \tag{4-3}$$

$$\frac{dN_1}{dt} = +\beta_1 C_1 - \beta_2 N_1 + \beta_0 \tag{4-4}$$

with:

$$\alpha_1 = k_{CN} N + k_1 M + \delta_c + n_e r'$$

$$\alpha_2 = k_{NC} C$$

$$\alpha_0 = n_e r' C$$

$$\beta_1 = k_{CN} N$$

$$\beta_2 = k_{NC} C + \delta N + n_e r'$$

$$\beta_0 = n_e r' N$$

The level populations $C_0$ and $N_0$ can be considered to be constants under our experimental conditions. The coupled equations (4-3) and (4-4) can be solved in a straightforward fashion and yield [30]:

$$C_1(t) = a_0 + a_1 e^{-t/\tau_f} + a_2 e^{-t/\tau_s} \tag{4-5}$$

$$N_1(t) = b_0 + b_1 e^{-t/\tau_f} + b_2 e^{-t/\tau_s} \tag{4-6}$$

where $a_0$, $a_1$, $a_2$, $b_0$, $b_1$ and $b_2$ are constants to be determined by the initial conditions in terms of $\alpha_0$, $\alpha_1$, $\alpha_2$, $\beta_1$ and $\beta_2$. The decay rates $1/\tau_f$ and $1/\tau_s$ are given by:

$$\frac{1}{\tau_f} = \alpha_1 + \beta_2 \tag{4-7}$$
\[
\frac{1}{\tau_f} = \frac{a_2 \beta_2 - a_1 \beta_1}{a_1 + \beta_2}
\]  
(4-8)

provided that \(4(a_2 \beta_2 - a_1 \beta_1)/(a_1 + \beta_2)^2 = \tau_f/\tau_s \ll 1\). The experimental results described in Section 4.5 show that \(\tau_f \ll 20 \tau_s\) and the experimental double exponential decay is well described by Eqs. (4-7) and (4-8).

These equations can be rewritten as:

\[
\frac{1}{\tau_f} = \frac{k_{NC} C + k_{CN} N + k_{1} M + \delta C + \delta N + n_e (r'_C + r'_N)}{k_{NC} + k_{CN} N + k_{1} M + \delta C + \delta N + n_e (r'_C + r'_N)}
\]  
(4-9)

\[
\frac{1}{\tau_s} = \frac{k_{NC} C + k_{CN} N + k_{1} M + \delta C + \delta N + n_e (r'_C + r'_N)}{k_{NC} + k_{CN} N + k_{1} M + \delta C + \delta N + n_e (r'_C + r'_N)}
\]  
(4-10)

where we have approximated \(C_0\) and \(N_0\) to \(C\) and \(N\) in \(a_2\) and \(\beta_1\), and neglected small terms in the numerator of Eq. (4-10) which do not contain \(k_{NC}\) or \(k_{CN}\) [87]. In the absence of a discharge, \(n_e = 0\), and Eq. (4-9) reduces to:

\[
\frac{1}{\tau_f} = \frac{k_{NC} C + k_{CN} N + k_{1} M + \delta C + \delta N}{k_{NC} + k_{CN} N + k_{1} M + \delta C + \delta N + n_e (r'_C + r'_N)}
\]  
(4-11)

This equation will be used in Section 4.5. The fast relaxation rate, \(1/\tau_f\), is dominated by the energy exchange between \(CO_2(v_2)\) and \(N_2(v_4)\) modes. The slow relaxation rate, \(1/\tau_s\), depends on both diffusional and collisional de-excitations. Even in the absence of a discharge, \(1/\tau_s\) will still have a complex pressure dependence as shown in Fig. 4.4, where it can be seen that the effect of diffusion is significant.

For mixtures with no \(N_2\), all the terms in Eqs. (4-1) and (4-2) relating to nitrogen become zeros, we have only

\[
\frac{dC_1}{dt} = -(k_{1} M + \delta C + n_e r'_C)C_1 + n_e r'_C C_0
\]  
(4-12)
and the population \( C_1 \) decays with a single exponential of rate:

\[
\frac{1}{\tau} = k_4 M + \delta_C + n_e r'_C
\]  

(4-13)

This relationship has been verified experimentally (see Fig. 4.7). In the absence of a discharge, Eq. (4-13) reduces to:

\[
\frac{1}{\tau'} = k_4 M + \delta_C
\]  

(4-14)

where \( \tau' \) is the relaxation time in the absence of a discharge.

4.3 Relationships Between Relaxation Rates and Electron Excitation and De-excitation Rates

From Eqs. (4-13) and (4-14), it can be seen that by measuring relaxation rates with and without a discharge, one can obtain the effective electron de-excitation rate

\[
\frac{1}{n_e r'_C} = \frac{1}{\tau} - \frac{1}{\tau'}
\]  

(4-15)

in discharge mixtures with no \( N_2 \). In addition to determining electron de-excitation rates, one is also able to calculate the electron excitation rates. The relaxation rate measurements can be combined with \( T_3 \) measurements of the type described in Chapter 3 to determine the rate of loss of population from the upper laser level in the absence of lasing. Under steady state conditions, this rate of loss of population must be equal to the rate of production by electron excitation, i.e.,

\[
n_e C_0 = C_1/\tau
\]  

(4-16)
As \( \frac{C_1}{C_0} = \exp(-h\nu_3/kT_3) = x_3 \), Eq. (4-16) can be rewritten as:

\[
n_e r_C = x_3/\tau \tag{4-17}
\]

It will be shown in Section 4.6 that, to a very good approximation, the measured values of \( x_3/\tau \) do vary linearly with the discharge current according to Eq. (4-17).

The situation is more complicated when \( N_2 \) is present in the discharge. To determine the electron excitation and de-excitation rates from measurements of the relaxation rates, \( 1/\tau_s \), and the \( \nu_3 \) mode temperature, one must approximate Eq. (4-10) in the following form:

\[
\frac{1}{\tau_s} = \frac{k_{1M} + \delta_C + n_e r_C^t + \frac{k_{CH}}{k_{NC}} \left( \delta_N + n_e r_N^t \right)}{D} \tag{4-18}
\]

where the numerator and denominator have been divided by \( k_{NC} \), and the term \( n_e (r_C^t + r_N^t) \) in the denominator has been neglected in comparison with the much larger term \( k_{NC} + k_{CH} + k_{1M} + \delta_C + \delta_N = Dk_{NC} \). In the absence of a discharge, we obtain

\[
\frac{1}{\tau_s} = \frac{k_{1M} + \delta_C + \frac{k_{CH}}{k_{NC}} \delta_N}{D} \tag{4-19}
\]

Hence, the effective electron de-excitation rate is given by

\[
n_e r_C^t + \frac{k_{CH}}{k_{NC}^t} n_e r_N^t = D\left( \frac{1}{\tau_s} - \frac{1}{\tau_s} \right) \tag{4-20}
\]

The value of \( D \) varies only very slightly with the gas temperature and can be considered, for all practical purposes, to be constant. It will be
shown in Section 5.6.2 that the term \( \frac{1}{\tau_s} \) has a linear dependence upon the discharge current.

To determine the corresponding electron excitation rate in a CO\(_2\):N\(_2\):He mixture, we follow the same procedure as used with CO\(_2\):He mixtures, and equate the steady state rate of loss of population to the rate of production by electron excitation. Population is lost at a rate of \( l/\tau_s \) from all excited levels of CO\(_2\)(\( v_3 \)) and N\(_2\)(\( v_4 \)) modes, while direct electron excitation from the ground level to highly excited levels of the N\(_2\) molecule must also be considered. Hence, the equilibrium condition is

\[
\sum_{i} n_{ci} C_i + \left( \sum_{i} n_{ei} N_i \right) N = \frac{\tau_s}{\tau_s} \left( C_j + N_j \right)
\]

where \( i \) and \( j \) are summed over all excited \( v_3 \) or \( v_4 \) levels. Dividing each side by \( C \), we obtain

\[
n_{ci} C + \frac{N}{C} \left( \sum_{i} n_{ei} N_i \right) = \frac{x_3 + \frac{N}{C} x_4}{\tau_s}
\]

where \( x_4 = \exp(-\hbar \nu_4/kT_4) \), and is related to \( x_3 \) by [61]

\[
\frac{\hbar \nu_3}{kT_3} \cdot \frac{kT_4}{kT_4} = \frac{\tilde{n}(\nu_3 - \nu_4)}{kT}
\]

All terms on the right hand side of Eq. (4-22) are known experimentally as a function of discharge current, while the left hand side can be evaluated from the calculations of Judd [15]. The comparison will be given in Section 4.6.
4.4 **Experimental Apparatus**

Figure 4.2 shows a schematic diagram of the apparatus used for relaxation rate measurements; the same TDL system described in Chapter 3 is used. Basically, the set-up is similar to that in Fig. 3.10, but the CO₂ laser oscillator is now operated in a pulsed mode instead of a CW mode. The grating has been replaced by a rotating mirror for Q-switching the laser. The short discharge tube is now subject to a train of intense laser pulses with peak powers of several kilowatts/cm², pulse durations of 160 nsec full-width-half-maximum, and a frequency spectrum distributed over the 10 µm P(16), P(18), P(20), and P(22) lines. The effect of these pulses is monitored directly by the HgCdTe detector whose output is fed into a storage oscilloscope with signal averaging capabilities (Tektronix Model 468). A GeAu detector placed just behind the mirror M₁ monitors the Q-switched pulse and provides proper triggering for the oscilloscope.

The repetition rate of the Q-switched pulses is 200 pps. This relatively low repetition rate allows all the vibrational populations to return to equilibrium between pulses. For each measurement, the TDL is tuned to the linecenter of a selected transition in the ν₃ mode. The output signal from the HgCdTe detector is averaged in the oscilloscope up to a maximum of 256 sweeps. The signal-to-noise ratio after averaging varies from 10 to 100 depending on the operating conditions.

Gases and laser premixtures used in all the relaxation rate measurements are supplied by Canadian Liquid Air and are used with no further purification. Quoted pressures are measured at the gas outlet.
FIGURE 4.2 Schematic diagram of the apparatus used for all the relaxation rate measurements. The Q-switching of the CO$_2$ laser is achieved by a rotating mirror, and the changes in level populations as induced by the laser pulse are monitored by a HgCdTe detector. The output signal of the detector is fed into a storage scope which is triggered by a Au:Ge detector placed just behind the mirror M$_1$. 
of the discharge tube with a calibrated Edwards gauge. There is a negligible pressure drop across the short tube. Results obtained with the Q-switched pulses are presented in the next two sections.

