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Studies of nonequilibrium vibrational kinetics of carbon monoxide and nitric oxide in optical pumping experiments

Adamovich, Igor V., Ph.D.
The Ohio State University, 1993
STUDIES OF NONEQUILIBRIUM VIBRATIONAL KINETICS
OF CARBON MONOXIDE AND NITRIC OXIDE
IN OPTICAL PUMPING EXPERIMENTS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Igor Adamovich

The Ohio State University
1993

Dissertation Committee:

J. William Rich
K. Narahari Rao
T. Gustafson
L. Van Woerkom

Approved by

J. William Rich
Advisor

Chemical Physics Graduate Program
To My Parents, To My Wife Alla

And To My Daughter Sasha,

With Love And Gratitude
ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to Profs. J.W. Rich and S.A. Zhdanok for their help and advice throughout my work. I also wish to express my gratitude to Drs. S. DeBenedictis, C. Flament, A.A. Fridman, S.O. Macheret, J.-P. Martin, Yu.P. Raizer, V.V. Subramaniam, and C.E. Treanor, for many fruitful discussions. The assistance of L. Cortney, M. Grassi, S. Saupe, O. Schulz, and B. Zimering is gratefully acknowledged.
VITA

July 5, 1964 ........................................ Born in Tyumen, USSR

1987 ...................................................... Graduated from Moscow
                                   Institute of Physics
                                   and Technology, Moscow,
                                   USSR

1987-1991 ................................................. Research Associate,
                                   Lyukov Heat and Mass Transfer
                                   Institute, Minsk, Byelarus

1991-Present ........................................... Graduate Student,
                                   Chemical Physics Program,
                                   The Ohio State University,
                                   Columbus, Ohio, USA
PUBLICATIONS


FIELDS OF STUDY

Major Field: Chemical Physics

Studies in Molecular Energy Transfer with Prof. J. William Rich
TABLE OF CONTENTS

DEDICATION ........................................................................................................ ii
ACKNOWLEDGEMENTS ........................................................................................ iii
VITA ......................................................................................................................... iv
TABLE OF CONTENTS .......................................................................................... vii
LIST OF FIGURES ............................................................................................... ix
LIST OF TABLES ..................................................................................................... xiii

CHAPTER PAGE

I. INTRODUCTION ................................................................................................. 1

II. STUDIES OF VIBRATIONALLY STIMULATED IONIZATION

OF CARBON MONOXIDE ................................................................................. 7
2.1 Introduction ................................................................................................. 7
2.2 Experimental procedure ............................................................................. 10
2.3 Results and discussion .............................................................................. 18
  2.3.1 Infrared Measurements .................................................................. 18
  2.3.2 Ionization Measurements ............................................................... 26
  2.3.3 Vibration-to-electron coupling measurements ................................ 38
2.4 Conclusions ............................................................................................... 45

III. STUDIES OF VIBRATIONAL AND ELECTRONIC EXCITATION

OF NITRIC OXIDE .......................................................................................... 47
3.1 Introduction ............................................................................................... 47
3.2 Experimental procedure................................. 49
3.3 Results ....................................................... 53
3.4 Discussion .................................................. 62
  3.4.1 Vibrational excitation .............................. 62
  3.4.2 Electronic excitation ............................... 65
  3.4.3 V-T and V-V rates measurements .......... 69
3.5 Conclusions ............................................... 73

IV. STUDIES OF SPATIAL NONHOMOGENEITY EFFECTS IN NONEQUILIBRIUM
  VIBRATIONAL KINETICS ............................................. 75
  4.1 Introduction .............................................. 75
  4.2 Results and discussion ............................. 79
    4.2.1 Vibrational Excitation and Transport
        Coefficients .............................................. 79
    4.2.2 Diffusion and Vibrational Distribution
        Function .................................................... 84
    4.2.3 Spatial Integration ................................. 89
    4.2.4 Two-dimensional Kinetic Model
        of Vibrationally Nonequilibrium Gas Flows .... 95
    4.2.5 Results of calculation and comparison
        with experiments .................................... 104
  4.3 Conclusions ............................................. 114