4.5 Relaxation Rates of the $v_3$ Mode in Pure CO$_2$ and in CO$_2$ :N$_2$ :He Mixtures in Thermal Equilibrium

The initial experiments are performed on gas mixtures in the short tube in the absence of a discharge. The passage of an intense 10 $\mu$m CO$_2$ laser pulse through the gas transfers ~50% of the 10$^0$ population to the 00$^0$1 level. The TDL is tuned to a specific transition in the 00$^0$1 $\rightarrow$ 00$^0$2 band, and monitors the return of the 00$^0$1 population to thermal equilibrium, i.e., to its original state of approximately zero population. Typical signals are shown in the inserts of Figs. 4.3 and 4.4. Measurements on gas mixtures in thermal equilibrium serve two purposes: (i) one can compare the results with those reported previously and determine the reliability and accuracy of the technique; and (ii) one can evaluate the lifetime of the 00$^0$1 levels (including effects of temperature and diffusion) in the absence of a discharge, and then compare directly with the lifetime in a discharge.

4.5.1 Pure CO$_2$

The relaxation rate of the 00$^0$1 level in pure CO$_2$ is given by Eq. (4.14). The peak absorption induced in the 00$^0$1 transitions ranges from 30 to 95%, depending upon CO$_2$ pressure and the probe line used. Consequently, the TDL signals, such as that shown in Fig. 4.3, must be
FIGURE 4.3 Relaxation rate of the 0001 level in pure CO2 at room temperature. Measurements are shown for two different probe transitions. The solid line gives the contribution of collisional relaxation processes to the measured rate. The insert is a photograph of the storage oscilloscope display after 128 individual scans have been averaged. This photograph shows a typical signal observed in 4.3 Torr CO2 with the TDL tuned to the line center of the 0001 P(19) transition.
Relaxation rates of the $00^01$ level in a 9.2% CO$_2$:11% N$_2$:79% He mixture at room temperature. The insert shows a typical signal, taken with a TDL probe on the $00^01$ P(19) transition, illustrating the double exponential decay of the perturbed population. The fast ($1/\tau_f$) and slow ($1/\tau_s$) relaxation rates are both plotted as a function of pressure. Also, shown is the calculated collisional contribution to the slow rate.
corrected for the exponential variation of the transmission with absorption coefficient to determine the true decay of the 00^01 population. Once this correction is carried out, the 00^01 population is found to return to equilibrium with a single exponential rate. This rate is plotted as a function of pressure in Fig. 4.3. Note that the two different probe lines give identical results, confirming that rotational equilibrium is maintained. The trend of the experimental results closely follows that reported by Margottin-Maclou et al. [68]. At higher pressures, the collisional relaxation processes dominate and the results are in good agreement with the value of 350 s^{-1} Torr^{-1} reported in Reference [68].

4.5.2 CO_2:N_2:He Mixtures

A typical CO_2 laser mixture of 9.2% CO_2:11% N_2:79.8% He is used in this experiment. With the addition of N_2, the v_3 mode population of CO_2 decays with a double exponential, as illustrated in the insert of Fig. 4.4. The fast component of the relaxation rate, 1/\tau_f, represents the energy exchange rate between CO_2(v_3) and N_2(v_4) modes, and is given by Eq. (4-11), whereas the slow component, 1/\tau_s, is given by Eq. (4-19). The results of the measurements of 1/\tau_f and 1/\tau_s are shown in Fig. 4.4. The fast relaxation rate increases linearly with pressure, and by correcting the measured value of 1/\tau_f for the small contribution from (k_c^0 + \delta_c^0 + \delta_N^0) the CO_2 --> N_2 energy exchange rate is determined as (3.59 \pm 0.15) \times 10^3 s^{-1} Torr^{-1} [69] in our mixture. This value agrees well with the value of (3.57 \pm 0.18) \times 10^3 s^{-1} Torr^{-1} of Gueguen et al. [70] and is slightly larger than the (3.20 \pm 0.16) \times 10^3 s^{-1} Torr^{-1} of Rosser et al. [71]. (The results quoted in Refs. [70] and [71] have been adjusted for our mixture using Eq. (4-11)).
The slow relaxation rate, $1/r_s$, does not have a linear dependence upon pressure as relaxation by diffusion makes a significant contribution to the total relaxation rate. The effect of diffusion can clearly be seen by comparing the measured relaxation rate in Fig. 4.4 with the calculated collisional relaxation rate [4].

4.5.3 Temperature Dependence of $00^01$ Relaxation Rates

As a final stage in the measurements of gas mixtures in thermal equilibrium, an investigation of the temperature dependence of the slow relaxation rate is made. Several authors have carried out detailed investigations of the temperature dependence of the collisional relaxation rates of the $00^01$ level in pure CO$_2$ and mixtures [72], and measurements have also been made of the effect of temperature on diffusion in pure CO$_2$ [73]. However, we are now concerned with gas mixtures of CO$_2$, N$_2$, and He, where relaxation by collisions and diffusion occur with comparable rates. Consequently, the cooling jacket of the short tube is immersed in a bath of hot oil, and relaxation rates in typical CO$_2$ laser mixtures are measured over the temperature range from 260 to 400 K. The results of these measurements are shown in Figs. 4.5 and 4.6 for two mixtures, i.e., 9.1% CO$_2$:90.9% He at 10.4 torr and 9.2% CO$_2$:11% N$_2$:79.8% He at 19.4 Torr. A linear dependence on temperature is observed for both mixtures. The results of these measurements will be used in Section 4.6 to differentiate between electron effects and the unavoidable heating of the gas produced by an electrical discharge.
FIGURE 4.5 Variation of relaxation rate of the 00^1 level as a function of gas temperature in a 9.1\% CO\textsubscript{2}:90.9\% He mixture at 10.4 Torr. These measurements were made in the absence of a discharge and are used in Section 4.6.1 to account for the effects of temperature and diffusion on the relaxation rate.
$1/T \times 10^{3}$ vs. Temperature (K)

10.4 Torr
9.1% CO$_2$, 90.9% He
FIGURE 4.6 Variation of slow relaxation rate of the \( \text{O}_2^0 \) level as a function of gas temperature in a 9.2\% \( \text{CO}_2 \):11\% \( \text{N}_2 \):79.8\% He mixture at 19.4 Torr. These measurements were made in the absence of a discharge and are used in Section 4.6.2 to account for the effects of temperature and diffusion on the relaxation rate.
19.4 Torr
9.2% CO₂: 11% N₂: 79.8% He

\[ \frac{1}{T} \times \frac{1}{P} \]

Temperature (K)

[Graph showing a linear relationship between temperature (K) and a variable represented by \( \frac{1}{T} \times \frac{1}{P} \).]
4.6 Relaxation Rates of the $v_3$ Mode in a Discharge

The relaxation rates measured in the previous section for gas mixtures in thermal equilibrium are in good agreement with the results reported in the literature. Hence, we next studied relaxation rates in the presence of an electric discharge. In a typical CO$_2$ laser mixture, the discharge produces a substantial population in the $v_3$ mode, and creates gain at 10 μm. Thus the passage of a saturating 10 μm pulse through the discharge tube will transfer population from the 00$^0$1 level to the 10$^0$0 level. The TDL probe monitors this population transfer, and then measures the rate of recovery of the 00$^0$1 population to its unperturbed value. Similar measurements can be made on the 00$^0$2 → 00$^0$3 and 00$^0$3 → 00$^0$4 transitions. In most cases, the absorption is so strong on the 00$^0$1 P(19) line that the TDL must be tuned to the 00$^0$1 P(45) line, or lines in the 00$^0$2 and 00$^0$3 bands, in order to make accurate measurements.

4.6.1 CO$_2$:He Mixture

The initial measurements were made without N$_2$ in the mixture to avoid the complication of CO$_2$ <-> N$_2$ energy exchange. In this case, the 00$^0$1 population returns to its unperturbed value with a single exponential rate, 1/τ, as given by Eq. (4-13). As one is interested in the electron de-excitation, experiments are performed at a fixed gas pressure and 1/τ is measured as a function of discharge current. Results are shown in Fig. 4.7. Note the very substantial increase in the relaxation rate of the $v_3$ mode as the discharge current is increased to 25 mA. The value of 1/τ increases by almost a factor of 3. By comparing Eq. (4-13) to Eq. (4-14),
FIGURE 4.7 Relaxation rate of the $v_3$ mode population in a 9.1% CO$_2$: 90.9% He mixture at 10.4 Torr. Curve (a) shows recovery rates measured in a discharge using a TDL operating on the 00$^01$ P(45) transition. Curve (b) shows relaxation rates measured in unexcited gas thermally heated to correspond to the measured discharge gas temperature. Curve (c) gives the difference between curves (a) and (b), and shows the contribution of electron de-excitation.
one might conclude that the entire change in $1/\tau$ is caused by the term $n_e r_c^4$. However, the TDG measurements also show that the discharge causes an increase in gas temperature at the center of the discharge (see Chapter 3). At 25 mA the gas temperature has increased from 260 to 347 K. As the terms $k_i M$ and $s_c$ in Eqs. (4.13) and (4.14) are slightly temperature dependent, one must use the results shown in Fig. 4.5 to account for the thermal effects. This correction is shown in Fig. 4.7, giving the final result that the electron de-excitation term depends linearly on current, and has a slope of $113 \pm 10$ s$^{-1}$ mA$^{-1}$.

As discussed in Section 4.3, the relaxation rate measurements of Fig. 4.7 can be combined with the $v_3$ mode temperature measurements to determine the electron excitation rate. Therefore, the measured values of $x_3/\tau$ (see Eq. 4.11) are plotted against the discharge current in Fig. 4.8. A least-squares fit to the experimental data gives a straight line through the origin with the slope giving an electron excitation rate of $34.2 \pm .3$ s$^{-1}$ mA$^{-1}$.