APPENDIX .......................................................... 115
LIST OF REFERENCES .............................................. 118
LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Vibrational energy exchange between two molecules A (vibrational quantum $E^1_v$) and B (vibrational quantum $E^2_v$)</td>
<td>3</td>
</tr>
<tr>
<td>1.2 Boltzmann, Treanor, and &quot;real&quot; vibrational distributions of nitrogen; $T = 300K$, $T^v = 2500K$</td>
<td>3</td>
</tr>
<tr>
<td>2.1 Schematic of the experimental setup: 1, infrared CO laser; 2, d.c. power supply; 3, microammeter; 4, gas supply and gas mixing manifold; 5, impurity trap; 6, cell; 7, exhaust pump; 8, infrared spectrometer; 9, laser power meter</td>
<td>11</td>
</tr>
<tr>
<td>2.2 Typical CO laser spectrum</td>
<td>13</td>
</tr>
<tr>
<td>2.3 Cell with probe</td>
<td>15</td>
</tr>
<tr>
<td>2.4 CO first overtone emission spectra at different He pressures</td>
<td>19</td>
</tr>
<tr>
<td>2.5 Comparison of experimental and synthetic CO vibrational spectra</td>
<td>21</td>
</tr>
<tr>
<td>2.6 Comparison of experimental and synthetic CO rotational spectra</td>
<td>22</td>
</tr>
<tr>
<td>2.7 Inferred CO vibrational distribution functions at different He pressures</td>
<td>24</td>
</tr>
</tbody>
</table>
2.8 Experimental and theoretical voltage-current characteristics of the Thomson discharge .......................... 27

2.9 Saturation current and number of "active CO molecules" dependence on the He pressure .......................... 34

2.10 Charged species distributions in the Thomson discharge in the absence of the field and in the saturation regime. P = 100 Torr, CO:Ar = 3:97, d/L = 0.25; q(0) = 10^-21 cm^3/s (see Eqs. (2.8), A2-A4). L - interelectrode distance ................................................................. 39

2.11 Electric field influence on different CO vibrational level populations ....................................................... 41

2.12 Qualitative demonstration of the V→e→V-ΔV effect (strongly exaggerated). ε - electron energy, T_e - electron temperature ................................................................. 42

3.1 The experimental setup. 1, CO laser; 2, laser mirror, 3, grating; 4, focusing mirror; 5, absorption cell; 6, monochromator, 7, InSb infrared detector, 8, photomultiplier, 9, lock-in amplifier; 10, computer; 11, powermeter ................................................................. 50

3.2 The first overtone infrared NO spectra; solid lines - experimental spectra, dashed line - synthetic spectrum ..... 54

3.3 Einstein coefficients for NO infrared spontaneous radiation; 1,2 - [47], 1',2' - [48]; 1,1' - Δν=1, 2,2' - Δν=2 ................................................................. 57

3.4 The experimental NO vibrational distribution functions (points); 1,2, Treanor distributions for T_v = 2500K, x
T = 300K, and $T_v = 2500K$, $T = 700K$, respectively; 3, Boltzmann distribution, $T = 700K$ ......................... 58

3.5 The visible/ultraviolet NO spectrum ......................... 60

3.6 The experimental profile of the NO $0,2 \gamma$ band (points); the synthetic profile at different temperatures (lines) .... 61

3.7 Comparison of the master equation calculation with the experiment of Ref. [43] ................................. 66

3.8 Comparison of the NO V-T rates measured by optical pumping, Ref. [16] and by SEP, Ref. [38] (the point for $v=1$ is the result of Ref. [36]) ......................... 72

4.1 Measured vibrational distribution functions of CO (points) and Treanor distributions (curves): a, CO-N$_2$-He glow discharge, Ref.[31]; b, c, d, CO-Ar-He optical pumping, Refs. [8,14,30], respectively .................. 77

4.2 Vibrational quantum number function $L(v)$ in the diffusion correction, Eq. (4.17), for different plateau solutions ................................. 88