This experimental excitation rate can be compared with calculations based on the solution of the Boltzmann transport equation [13]. We have chosen to compare our results with the calculations of Judd [15], who gives rates for a wide range of mixtures and E/N values (ratio of electric field to total number density). However, to compare experiment with calculation, one must estimate the electron density per unit of discharge current at the center of the discharge. If we assume that the radial distribution of electron density and gas temperature across the discharge follows a parabolic function [74], then the peak current density at the
FIGURE 4.8 Variation of $x_3/\tau$ as a function of discharge current in a 9.1% CO$_2$:90.9% He mixture at 10.4 Torr. The slope of the linear increase gives the electron excitation rate.
10.4 Torr
9.1% CO₂ : 90.9% He

\[ \frac{x_3}{\tau} \times 10^3 \text{ s}^{-1} \]

Slope = 34.2 ± 0.3 s\(^{-1}\) mA\(^{-1}\)
center of the tube is approximately twice the average current density (see Appendix B). For a 10% CO₂:90% He mixture, the E/N ratio is $1.7 \times 10^{-16}$ V·cm$^{-2}$ [19]. From the calculations of Judd, the electron excitation rate is determined to be $\sim 17$ s$^{-1}$ mA$^{-1}$, i.e., about half the measured value. Part of this discrepancy may be caused by the fact that Judd used electron excitation cross sections compiled by Lowke et al. [14]; larger cross sections have been measured recently by Bulos et al. [27].

4.6.2 CO₂:N₂:He Mixture

This section is concerned with the presence of N₂ in a typical CO₂ discharge. The measurements are performed with a 9.2% CO₂:11% N₂:79.8% He mixture at 19.4 Torr. Once again, after the passage of the Q-switched pulse the $v_3$ mode returns to its unperturbed population with a double exponential of fast and slow rates given by Eqs. (4-9) and (4-10) respectively. At present we are only interested in the slow relaxation rate, $1/\tau_s$, associated with the combined energy in the CO₂($v_3$) and N₂($v_4$) because the measurements of $1/\tau_s$ can be used to determine the electron excitation and de-excitation rates. The added N₂ also produces an experimental complication; the absorption in the 00^01 band and on the stronger lines of the 00^02 band is very large. Therefore the relaxation rates are measured with probe lines 00^02 P(44), 00^03 R(11) and 00^03 P(19). Results are shown on the upper curve of Fig. 4.9. As expected, the 00^02 and 00^03 bands display the same recovery rate, confirming that the $v_3$ mode can be described by a single vibrational temperature during the slow
FIGURE 4.9 Slow relaxation rate of the $v_3$ mode population in a CO$_2$ : N$_2$:He mixture. Curve (a) shows recovery rates measured in a discharge using a TDL operating on the $^0Q^0_2 P(44)$ line ($\Delta$), the $00^0_3 R(11)$ line (x) and the $00^0_3 P(19)$ line (o); curves (b) and (c) are obtained in the same way as in Fig. 4.7.
19.4 Torr
9.2% CO₂ : 11% N₂ : 79.8% He

\[ \frac{1}{\tau_s} \times 10^3 \, \text{s}^{-1} \]

\[ \text{CURRENT (mA)} \]

Slope = 136 ± 14 s⁻¹ mA⁻¹
recovery phase. The 000 1 population will also have the same relaxation rate.

In Fig. 4.9, a dramatic increase in the relaxation rate of the \( v_3 \) mode is seen as the discharge current increases. Thermal effects only make a minor contribution to this increase; the dominant effect is one of electron de-excitation. The slope of curve (C) is 136 s\(^{-1}\) mA\(^{-1}\). The constant D in Eq. (4.20) has a measured value of \( \approx 2.5 \) in our mixture, and thus we deduce an electron de-excitation rate of 340 \( \pm 35 \) s\(^{-1}\) mA\(^{-1}\).

By combining \( T_3 \) measurements with curve (a) of Fig. 4.9 we can also determine from Fig. 4.10 that the electron excitation rate is 92 \( \pm 8 \) s\(^{-1}\) mA\(^{-1}\) (see Eq. 4-22). The measured value of E/N for this mixture is \( 2.7 \times 10^{-16} \) V cm\(^{-2}\) [19], and following the same procedure as in Section 4.6.1 the calculations of Judd give an electron excitation rate of 80 s\(^{-1}\) mA\(^{-1}\).

The agreement between experiment and theory is now much better for a CO\(_2\):N\(_2\):He mixture, suggesting that the electron excitation cross sections used by Judd for the N\(_2\) molecule may be better than those used for CO\(_2\).

In view of all the uncertainties involved (e.g. e-CO\(_2\) excitation cross sections, electron distribution in the discharge, etc....) in comparing the experimental measurements to theoretical calculations of electron excitation rates, too much emphasis should not be placed upon comparisons of this type. A more useful parameter is the efficiency of excitation into the combined CO\(_2\)(\( v_3 \)) and N\(_2\)(\( v_4 \)) modes. The percentage of input power available to excite the upper laser level has been calculated by several authors. The present experiment enables the evaluation of this
Variation of \((x_3 + x_4 \text{ N/C})/\tau_s\) as a function of discharge current in a 9.2% CO\textsubscript{2}:11% N\textsubscript{2}:79.8% He mixture at 19.4 Torr. The slope of the linear increase gives the electron excitation rate.
19.4 Torr
9.2% CO₂ : 11% N₂ : 79.8% He

\[ \frac{(x_3 + x_4) N/C}{\tau_5} \times 10^3 \text{s}^{-1} \]

Slope = 92±8 s⁻¹ mA⁻¹
parameter by two almost independent methods. In the absence of 10 \( \mu \text{m} \) lasing, the energy stored in the combined \( \nu_3 \) and \( \nu_4 \) modes is given by:

\[
E_3(T_3) + E_4(T_4) = \left( C \nu_3 \frac{x_3^{\nu_3}}{1-x_3} + N \nu_4 \frac{x_4^{\nu_4}}{1-x_4} \right)
\] (4-24)

where \( x_4 = \exp(-\nu_4/kT_4) \) and the value of \( T_4 \) can be determined from the measured value of \( T_3 \) by \([61]\):

\[
\frac{\nu_3}{kT_3} - \frac{\nu_4}{kT_4} = \frac{\hbar(\nu_3 - \nu_4)}{kT}
\] (4-25)

where \( T \) is the background gas temperature. However, the rate of loss of energy from the combined mode is simply given by \( 1/\tau_s \) as plotted in Fig. 4.9. Hence, Fig. 4.9 and the \( T_3 \) measurements of Fig. 3.17 can be combined to give the total rate of loss of energy from the \( \nu_3 \) and \( \nu_4 \) modes in the steady state non-lasing case. This power loss must be equal to the rate of excitation by electrons in the discharge, i.e., the input power to the \( \nu_3 \) and \( \nu_4 \) modes, \( P_3 \) is given by

\[
P_3 = \frac{E_3(T_3) + E_4(T_4)}{\tau_s}
\] (4-26)

Fig. 4.11 shows a plot of \( P_3 \) as a function of total electrical input power at the center of the discharge. The total input power is calculated by using measured discharge currents and voltages, and assuming the current density at the center of the discharge is twice the average current density.

This first method equates \( P_3 \) to the rate of loss of energy by collisions and diffusion in the discharge. However, in Section 3.5,
FIGURE 4.11 Input power to the combined $\text{CO}_2(\nu_3)$ and $\text{N}_2(\nu_4)$ modes, $P_3$, as a function of the total electrical input power to the discharge. Data points labelled lasing refer to calculations using Eq. (4-27); non-lasing refer to Eq. (4-26).
19.4 Torr
9.2% CO₂: 11% N₂: 79.8% He

- Lasing
+ Non-lasing

P₃ (W/cm³)

INPUT POWER DENSITY (W/cm³)
measurements have been made under conditions where stimulated emission accounts for more than 80% of the energy loss from the \( \nu_3 \) and \( \nu_4 \) modes. Results of these measurements on 10 \( \mu \)m power extraction \( P_s \) were given in Fig. 3.18. To determine \( P_3 \) it must be recognized that each laser photon of energy \( h\nu_L \) requires a molecular excitation of \( h\nu_3 \) via electron excitation. In addition, one must still account for the relaxation of the \( \nu_3 \) and \( \nu_4 \) modes by collisions and diffusion. Thus,

\[
P_3 = \frac{h\nu_3}{h\nu_L} P_s + \frac{E_3(T_3') + E_4(T_4')}{\tau_s}
\]  

(4-27)

where \( T_3' \) refers to the mode temperature in the presence of lasing, i.e., the lower curve of Fig. 3.16, and \( T_4' \) is calculated from \( T_3' \) using the relation (4-25) [75]. The second term in Eq. (4-27) ranges from 5 to 20% of \( P_3 \). Results obtained using Eq. (4-27) are shown in Fig. 4.11.

The results shown in Fig. 4.11 illustrate three very important points: (i) The rate of loss of energy by collisions and diffusion from the \( \nu_3 \) and \( \nu_4 \) modes is very different in the lasing and non-lasing case. However, at all discharge currents, this difference is found to be equal to the measured rate of loss of energy via stimulated emission. The excellent agreement of the two data sets shown in Fig. 4.11 confirms the validity of our measurement techniques and analysis. (ii) The linear increase of \( P_3 \) with input power observed in Fig. 4.11 should be contrasted with the saturation of \( T_3 \) displayed in Fig. 3.17. Clearly, electron de-excitation substantially reduces the lifetime of the \( \nu_3 \) and \( \nu_4 \) modes at high discharge currents, and counteracts the effect of increased electron excitation. We can now account in a detailed and quantitative fashion for
the saturation of $T_3$ in CO$_2$ discharges [2,3]. (iii) The slope efficiency of 70% measured in Fig. 4.11 is typical of the high values calculated for CO$_2$:N$_2$:He mixtures. As measurements are made by probing only the central portion of a 1 cm bore discharge, any direct comparison with theory requires a knowledge of the radial dependence of electron density, etc. Nevertheless, a value of 70% is in reasonable agreement with the $\sim 50\%$ predicted by Bullis et al. [74] and Lowke et al. [14] for a 1:1:8 mixture with an $E/N$ ratio of $\sim 2.7 \times 10^{-16}$ V·cm$^2$.