4.3 Effective vibrational temperatures of the first level, $T^*_v$, and of the plateau, $T^{**}_v$, Eqs. (4.30,4.31) as functions of the spatial nonhomogeneity $\Delta T_v = T_{v2} - T_{v1}$ and temperature ................................................. 93

4.4 Integrated VDF (solid line) and Treanor distributions with two effective vibrational temperatures (dashed lines) ....................... 94

4.5 Vibrational quanta diffusion coefficient .......................... 99
4.6 Experimental CO VDF’s, Ref. [8] (points) and results of quasi-1-D model calculations (curves) .................. 106

4.7 Experimental CO VDF, Ref. [31] (points) and the distribution function obtained from two-dimensional model (curves). Solid line, zero efficiency of the radiative energy loss; dashed line, 100% energy loss by V-E/radiation mechanism ....................................................... 109

4.8 Calculated normalized radial profiles of temperature and vibrational temperature for the experimental conditions of Ref. [31]; no energy loss by radiation ..................... 111
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Typical laser conditions</td>
<td>12</td>
</tr>
<tr>
<td>3.1 Laser parameters optimized for P(11) 8→7</td>
<td>51</td>
</tr>
<tr>
<td>3.2 Experimental regimes</td>
<td>55</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

Nonequilibrium molecular vibrational mode distributions, maintained by the processes of excitation of molecular vibrations, vibration-to-vibration (V-V), vibration-to-translation (V-T), and vibration-to-electronic (V-E) collisional energy transfer, as well as by chemical reactions in gases, have been widely studied for various species. These processes are of great interest due to their applications to plasma chemical reactors, environmental clean-up in gas discharges, molecular lasers, high-enthalpy gas dynamic flows and upper atmosphere chemistry.

There is an extensive literature discussing vibrational and electronic molecular energy transfer in gases. Recent developments in this field have been analyzed and summarized in reviews by Gordiets, Osipov, and Shelepin [1], Slovetskii [2], Nikitin [3], by Rusanov and Fridman [4], and by Capitelli [5], where a great deal of theoretical results and experimental data are discussed.

For some energy transfer processes involving vibrationally and electronically excited molecules, theoretical models to date are either unavailable or give only qualitative interpretation of their mechanisms. One may mention vibrational relaxation of molecules in degenerate electronic states, collisional V-E transitions, non electron
impact ionization of molecules at high vibrational levels and so on. Further research and developments in these fields require careful experimental studies of the molecular energy transfer processes at strong vibrational nonequilibrium.

One of the most efficient methods of creating vibrationally nonequilibrium conditions is the use of the effect of anharmonic V-V pumping [6], first predicted by Treanor, Rich and Rehm [7]. The main idea of this effect is that V-V exchange between two vibrationally excited molecules leads to preferential population of higher vibrational levels, since the vibrational energy level spacings decrease with vibrational quantum number v. For example, consider a collision of two diatomic molecules, one of which (A) is in the $v^\text{th}$ vibrational level, and the other (B) is in vibrational level $w$. There is some probability, $P_1$, that molecule A will relax to a lower vibrational level $v-1$, while molecule B will be excited to a higher level $w+1$ (see Fig. 1.1, solid arrows). The reverse process, when A makes the transition $v-1 \rightarrow v$, and B goes down from level $w$ to $w-1$, has some probability $P_2$ (Fig. 1.1, dashed arrows). In equilibrium at a temperature $T$, the rates of these two processes are related by detailed balance. Therefore, one can write the equation

$$k_{f_1} f(A)f(B) - k_{f_2} f_{v-1}(A)f_{w+1}(B) = 0 \quad (1.1)$$

where

$$f_{1}(A,B) = f_{0}(A,B)\exp(-E_{1}(A,B)/T) \quad (1.2)$$

is the equilibrium relative population of $i^{th}$ vibrational level of the
Figure 1.1 Vibrational energy exchange between two molecules A (vibrational quantum $E_1$) and B (vibrational quantum $E_2$)

\[ k_1/k_2 = e^{(E_1-E_2)/T} \]