4.7 Summary

This chapter has reported relaxation measurements of the $v_3$ mode levels after perturbation induced by 10 µm Q-switched laser pulses under a wide variety of experimental conditions. In particular, the effect of electrons on the lifetime of the CO$_2$ $v_3$ mode in a discharge is investigated; the electron de-excitation makes a substantial contribution to the relaxation rate of the $v_3$ mode, and dominates other relaxation processes at high current. These findings account quantitatively for the saturation of $T_3$ observed in previous measurements on CO$_2$ lasers. Detailed measurements have been made on two CO$_2$:N$_2$:He mixtures, $\sim 1:0:9$ and $\sim 1:1:8$. In each case, the ratio of electron de-excitation rate to electron excitation rate was $\sim 3.5:1$. This ratio is much smaller than that measured by Gower and Carswell [30] or Christophe and Offenberger [29], but is in reasonable agreement with the principle of detailed balance [29]. The measured electron excitation rates and discharge efficiency are also in reasonable agreement with calculated values.
The occurrence of substantial electron-de-excitation in CO\(_2\) laser discharges limits the attainable \(T_3\) to 2000 to 3000 K, depending upon gas mixture. This limitation appears unavoidable in electric discharge excited CO\(_2\) lasers; much higher temperatures may be attainable in an optically pumped CO\(_2\) medium. The limitation on \(T_3\) does not severely affect CW CO\(_2\) laser operation, as the presence of a 10 \(\mu\)m field significantly lowers \(T_3\) and reduces the effect of electron de-excitation. However, in pulsed TE lasers, the current pulse generally ends before lasing begins, and electron de-excitation severely limits the energy which can be stored in the discharge medium.

The next chapter deals with the relaxation of the lower laser level and its effects on the dynamics of various types of CO\(_2\) lasers.
CHAPTER 5

VIBRATIONAL RELAXATION OF THE CO₂ LOWER LASER LEVELS

5.1 Introduction

This chapter is concerned with the dynamics of the lower laser levels in CO₂. As mentioned in Section 2.4, reported values of the rate constants for the vibrational relaxation of the lower laser levels, i.e., \(1^0\)\(^0\) and \(02^0\) vary over an order of magnitude, from \(\approx 10^5\) to \(\approx 10^6\) s\(^{-1}\) Torr\(^{-1}\). Much of the difficulty in determining the relaxation rates of the \(1^0\)\(^0\) and \(02^0\) levels arises from the fact that many different energy transfer processes are involved. First one must consider the vibration-vibration (V-V) processes involving the three levels \(1^0\)\(^0\), \(02^0\) and \(02^2\), i.e.,

\[
\begin{align*}
\text{CO}_2(1^0\text{O}) + M & \leftrightarrow \text{CO}_2(02^0) + M \quad (5-1) \\
\text{CO}_2(1^0\text{O}) + M & \leftrightarrow \text{CO}_2(02^2) + M \quad (5-2) \\
\text{CO}_2(02^0) + M & \leftrightarrow \text{CO}_2(02^2) + M \quad (5-3)
\end{align*}
\]

where \(M\) denotes any molecule in the gas mixture. All three levels are coupled to the \(01^1\) level by

\[
\begin{align*}
\text{CO}_2(01^1) + \text{CO}_2(01^1) & \rightarrow \text{CO}_2(1^0\text{O}) + \text{CO}_2(00^0) \quad (5-4) \\
& \rightarrow \text{CO}_2(02^0) + \text{CO}_2(00^0) \quad (5-5) \\
& \rightarrow \text{CO}_2(02^2) + \text{CO}_2(00^0) \quad (5-6)
\end{align*}
\]
In addition to the V-V processes (5-1)-(5-6), all $v_1$ and $v_2$ mode levels ultimately relax by the slower vibration-translation (V-T) processes represented by

$$\text{CO}_2(01^10) + M \rightarrow \text{CO}_2(00^00) + M \quad (5-7)$$

In view of the complexity of the lower laser level relaxation mechanism, one would like ideally to monitor the populations of all levels on an individual basis during the relaxation period. To date this has not been possible, and most reported experiments have required many assumptions and approximations before relaxation rates can be extracted from observed laser pulse decays [42], fluorescence measurements [45], photo-acoustic measurements [76] and Raman scattering [48]. The most direct experimental technique used to date involved the use of saturating and probe lasers operating in the 10.4$\mu$m and 9.4$\mu$m bands [43,44], but even these experiments required a simultaneous account to be taken of the upper level population. It is not surprising that most experiments cannot differentiate between many of the processes (1) to (7), and often report inferred relaxation rates for a given process which differ by an order of magnitude. The limitation of previous experimental techniques is perhaps best illustrated by pointing out that no measurements have ever been made on the $02^20$ level, despite its importance in the relaxation processes.

In this chapter, we describe the use of a tunable diode laser to investigate the dynamics of the lower laser levels. The wide tunability of this probe laser enables us to monitor the populations in all levels of interest, including the $02^20$ and $01^10$ levels. The TDL monitors the
population changes caused by the passage of an intense Q-switched 10.4 \( \mu \text{m} \) laser pulse and then determines the rate at which the various vibrational levels return to their equilibrium value. We make measurements in both CW \( \text{CO}_2 \) discharge and thermal gas mixtures over a wide range of pressures, and for various gas mixtures containing \( \text{CO}_2 \), \( \text{N}_2 \) and \( \text{He} \). In particular, we monitor the populations in the four levels \( 1^20^0 \), \( 02^00 \), \( 02^20 \), and \( 01^10 \), and develop a simple model which enables us to relate the measured population changes to the rates of processes (5-1) to (5-7). This model is described in Section 5.4, and compared with experimental results in Section 5.5. Sections 5.2 and 5.3 describe the experimental apparatus and measurements, while Section 5.6 gives our conclusions.

5.2 Experimental Apparatus

The experimental set-up is identical that illustrated in Fig. 4.2, so only a brief description is given here. Referring to Fig. 5.1, the short discharge is placed inside a V-shaped cavity and is subject to a train of intense Q-switched laser pulses with a peak power of \( \sim 5 \text{ kW/cm}^2 \), a pulsewidth at full-width-half-maximum of 150 nsec, and a frequency spectrum distributed over the 10.4 \( \mu \text{m} \) \( P(16) \), \( P(18) \), \( P(20) \) and \( P(22) \) lines. The effect of these pulses is monitored directly by the HgCdTe detector whose output is fed into a storage oscilloscope with signal averaging capabilities (Tektronix Model 468). The response time of the entire detection system is limited by the rise time of the HgCdTe detector and its preamplifier to \( \sim 60 \) nsec. This was not a significant limitation in any of the relaxation rate measurements. A Au:Ge detector placed just behind the mirror \( M_1 \) monitors the Q-switched pulse and provides
FIGURE 5.1 Schematic diagram of the apparatus used for all the relaxation rate measurements. The Q-switching of the CO$_2$ laser is achieved by a rotating mirror, and the changes in level populations as induced by the laser pulse are monitored by a HgCdTe detector. The output signal of the detector is fed into a storage scope which is triggered by a Au:Ge detector placed just behind the mirror M$_1$. 
a trigger for the oscilloscope. Results obtained with the Q-switched pulses are presented in the next section.

5.3 Relaxation Rate Measurements in the $v_1$ and $v_2$ Modes of CO$_2$

The passage of an intense 10 $\mu$m pulse through the short discharge tube transfers a substantial fraction of the molecules from the $00^01$ level to the $10^00$ level. (The molecules were initially excited to the $00^01$ level by the electric discharge.) The excess population in the $10^00$ level is then quickly transferred to the $02^00$, $02^20$ and $01^10$ levels by processes (5-1) to (5-6). Finally, the population in the $v_1$ and $v_2$ modes returns to equilibrium by V-T transfer of the type described by (5-7). These various energy transfer processes are indicated schematically in Fig. 5.2.

By tuning the diode laser to the linecentre of individual vibrational-rotational transitions in 4.3 $\mu$m bands such as $(10^00 \rightarrow 10^01)$, $(02^00 \rightarrow 02^01)$ ..., we can monitor the time dependent populations in levels $10^00$, $02^00$, .... Although the measured absorption coefficient only determines the population difference between the upper and lower levels in the 4.3 $\mu$m bands, the upper level population is usually very small, changes slowly with time, and does not affect the analysis. Note that this is not always true when 9 $\mu$m and 10 $\mu$m lasers are used to monitor populations. The short discharge tube is generally operated at a current of 5 mA. This current produces a reasonable equilibrium population in the $00^01$ level, but is low enough to give negligible CO$_2$ dissociation and to minimize the effects of electrons and ions on the lower laser levels.
FIGURE 5.2 Simplified energy level diagram of CO$_2$. The six V-V energy transfer processes considered in the kinetic model are indicated, together with the V-T relaxation process.
CO₂
10 μm band laser
Measurements were made for a range of gas mixtures and pressures, and
the signal averaging capability of the oscilloscope was used to average
the effect of many Q-switched pulses. Figures 5.3 and 5.4 show some
typical time-dependent absorption traces. Figure 5.3 displays the Q-
switched laser pulse, and the short and long-term behaviour of the $10^0_0$
population. For these traces the diode laser was tuned to the $P(22)$
transition of the $10^0_0 + 10^0_1$ band. Identical results were obtained
for different transitions of the same band confirming that rotational
equilibrium is maintained \cite{33,77}. The return of the $10^0_0$ level popula-
tion to equilibrium is well-described by a double exponential. In Fig.
5.4 a variety of tunable diode laser traces are shown. These represent
the time-dependent populations in the $10^0_0$, $02^0_0$, $02^2_0$ and $01^1_0$
levels. In all cases, there is an initial reduction in transmission of the probe
laser as the population transferred by stimulated emission spreads through
the levels. All level populations then slowly relax back to their equili-
brum values.

A detailed analysis of the traces of Figs. 5.3 and 5.4 showed that
all populations have a slow exponential recovery after the first few $\mu$s.
This slow relaxation rate is the V-T rate represented by (5.7) and is
plotted as a function of pressure in Fig. 5.5. Note that all three levels,
$10^0_0$, $02^0_0$ and $02^2_0$, have the same recovery rate. Despite the poor signal-
to-noise ratio, the $01^1_0$ population can also be determined to recover at
a similar rate. From Fig. 5.5, we measure a rate constant of $(3.30 \pm 0.11)$
$\times 10^3 \ s^{-1} \ Torr^{-1}$ \cite{69} for a 10% CO$_2$: 90% He mixture. This is in good
agreement with the photo-acoustic measurements of Lepoutre et al. \cite{39,41}
FIGURE 5.3 Time dependent behavior of the \( 10^0 \) level after the passage of Q-switched laser pulses. The tunable diode laser is set to linecenter of the \((10^0_0 \rightarrow 10^0_1)\) \(P(22)\) transition. The upper photograph shows the Q-switched pulse and the early time behavior of the \(10^0\) population. The lower photograph shows the double exponential relaxation of the \(10^0\) population for a discharge current of 5 mA in a 10% CO\(_2\)-90% He mixture at 19.6 Torr.
FIGURE 5.4 Repeat of Fig. 5.3 for the $O_2^0$, $O_2^2$ and $O_2^{1}$ levels. The diode is tuned to linecenter of the $(O_2^0 \rightarrow O_2^0) \ P(30)$, $(O_2^2 \rightarrow O_2^2) \ P(19)$ and $P(26)$, and $(O_2^{1} \rightarrow O_2^{1}) \ P(44)$ transitions as indicated, and 256 individual pulses are averaged for each trace. Discharge current is 5 mA in a 10% CO$_2$:90% He mixture at 10.4 Torr. The behavior of the $O_2^0$ level is also shown for comparison.
FIGURE 5.5 Slow V-T recovery rate of the $10^0_0$, $02^0_0$ and $02^2_0$ level populations as a function of pressure. All measurements are made in a discharge excited mixture of 10% CO$_2$: 90% He.
$10\% \text{ CO}_2 : 90\% \text{ He}$

at 5 mA

$(3.30 \pm 0.11) \times 10^3 \text{ s}^{-1} \text{ Torr}^{-1}$

PROBE LINES
- $10^\circ 0$ P(22)
- $02^\circ 0c$ P(26)
- $02^\circ 0d$ P(19)
- $02^\circ 0$ P(30)
who determined the V-T rate constant as \((3.21 \pm 0.16) \times 10^3 \text{ s}^{-1} \text{ Torr}^{-1}\) for our mixture at 280 K. Thus, after the passage of the Q-switched pulse, the \(v_1\) and \(v_2\) modes quickly redistribute the excess energy and attain a new Boltzmann distribution at a higher mode temperature. The populations in all levels then slowly return to equilibrium with the same V-T rate.

In the present study we are more interested in the fast redistribution of energy in the \(v_1\) and \(v_2\) modes; the V-T relaxation process has been well-characterized in previous work [39,41]. We are mainly concerned with the first few \(\mu s\) in the traces of Figs. 5.3 and 5.4, and the relaxation processes (5-1) to (5-6). The simplest rate to measure from Figs. 5.3 and 5.4 is the fast decay of the 10\(^0\)0 population as it couples to all other \(v_1\) and \(v_2\) mode levels. Within experimental error, this decay is well described by an exponential with a time constant which is inversely proportional to pressure. This V-V relaxation rate is plotted in Fig. 5.6 for the 40\% CO\(_2\):90\% He mixture in the discharge. Also shown in Fig. 5.6 are results for a 9.2\% CO\(_2\):11\% N\(_2\):79.8\% He mixture. No significant difference is observed for the rate in the two mixtures, i.e., N\(_2\) and He have a similar effect. This result is in contrast to the measurements of Jacobs et al. [44] who found that N\(_2\) is \(~4\) times as effective as He. To evaluate the relative effectiveness of CO\(_2\) and He we also made measurements in pure CO\(_2\) at room temperature. In this case the Q-switched pulse initially reduces the 10\(^0\)0 population, which then recovers to its equilibrium value. These results are also shown in Fig. 5.6, and indicate that CO\(_2\) is \(~17\) times as effective as He in coupling the 10\(^0\)0 level to the \(v_1\) and \(v_2\) modes.
FIGURE 5.6. Fast recovery of the 10\textsuperscript{0} level population as a function of pressure. Measurements are made for pure CO\textsubscript{2} at room temperature, and for two different mixtures in a discharge.
Slope = $4.31 \times 10^5 \text{ s}^{-1} \text{Torr}^{-1}$

**PURE CO$_2$**

Slope = $6.58 \times 10^4 \text{ s}^{-1} \text{Torr}^{-1}$

**MIXTURES**

- pure CO$_2$ at 297K
- 10%CO$_2$:90%He at 5mA
- 9.2%CO$_2$:11%N$_2$:79.8%He at 5mA
The fast V-V relaxation of the 10\textsuperscript{0}0 level can take place directly by processes (5-1), (5-2) and (5-4), and indirectly by processes (5-3), (5-5) and (5-6). To evaluate the rate constants of these individual processes, we use the additional data provided by the time-dependent 02\textsuperscript{0}0, 02\textsuperscript{2}0 and 01\textsuperscript{1}0 populations shown in Fig. 5.4. We have developed a simple kinetic model to describe the fast V-V coupling and slower V-T relaxation of the ν\textsubscript{1} and ν\textsubscript{2} modes. By comparing the predictions of this model with experiment, we are able to determine the rate constants for processes (5-1) to (5-7). Details are given in the next two sections.

5.4 Six-level Kinetic Model

The six levels in CO\textsubscript{2} which are used to describe the relaxation processes involved in the recovery of the lower laser level population are shown in Fig. 5.2. In the present series of experiments, the slowest time scale under consideration is the V-T relaxation plotted in Fig. 5.5. On this time scale, one can neglect relaxation due to spontaneous emission, diffusion and collisions with electrons and ions. Collisional relaxation of the 00\textsuperscript{0}1 level can also be neglected. Thus, the only relaxation processes of importance are the six V-V processes corresponding to (5-1) to (5-6) and the V-T relaxation. Referring to Fig. 5.2, we label the six V-V processes with rate constants \( k_i \) (i = 1 to 6) corresponding to the left to right process in Eqs. (5-1) to (5-6). The reverse rate constants \( k_i \) are related to \( k_i \) by the principle of detailed balance, i.e.,

\[
\frac{k_i}{k_i} = \frac{N_i^0}{N_i^0} = \mu^2
\]
\[
\frac{\dot{N}_2^0}{k_2} = \frac{N_4^0}{N_2^0} = \frac{1}{2} \mu \\
\frac{\dot{N}_3^0}{k_3} = \frac{N_3^0}{N_2^0} = \frac{1}{2} \mu \\
\frac{\dot{N}_4^{102}}{k_4} = \frac{N_1^{102}}{N_4^0 N_0^0} = \frac{4}{\mu} \\
\frac{\dot{N}_5^{102}}{k_5} = \frac{N_1^{102}}{N_3^0 N_0^0} = 4 \mu \\
\frac{\dot{N}_6^{102}}{k_6} = \frac{N_1^{102}}{N_2^0 N_0^0} = 2
\] (5-8)

where \( N_i^0 \) represents the equilibrium population in level \( i \) at temperature \( T \), \( \mu = \exp(-\delta/kT) \) where \( \delta \) is the average energy spacing between levels 4 and 2, and 2 and 3 (51.3 cm\(^{-1}\)). In addition the populations in levels 1 to 4 decay with the slow V-T rate constant, \( k_{VT} \) (see Fig. 5.2). If we define the time-dependent population in level \( i \) as \( N_i \), and assume it is trying to relax to an equilibrium value \( N_i^0 \), then the rate of change of population in each level is given by:

\[
\frac{dN_5}{dt} = -KI (N_5 - N_4)
\]

\[
\frac{dN_4}{dt} = +KI (N_5 - N_4) - (k_1 N + k_2 N + k_{VT} N)(N_4 - N_4^0) - \frac{4}{\mu} k_4 (N_0 N_4 - N_0^0 N_4^0) + \mu^2 k_1 N(N_3 - N_3^0) + \frac{1}{2} \mu k_2 N(N_2 - N_2^0) + k_4 (N_1^2 - N_1^2)
\]
$$\frac{dN_3}{dt} = k_1 N(N_4 - N_4^e) - \left(\mu^2 k_1 N + k_3 N + k_{VT} N\right) (N_3 - N_3^e)$$

$$- 4\mu k_5 (N_0 N_3 - N_0^e N_3^e) + \frac{1}{2\mu} k_3 N(N_2 - N_2^e) + k_5 (N_1^2 - N_1^{e2})$$

$$\frac{dN_2}{dt} = k_2 N(N_4 - N_4^e) + k_3 N(N_2 - N_2^e)$$

$$- \frac{1}{2\mu} \mu k_2 N + \frac{1}{2\mu} k_3 N + k_{VT} N)(N_2 - N_2^e)$$

$$- 2 k_6(N_0 N_2 - N_0^e N_2^e) + k_6(N_1^2 - N_1^{e2})$$

$$\frac{dN_1}{dt} = \frac{8}{\mu} k_4(N_0 N_4 - N_0^e N_4^e) + 8\mu k_5(N_0 N_3 - N_0^e N_3^e)$$

$$+ 4k_6(N_0 N_2 - N_0^e N_2^e) - 2(k_6 + k_5 + k_4)(N_1^2 - N_1^{e2})$$

$$+ k_{VT} N[N(N_4 - N_4^e) + (N_3 - N_3^e) + (N_2 - N_2^e) - (N_1 - N_1^e)]$$

$$\frac{dN_0}{dt} = -\frac{4}{\mu} k_4(N_0 N_4 - N_0^e N_4^e) - 4\mu k_5(N_0 N_3 - N_0^e N_3^e)$$

$$- 2k_6(N_0 N_2 - N_0^e N_2^e) + (k_6 + k_5 + k_4)(N_1^2 - N_1^{e2})$$

$$+ k_{VT} N(N_1 - N_1^e)$$

where $k$ is a constant related to the stimulated emission cross section of the laser levels and $I$ is the intensity of the 10$\mu$m laser pulse used to
perturb the probed medium. $N$ is the total number density of CO$_2$ molecules. In writing down expressions for $dN_5/dt$ and $dN_4/dt$, we have assumed rotational equilibrium in each vibrational level and neglected the small difference between the rotational factors of $N_4$ and $N_5$. The system of differential equations (5-9) is solved using a Runge-Kutta routine after normalising all populations by dividing throughout by $N$. We use the initial condition that $(N_i - N_i^e)$ is zero for all $i$, and ensure that $Z(N_i - N_i^e)$ remains zero at all times.