Figure 1.2 Boltzmann, Treanor, and "real" vibrational distributions of nitrogen; $T = 300K$, $T_v = 2500K$
molecule A or B, respectively, $E_1$ is its energy, $k_j = P_j Z$ is the rate constant of $j^{th}$ process, and $Z$ is gas-kinetic collision frequency. Now, one can see that the excitation of molecule B ($w-1 \rightarrow w$, rate constant $k_1$) is a faster process than the excitation of A ($v-1 \rightarrow v$, rate constant $k_2$), if the vibrational level spacing of B, $E_2$, is closer than that of A, $E_1$ (see Fig. 1.1). Obviously, this effect becomes especially significant when the translational temperature $T$ decreases.

The vibrational distribution function (VDF), created by V-V exchange, follows the Treanor distribution (see Ref. [7]),

$$f_v = f_0 \exp\left\{-v\left[\frac{E_1}{T_v} - \frac{(v-1)\Delta E}{T}\right]\right\}, \quad (1.3)$$

where

$$T_v = \frac{E_1}{\ln\left\{f_0/f_1\right\}} \quad (1.4)$$

is the vibrational temperature of the first vibrational level. In Eqs. (1.3, 1.4), $E_1 = \omega e e (1 - 2\omega e e e / \omega)$ is the energy of vibrational transition $1 \rightarrow 0$, $\Delta E = \omega e e e$. If the vibrational temperature of a gas exceeds $T$, then the Treanor distribution has higher values than Boltzmann distribution with temperature $T_v$. Figure 1.2 shows Boltzmann and Treanor distributions of $N_2$ at $T = 300K$ and $T_v = 2500K$.

Since the V-T relaxation rates strongly increase with vibrational quantum number, at levels higher than

$$v_0 = 0.5 + \frac{E_1 T}{2\Delta E T_v} \quad (1.5)$$
the Treanor distribution transforms into the so-called "plateau" with a nearly constant slope and a sharp fall-off at very high v's, where the V-T processes are faster than the V-V exchange (see Fig. 1.2). Thus, at low temperatures, when the vibration-translation (V-T) relaxation becomes much slower, this mechanism creates strongly nonequilibrium relative populations even for very high vibrational levels.

Note that in spite of the fact that the V-V energy transfer processes with Δv > 1 are not forbidden, usually their probabilities are much smaller compared to those of one-quantum transitions, at least for not very high v's. This means that the vibrational excitation of a molecule primarily occurs in a number of consecutive one-quantum jumps, starting from the 0 → 1 transition, or by means of climbing the so-called "vibrational ladder".

Strong vibrational excitation by V-V pumping can occur in molecular gas flows with a high vibrational energy content and a low translational temperature. For example, this can be in an electric discharge, where excitation of molecular vibrations occurs by electron impact (see Ref. [2] and Chapter 11 of Ref. [5]). Unfortunately, discharge electrons are also known to excite a variety of electronic levels of atoms and molecules, which makes isolation of key processes and interpretation of experimental data difficult. Another problem is that in a self-sustained discharge, the energy loading per molecule cannot be arbitrarily varied without changing other parameters, such as gas temperature, pressure, flow rate and so on.

Another experimental technique which allows V-V pumping is fast cooling of a hot gas in a shock tube / supersonic nozzle flow,
where vibrational energy remains "frozen" due to a slow rate of vibrational relaxation. The most serious disadvantage of this technique is the short test time available, ~1 ms.

An alternative approach, which allows the selective excitation of molecular vibrations at the low levels with the following V-V up-pumping, is optical pumping of a gas by absorption of laser radiation. This method has first been developed for strong vibrational excitation of CO [8-14] and NO [15-17] by resonance absorption of CO laser radiation, and of N$_2$ [18] by Raman absorption of ruby laser radiation. It allows reliable measurements of kinetic rates in a fully controlled discharge-free environment, operable for hours. It has been successfully used for measurements of V-V and V-T rates for CO-CO, CO-Ar, CO-He [8,11], and NO-NO [16], V-E rates in CO and NO [12,13,15,16], vibrationally-induced ionization rate of CO [15], as well as for studies of isotope separation by V-V pumping in CO [9,10] and N$_2$ [18].