In solving (5-9) we use the value of $k_{VT}$ determined in Fig. 5.5. This leaves six unknown V-V rates. Fortunately, the mixing of the Fermi levels 10$^0$0 and 02$^0$0 allows us to treat these two levels in a similar fashion, and set [44,49]

$$\frac{k_3}{k_2} = \frac{k_4}{k_5} = \mu \quad (5-10)$$

Thus, we are left with four unknown rate constants in the model. We shall show in the next section that these four constants can be determined from the experimental measurements of the type shown in Figs. 5.3 and 5.4.

5.5 Determination of the V-V Rate Constants

The experimental data of Figs. 5.3 and 5.4 is converted into time-dependent populations, $N_i$, using the techniques described in [77]. For one set of experimental conditions, the perturbed populations $(N_i - N_i^e)$ are normalized by $N_i^e$ and plotted in Fig. 5.7. Note the large population change in the directly pumped 10$^0$0 level, and the much smaller fractional
FIGURE 5.7. Experimental 10 μm laser pulse and perturbed populations in levels 10°0, 02°0, 02°0 and 01°0. The data points are derived from photographs such as in Fig. 5.4, and refer to a 10% CO₂:90% He mixture at 10.4 Torr with a discharge current of 5 mA. The extent of the peak-to-peak noise is indicated by the hatched area on the O1°0 trace. Also shown in the figure by solid lines are the calculated population changes using the model of Section 5.4 and the V-V rates given in Table 5.1.
change in the other three levels. We have used the computer model to
fit the populations in the first 12 μs. The best-fit set of V-V rate
constants is given in Table 5.1. These rate constants produce the cal-
culated curves shown in Fig. 5.7. Both theory and experiment agree that
after ~ 6 μs all four level populations are close to equilibrium at a
common mode temperature, and the mode energy then relaxes at the V-T
rate. The peak intensity of the 10.6 μm pulse is used as a scaling para-
meter to arrange that experiment and theory give the same energy in the
(v_1 + v_2) mode at time > 6 μs. This procedure is equivalent to ensuring
that the total population transferred by stimulated emission in the model
agrees with experiment.

At very early times, almost all the transferred population appears
in the 10^00 level. There is a significant discrepancy between theory and
experiment at the peak of the 10^00 population. However, the finite line-
width of the TDL causes the experimental measurement to underestimate the
value of the population peak [78,79] by about the observed amount. The
remaining difference between calculation and experiment in the 01^10 popu-
lation lies within experimental error, as this population can only be
measured with a poor signal-to-noise ratio (see Fig. 5.4). The agreement
between theory and experiment demonstrated in Fig. 5.7 confirms that the
model described in Section 5.4 can account for the observed population
changes. However, it is appropriate to describe some aspects of our
fitting procedure, and to point out the experimental parameters which
are most sensitive to changes in the V-V rates. We start by considering
the fast decay of the 10^00 population. During this decay period, the
**TABLE 5.1**

V-V Coupling Rate Constants in CO$_2$ \(^{(a)}\) at \(\sim 280\) K

(unit in \(s^{-1}\) Torr$^{-1}$)

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Present Study</th>
<th>Seeber (b)</th>
<th>Sharma (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>((4.8 \pm 0.8) \times 10^4)</td>
<td>(7.4 \times 10^4)</td>
<td>(\geq 1 \times 10^6)</td>
</tr>
<tr>
<td>(k_2)</td>
<td>((1.6 \pm 0.2) \times 10^5)</td>
<td>(1.6 \times 10^5)</td>
<td>(5.9 \times 10^5)</td>
</tr>
<tr>
<td>(k_4(d))</td>
<td>((4.5 \pm 1.5) \times 10^4)</td>
<td>(2.6 \times 10^4)</td>
<td>(3.3 \times 10^4)</td>
</tr>
<tr>
<td>(k_6(d))</td>
<td>((8.0 \pm 2.0) \times 10^5)</td>
<td>(5.5 \times 10^5)</td>
<td>(1.8 \times 10^6)</td>
</tr>
</tbody>
</table>

(a) Rate constants of processes (5-1) to (5-3) for He and N$_2$ are each equal to \(\sim 1/8\) of the values for CO$_2$.

(b) Calculations at 300 K based upon short range interaction forces.

(c) Calculations at 300 K based upon long range interaction forces.

(d) Rate constants \(k_3\) and \(k_5\) can be determined from \(k_2\) and \(k_4\) respectively using (5-10).
changes in the populations of levels 0 to 3 are small, and we can approximate \((N_i - N_i^0)/N = 0\) for \(i = 0, 1, 2, 3\). Thus, immediately after the 10 \(\mu\)m laser pulse we can write the rate of change of \(N_4\) as:

\[
\frac{dN_4}{dt} = \left[ (k_1 + k_2)N_4 + \frac{4}{\mu} k_4 N_0 \right] (N_4 - N_4^0)
\]  \(5.11\)

Thus, with \(\mu = 0.77\) and \(N_0/N = 0.89\) the fast decay rate of level 4 in a 10% CO\(_2\)-90% He mixture is:

\[
0.1(k_1^C + k_2^C + 4.6 k_4^C) + 0.9(k_1^H + k_2^H) = 6.58 \times 10^4 \text{ s}^{-1} \text{ Torr}^{-1}
\]  \(5.12\)

from Fig. 5.6. Similarly, in pure CO\(_2\) the slope in Fig. 5.6 gives

\[
k_1^C + k_2^C + 4.6 k_4 = 4.31 \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}
\]  \(5.13\)

where the superscripts \(c\) and \(H\) indicate that the collision partners are CO\(_2\) and He, respectively. We can rewrite (5.12) and (5.13) as

\[
k_1^C + k_2^C + 4.6 k_4 = 4.31 \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}
\]  \(5.14\)

\[
k_1^H + k_2^H = 2.52 \times 10^4 \text{ s}^{-1} \text{ Torr}^{-1}
\]  \(5.15\)

To check that the approximations involved in deriving (5.14) and (5.15) are valid, we have run the full computer model with a variety of different values of \(k_1^C, k_2^C\) etc. which satisfy (5.14) and (5.15). In all cases, the calculated 1000 population has an exponential decay rate which agrees with experiment. Thus the data of Fig. 5.6 enable us to determine a relationship between the V-V constants given by (5.14) and (5.15). The next step is to obtain an estimate for \(k_1^C/k_2^C\) (assumed equal to \(k_1^H/k_2^H\)), i.e., to determine the branching ratio from the 1000 level to the nearby
$O_2^0O$ and $O_2^2O$ levels. We find that the most sensitive experimental parameter is the time-delay between the peak of $N_2$ and $N_3$. In Fig. 5.4 this parameter, $t_{32}$, has an experimental value of $1.2 \pm 0.2$ μs. In Fig. 5.8 we plot calculated values of $t_{32}$ as a function of $k_1/k_2$ with $k_6$ as a parameter and $k_4$ fixed ($t_{32}$ is insensitive to $k_4$). The chosen rate constants still satisfy (5-14) and (5-15). From Fig. 5.8 we can set $k_1/k_2$ as $0.30 \pm 0.05$ [80]. Thus the $1^0O$ level is more strongly coupled to the $O_2^2O$ level than to the $O_2^0O$ level, and the $O_2^2O$ population peaks earlier in time. If $k_1/k_2 > 1.0$, then calculations predict that the $O_2^0O$ population would peak first, in contradiction to experiment.

In a similar fashion, we use the magnitude of the peak populations transferred to the $O_2^0O$ and $O_2^2O$ levels to systematically estimate $k_6$ and $k_4$. Figs. 5.9 and 5.10 show the variation of the population peak of the $O_2^0O$ level, $P_3$, with $k_6$ and $k_4$ respectively. It can be seen from Fig. 5.9 that $P_3$ is insensitive to $k_6$. From the variation of $P_3$ with $k_4$ shown in Fig. 5.10, together with the value of $k_1/k_2$ and the experimental measurement of $P_3$, $k_4$ is determined to be $(4.5 \pm 1.5) \times 10^4 \text{s}^{-1} \text{Torr}^{-1}$. Similarly, the variation of the population peak of the $O_2^2O$ level, $P_2$, with $k_6$ and $k_4$ is depicted in Figs. 5.11 and 5.12 respectively. We can see that $P_2$ depends on both $k_4$ and $k_6$, and the value of $k_5$ is determined to be $(8.0 \pm 2.0) \times 10^5 \text{s}^{-1} \text{Torr}^{-1}$. The rate constants as determined from above are summarized in Table 5.1. These rate constants have been used to compare experiment and model calculations over a wide range of pressure. Good agreement was obtained at all pressures, as illustrated in Table 5.2.
FIGURE 5.8  Calculated values of the time-delay, $t_{32}$, between the peak population in levels 2 and 3. The kinetic model described in Section 5.4 is run for a range of values of $k_1/k_2$ with $k_6$ as a parameter and $k_4$ fixed at $4.5 \times 10^4 \text{ s}^{-1} \text{ Torr}^{-1}$. The experimental values of $t_{32}$ are within the range indicated by the two horizontal dashed lines.
10.4 Torr
10% CO₂ : 90% He

X $k_6 = 9.5 \times 10^5 \text{ s}^{-1} \text{Torr}^{-1}$
• $k_6 = 7.5 \times 10^5 \text{ s}^{-1} \text{Torr}^{-1}$
+ $k_6 = 5.5 \times 10^5 \text{ s}^{-1} \text{Torr}^{-1}$

$t_{32}$ (μsec) vs $k_1 / k_2$
FIGURE 5.9  Calculated values of the population peak, $P_3$ of the level 3 as a function of $k_1/k_2$ with $k_6$ as a parameter and $k_4$ fixed at $4.5 \times 10^4$ s$^{-1}$ Torr$^{-1}$. $P_3$ is insensitive to the variation of $k_6$. 
$k_e = 5.5 \times 10^5 \text{s}^{-1} \text{Torr}^{-1}$

10.4 Torr

10% CO$_2$ : 90% He
FIGURE 5.10  Calculated values of the population peak, $P_3$, of the level 3 as a function of $k_1/k_2$ with $k_4$ as a parameter and $k_6$ fixed at $7.5 \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$. The horizontal and vertical dashed lines indicate the range of values of $P_3$ and $k_1/k_2$, respectively.
$k_4 = 3.5 \times 10^4 \text{ s}^{-1} \text{Torr}^{-1}$

$10.4 \text{ Torr}$

$10\% \text{ CO}_2 : 90\% \text{ He}$
FIGURE 5.11 Calculated values of the population peak, $P_2$, of the level 2 as a function of $k_1/k_2$ with $k_6$ as a parameter and $k_4$ fixed at $4.5 \times 10^4$ s$^{-1}$ Torr$^{-1}$. The horizontal and vertical dashed lines indicate the range of values of $P_3$ and $k_1/k_2$, respectively.
$k_e = 5.5 \times 10^5 \text{ s}^{-1} \text{ Torr}^{-1}$

$10.4 \text{ Torr}$

$10\% \text{ CO}_2 : 90\% \text{ He}$
FIGURE 5.12 Calculated values of the population peak, $P_2$, of the level 2 as a function of $k_1/k_2$ with $k_4$ as a parameter and $k_6$ fixed at $7.5 \times 10^5$ s$^{-1}$ Torr$^{-1}$. The horizontal and vertical dashed lines indicated the range of values of $P_3$ and $k_1/k_2$, respectively.
The graph shows a plot of $p_2$ against $k_1 / k_2$ with lines for $5.5 \times 10^4$, $4.5 \times 10^4$, and $3.5 \times 10^4$ Torr$^{-1}$. The graph is labeled with conditions: 10.4 Torr, 10% CO$_2$, 90% He.
TABLE 5.2
Peak Values of \( \frac{(N_i - N_i^e)}{N_i^e} \) for a 10% CO₂:90% He Mixture as a Function of Pressure

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>10⁰₀ Expt.(a)</th>
<th>10⁰₀ Calc.(b)</th>
<th>0₂⁰₀ Expt.</th>
<th>0₂²₀ Expt.</th>
<th>0₁¹₀ Expt.</th>
<th>0₁¹₀ Calc.(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4</td>
<td>5.9</td>
<td>7.5</td>
<td>0.59</td>
<td>0.51</td>
<td>0.47</td>
<td>0.46</td>
</tr>
<tr>
<td>10.4</td>
<td>6.2</td>
<td>8.3</td>
<td>0.61</td>
<td>0.60</td>
<td>0.53</td>
<td>0.54</td>
</tr>
<tr>
<td>13.5</td>
<td>5.1</td>
<td>7.1</td>
<td>0.52</td>
<td>0.53</td>
<td>0.48</td>
<td>0.49</td>
</tr>
<tr>
<td>16.6</td>
<td>3.9</td>
<td>6.1</td>
<td>0.50</td>
<td>0.47</td>
<td>0.41</td>
<td>0.43</td>
</tr>
<tr>
<td>19.6</td>
<td>3.4</td>
<td>5.3</td>
<td>0.43</td>
<td>0.43</td>
<td>0.34</td>
<td>0.38</td>
</tr>
</tbody>
</table>

\( \pm 7\% \) \( \pm 7\% \) \( \pm 20\% \)

(a) See Refs. 78 and 79.

(b) Using the rate constants given in Table 5.1 and normalizing the total population transferred by stimulated emission in the model to agree with the experiment.
The significance of our results, as well as a comparison with previous work, is described in the next section.

5.6 Discussion and Conclusions

The tunable diode laser measurements described in this chapter provide a great deal of experimental information on the relaxation processes involved in emptying the CO₂ lower laser levels. For the first time, the populations in the 02^0 and 01^0 levels have been monitored during the relaxation period. The use of a tunable diode laser allows a very simple and direct determination of the absolute population in all the vibrational levels of interest. We have used our experimental results to determine all the V-V rates of importance; this was not possible with the limited experimental data previously available. Hence our experimental results are more easily compared with theoretical calculations, as shown in Table 5.1. In general our results are in much better agreement with the theory of Seeber [49] which considers the strong, short-range repulsive forces for the energy exchange. The other approach developed by Sharma [50] is a Born-approximation formulation in which long-range forces determine the V-V transfer. This approach does not give good agreement with our results; in particular Sharma predicts \( k_1 > k_2 \) which would result in the 02^0 population peaking earlier than the 02^2 population, in contradiction to experiment.

It is more difficult to compare our results with previous experiments, as many experiments only measured a combination (often uncertain) of rates (5-1) to (5-7). The most direct measurements were made by
Stark [43] and Jacobs et al. [44]. Stark quotes

\[ k_1 = (1.42 \pm 0.5) \times 10^5 \left[ P_{CO_2} + 0.46 P_{N_2} + 0.054 P_{He} \right] \text{s}^{-1} \]

at 400 K where all pressures are in Torr. Jacobs et al. find

\[ k_1' (\sim 0.77 k_1) = (3 \pm 1) \times 10^5 \left[P_{CO_2} + P_{N_2} + 0.27 P_{He} \right] \text{s}^{-1}. \]

Thus our value for \( k_1 \) in CO\(_2\) is smaller than either of these measurements, but neither Stark nor Jacobs et al. could distinguish between process (5-1) and process (5-2) followed by the reverse of process (5-3). Both energy transfer routes presumably contributed to their measured rates.

Although we have only studied a limited range of gas mixtures, the results given in Table 5.1 suggest that He and N\(_2\) are much less effective than CO\(_2\) in causing the near-resonant V-V energy exchange. Several other experimental measurements are reviewed by Jacobs et al. [44], and will not be analyzed here.

It is worth emphasizing that our results clearly demonstrate the importance of relaxation processes via the 02\(^2\)O level. Thus, it is inappropriate to consider the relaxation of either of the lower laser levels 10\(^g\)O or 02\(^g\)O without regard for the coupling to the 02\(^2\)O level and thence to the 01\(^1\)O level. A good deal of care must be taken before one can extract rate constants from relaxation processes involving the lower laser levels — as evidenced by the very wide variation in the published rate constants.
5.7 Summary

The tunable diode laser has been used to monitor the temporal variation of populations in the $10^00$, $02^00$, $02^20$ and $01^10$ levels. The conjunction of these measurements and an appropriate kinetic model has allowed us to determine the rate constants associated with processes (5-1) to (5-6). Accurate values of these rate constants are very important in the modelling of the 14 μm and 16 μm CO$_2$ lasers.
CHAPTER 6

CONCLUSIONS

In this chapter, we outline the major conclusions that can be drawn from the work reported in this thesis, and then discuss some additional applications of the present experimental technique. The work described in this thesis was aimed at a detailed examination of the mode temperature model used in CO$_2$ laser modelling, and at resolving two of the outstanding issues in CO$_2$ laser dynamics: (i) the ultimate limitation on energy storage in the v$_3$ mode, and (ii) the mechanisms controlling the relaxation of the lower laser level. All the important conclusions are covered in Chapters 3, 4 and 5; this chapter is concerned with giving a brief account of the overall significance of the research.

In Chapter 3, we have determined the absolute population in more than 25 vibrational levels of CO$_2$ in a CW discharge and have compared these to the prediction of the mode temperature model. In general, the results supported the use of mode temperatures in the modelling of CO$_2$ lasers. However, it was necessary to use the Treanor distribution to describe the population of the highly excited levels as a result of the anharmonicity of the CO$_2$ molecule. This quasi-equilibrium Treanor distribution has general validity in molecular systems where the energy transfer by collisions prevails and the intramode coupling is much faster than the intermode coupling and the V-T relaxation. For the case in which other relaxation processes become comparable to the intramode coupling,
substantial deviations from the quasi-equilibrium distribution are expected. Such a situation is common to the laser medium where the stimulated emission process dominates the relaxation of the laser levels (see Section 3.5).

In Chapter 4, the relaxation rate of the upper laser level is investigated with and without the presence of a discharge under a variety of experimental conditions. The relaxation rates induced by molecular collisions and diffusion obtained by the present work were in good agreement with previous measurements. Diffusion was found to be significant for typical CW laser mixtures and dominated the relaxation processes at low pressure. The most important outcome of the relaxation rate measurements of the upper laser level was the experimental determination of electron excitation and de-excitation rates in typical CO₂ discharges. Previous attempts at measuring these electron rates were indirect and gave results incompatible with theoretical calculations and experimental gain measurements. By contrast, our results are consistent with the calculations and the experimental measurements of level populations and power density (see Section 4.6). Furthermore, it was shown that electron de-excitation is responsible for the observed saturation of the v₃ mode temperature in CO₂ discharges. The existence of electron de-excitation does not affect significantly the operation efficiency of CW CO₂ lasers, but it reduces dramatically the efficiency of optical energy extraction from TE CO₂ oscillators and amplifiers operating at high input energies. The effects of electron de-excitation and electron quenching in general are unavoidable in electric discharge excited lasers.
Chapter 5 deals with the relaxation processes of the lower laser level. The situation concerning the rate constants of the V-V relaxation of the lower laser level has been the subject of several contradictory experimental and theoretical investigations; these studies were hindered by indirect measurement methods, incomplete diagnoses or misinterpretations (see Section 2.4). Our results were based upon direct measurements of the temporal variation of populations in the four connecting levels, i.e., 10^0, 02^0, 02^2 and 01^10. These simultaneous measurements provided a basically complete picture of the relaxation processes of the lower laser level. Moreover, a kinetic model was developed and used to evaluate the rate constants associated with different decay channels. These rate constants are not only important for modelling the regular CO_2 lasers, but are also valuable in the characterisation of 4.3 \mu m [8],82 and 16 \mu m [83,84] CO_2 lasers.

Several applications of the experimental techniques reported in this thesis are discussed below. In general, the TDL is very useful for investigating the dynamics of molecular gas lasers. A couple of concrete examples illustrate the potential usefulness of the technique.

Measurements can be made of the intramode V-V coupling rate of the \nu_3 mode in CO_2, such as 00^0_2 + 00^0_0 \rightarrow 2(00^0_1) using the TDL. This fast relaxation rate requires a much shorter pulse (<10ns) than that used in the present experiment, in order to perturb the population of a selected level in the \nu_3 mode manifold. Likewise, the relaxation rate of the 10^0_1 and 02^0_1 levels can be determined. These V-V relaxation rates are of primary importance to the dynamics of the recently developed 4.3 \mu m CO_2 lasers.
Thus far the cited applications are concerned with CO₂ laser dynamics. In recent years, the CO₂ laser has been used extensively in the production of optically pumped mid-infrared (MIR) and far-infrared (FIR) molecular gas lasers. The complex interaction between the two laser fields and the molecules can be studied in detail with the TDL technique; the co-propagating and counter-propagating gain characteristics of the optically pumped medium can be measured in a straightforward fashion [85]. In addition, other IR laser systems such as CO, HF, DF and HBr can be studied.

In conclusion, we have made use of a TDL to investigate in detail the dynamics of CO₂ lasers. The results described in this work have increased our understanding of the operation of electrically excited CO₂ lasers. Further, we have demonstrated the versatility of the TDL-based experimental technique. It is expected that this technique will be used extensively in the near future for studying the physics of infrared gas lasers.
APPENDIX A

RELATIONSHIP BETWEEN ABSORPTION COEFFICIENT AND VIBRATIONAL LEVEL POPULATIONS

In a gas, the absorption coefficient between a lower level, \( \ell \), and an upper level, \( u \), can be written as \([86]\).\n
\[
\alpha(\nu) = \frac{\lambda_0^2}{8\pi} A_{\ell u} \frac{g_u}{g_\ell} \left( n_u - n_\ell \right) g(\nu)
\]  
(A-1)

where \( \lambda_0 \) is the wavelength at line center, \( A_{\ell u} \) is the spontaneous transition probability, \( n_u \) and \( n_\ell \) are the population densities of the upper and lower levels having statistical weights \( g_u \) and \( g_\ell \) respectively, and \( g(\nu) \) is the normalized lineshape function evaluated at the frequency \( \nu \).

The spontaneous transition probability is given by \([86]\)

\[
A_{\ell u} = \frac{64\pi^4}{3h\lambda_0^3} |R_{\ell u}|^2 S_J F_J
\]

(A-2)

where \( |R_{\ell u}|^2 \) is the vibrational contribution to the transition moment, \( S_J \) is the rotational contribution, \( F_J \) is the interaction factor between vibration and rotation, and \( h \) is the Planck's constant. For \( \Sigma \) transitions, \( S_J \) (P branch) = \( J \), \( S_J \) (R branch) = \( J + 1 \), and \( g_u = 2J + 1 \) with \( J \) and \( J_u \), the rotational quantum numbers; for other transitions, values of \( S_J \) and \( g_u \) are given in Ref. \([87]\). The interaction factor differs little from unity; it is set to this value for all transitions. For the 4.3 \( \mu \)m \( 00^01 - 00^00 \) band, we have \( |R_{\ell u}|^2 = |R_{00^01 00^00}|^2 = 1.103 \times 10^{-37} \) esu-cm \([56]\); for all other transition bands, \( (i_j^k + 1)-(i_j^k) \), probed by the TDL, we use the relation \([87]\).
\[
\frac{R_{ij}^2k + 1}{R_{ij}^2k} = k + 1
\]  
(A-3)

This relation was experimentally verified for the CO molecule [88].

At line center, the normalized lineshape function can be expressed as [86]

\[
g(v_0) = \frac{1}{\pi \Delta v_C} \frac{a e^{a^2}}{n v_0} \text{erfc}(a) \]  
(A-4)

where \( a = (\ln 2)^{1/2} \Delta v_C / \Delta v_D \), \( \Delta v_C \) and \( \Delta v_D \) are the collision and Doppler linewidths (half width at half maximum). The Doppler linewidth is given by

\[
\Delta v_D = \frac{v_0}{c} \left( 2 \frac{kT}{M} \ln 2 \right)^{1/2} \]  
(A-5)

where \( T \) is the translational temperature, \( M \) is the mass of the CO\(_2\) molecule, and \( c \) and \( k \) are the speed of light and the Boltzmann constant.

No reliable measurements on the collision linewidth are available, hence we use the calculated values of Yamamoto et al. [57]. For \( J \) values in the range of 10-30, we have

\[
\Delta v_C (\text{Hz}) = 2.85 \times 10^7 (11.98 - 0.092 J) P_T \times (P_{CO_2} + 0.73 P_{N_2} + 0.64 P_{He}) T^{-3/4} \]  
(A-6)

where \( P_T \) is the total gas pressure in Torr and \( P_i \) is the fractional content of gas component \( i \) in the mixture. In Eq. (A-6), we have assumed that the effect of broadening by \( N_2 \) and \( He \) can be described by a scaling constant [89].
this is used for all transition lines and all transition bands. Moreover, the temperature dependence of $\Delta \nu_C$ is chosen to be the same as that for the CO molecule \cite{57,90}:

Finally, the vibro-rotational level population, $n_i$ (i.e. $n_\nu$ and $n_u$ in Eq. (A-1)), is related to the vibrational level population, $N_i$, by \cite{86}

$$n_i = N_i \frac{e^{-E_j/kT}}{Q_R} \quad (A-7)$$

where $E_j$ is the rotational energy of the level and $Q_R$ is the rotational partition function.

From the measurements of absorption coefficient in the transition bands \((ij^z_{k+1}) - (ij^z_k)\), Eqs. (A-1)-(A-7) can be combined together to calculate the population difference \((N_{ij^z_{k}} - N_{ij^z_{k+1}})\). Then, using the summing relation

$$N_{ij^z_{k}} = \sum_{k' \geq k} (N_{ij^z_{k'}} - N_{ij^z_{k'+1}}) \quad (A-8)$$

we can determine the absolute population of the vibrational level, i.e., $N_{ij^z_{k}}$. 
APPENDIX B

CURRENT DENSITY DISTRIBUTION IN A CYLINDRICAL DISCHARGE TUBE

The current density is:

\[ j(R) = e n_e(R) v_d(R) \]  \hspace{1cm} (B-1)

where \( j(R) \), \( n_e(R) \) and \( v_d(R) \) are the radial distributions of the current density, the electron density and the drift velocity, respectively, and \( e \) is the charge of the electron.

According to Judd's calculations [15], the drift velocity varies almost linearly with the ratio of electric field to total gas density, \( E/N \), and has the expression

\[ v_d(R) = 1.45 \times 10^{22} \left( \frac{E}{N} \right) \frac{T(R)}{T(0)} + 2.25 \times 10^6 \]  \hspace{1cm} (B-2)

for a 10% \( \text{CO}_2 \):10% \( \text{N}_2 \):80% He mixture, where \( v_d \) has the unit of cm/s, \( E/N \) has the unit of V-cm\(^2\) and \( T(R) \) is the radial distribution of the gas temperature with \( T(0) \), the central line temperature.

Bullis et al. have shown that in a wall dominated \( \text{CO}_2 \) electric discharge laser, the radial variation of electron density and gas temperature is nearly parabolic [74], i.e.

\[ n_e(R) = n_e(0)(1 - R^2) \]  \hspace{1cm} (B-3)

and

\[ T(R) = 1 + [T(0) - 1](1 - R^2) \]  \hspace{1cm} (B-4)

where \( R \) is the radial distance normalised to the radius of the discharge tube, and \( T \) is the gas temperature normalised to the wall temperature.
Substituting Eqs. (B-2)-(B-4) into Eq. (B-1), and letting $E/N$ equal to $2.7 \times 10^{-16}$ V-cm$^2$ [19], we obtain

$$j(R) = e n_e(o) v_d(o) [1 - (0.63) \frac{T(o)-1}{T(o)} R^2](1 - R^2)$$  \hspace{1cm} (B-5)

The average current density is:

$$j_{av} = 2 \int_0^1 j(R) R \, dR$$  \hspace{1cm} (B-6)

After the integration, we obtain

$$j_{av} = e n_e(o) v_d(o) [0.5 - (0.106) \frac{T(o)-1}{T(o)}]$$  \hspace{1cm} (B-7)

The peak current density $j_o = e n_e(o) v_d(o)$, hence

$$j_o = 2 j_{av}$$  \hspace{1cm} (B-8)

as $T(o)$ varies from $\sim 1$ to 1.7 in our experiment.
REFERENCES


58. For example, the square of the vibrational matrix element for the (00'9-00'8) band is assumed to be 9 times the corresponding value for the (00'1-00'0) band.
60. In writing down Eqs. (3-3) and (3-4), the harmonic oscillator approximation is assumed.
67. The neglected terms and approximations made have generally less
than ~ 10% contribution to the total value.
69. The error estimate on the slope given here, and in other parts of
this thesis, is simply one standard deviation obtained from a
linear least-squares fit to the data. These error limits are only
intended to give a rough estimate of the accuracy of the data.
70. Gueguen, H., F. Yzambart, A. Chakroun, M. Margottin-Maclou,
73. Doyennette, L., M. Margottin-Maclou, H. Gueguen, A. Carion, and
74. Bulis, R. H., W. L. Nighan, M. C. Fowler, and W. J. Wiegand, AIAA
75. In evaluating Eq. (4-27), we assume $T'$ is related to $T$ by the
expression (4.25). However, it is very likely that $T'_{A}$ is sub-
stantially higher than $T$ under lasing conditions. Nevertheless,
even if this is indeed the case, the rate of loss of energy
from the combined mode is still given by Eqs. (4-25) and (4-27).
78. For the experimental data shown in the upper trace of Fig. 5.3,
the TDL was tuned to linecenter of the $10^00 \rightarrow 10^01$ P(22) line.
The initial transmission of 64% was reduced to only 14% at the
population peak. The TDL linewidth was estimated as \( \sim 30 \text{ MHz FWHM} \), with small components as much as 200 MHz from the central value. In general, this linewidth was sufficiently narrow that it had a negligible effect on the measurements, except when the TDL transmission was \( < 20\% \). For small transmissions (i.e. strong absorption lines) the TDL linewidth results in an underestimate of the absorption coefficient. A similar effect is observed by J.A. Mucha, Appl. Spectrosc. 36, 141 (1982).

79. The linewidth effect described above has a negligible \(< 5\% \) effect on the measured relaxation rates in Fig. 5.6.

80. The error estimate on the ratio \( k_i/k_2 \), and on the rate constants \( k_i \) \( (i = 1,6) \) as shown in Table 5.1 is determined from the experimental errors on the time delay \( t \), the peak change in populations of the levels \( 02^00 \) and \( 02^20 \), and the value of the slopes in Fig. 5.6.