The present work discusses the results of recent optical pumping experiments carried out in The Molecular Energy Transfer Laboratory at the Ohio State University. Chapter II presents the studies of vibrationally-induced ionization and related phenomena in carbon monoxide. Chapter III addresses the investigation of vibrational and electronic energy transfer in nitric oxide. Finally, Chapter IV presents theoretical results of the two-dimensional simulation of spatially nonhomogeneous, vibrationally excited gas flows.
CHAPTER II
STUDIES OF VIBRATIONALLY STIMULATED IONIZATION
OF CARBON MONOXIDE

2.1 Introduction

Ionization mechanisms in diatomic gases are widely studied due to their applications to high-enthalpy gas dynamic flows, to electric discharge phenomena, and to gas laser development. There is a large amount of literature on the study of ionization in diatomics by electron impact and by photoionization (see, for example, Ref. [19] and references therein).

The present work discusses an additional ionization mechanism which may well be a major electron source in gas environments in which the vibrational mode energy is high. It can be described by the following kinetic equation:

\[
AB(v) + AB(v') \rightarrow \begin{cases} 
AB + AB^+ + e^- \\
(AB)^2 + e^-
\end{cases} \quad (2.1)
\]

and
\[ E_v + E_{v'} > E_1 \]  

(2.2)

Here, \( AB(v) \) represents a diatomic gas molecule in the \( v^{th} \) vibrational quantum state, \( AB(v') \) is the molecule in the \( v'^{th} \) state, \( E_v \) and \( E_{v'} \) are the energies of the molecule in the \( v^{th} \) and \( v'^{th} \) states, respectively. \( E_1 \) is the ionization energy of the molecule. Basically the preceding scheme states that ionization can occur by two-body collisions of the diatomics, if their total energy exceeds the ionization energy of \( AB \) (or the dimer \( (AB)_2 \)). Such ionization can occur in vibrationally nonequilibrium environments, for which the energy in the vibrational mode greatly exceeds the translational or rotational mode energies. Ionization can occur in gases where the translational/rotational modes are in equilibrium at near room temperature or lower, if the vibrational modes have sufficient energy. Such a situation can readily occur in supersonic expansion flows and in molecular gas glow discharges.

Ionization by this mechanism has been previously studied by Polak et al [20] in an \( N_2 \) glow discharge, and shown to be the dominant mode of ionization in the environment studied. A major difficulty with such measurements in a glow discharge, as has been said in Chapter I, is that alternative ionization channels, such as direct electron impact ionization or ionization by electronically excited molecular collisions, are simultaneously present. This makes isolation of key mechanisms difficult. A somewhat more recent study by Achasov et al [21] avoided this difficulty by studying the process in the supersonic expansion of a high-stagnation-enthalpy gas in a shock tunnel apparatus. In Ref. [21], both \( N_2 \) and CO were heated to stagnation temperatures in the 2000 to
4000 K range, and cooled in a rapid supersonic expansion. In the expansion, a substantial degree of the stagnation energy was frozen in the vibrational mode, and relatively low translation-rotation temperatures were achieved. The vibrational mode is vibration-vibration (V-V) pumped. Substantial amounts of ionization were measured in the expansion, and attributed to the associative ionization mechanism. Detailed exploration of the role of the vibrational nonequilibrium processes in the ionization mechanism was made difficult, however, due to the short test times available in the shock tunnel.

Theoretical studies of ionization by the vibrationally-induced mechanism of Eq. (2.1) have also been made by Cacclatore et al for a glow discharge in N₂ [22] and by Capitelli et al for a nitrogen afterglow [23], using the master equation simulation (see Ref. [6]) and the rate constant recommended in Ref. [20].

In the present experiments, the associative ionization mechanism is studied, again in a discharge-free environment, but one which can be operated for hours. Radiation from a carbon monoxide (CO) infrared gas laser is focused into a flowing-gas absorption cell. The cell contains a mixture of CO, Ar and He. Laser radiation is resonantly absorbed by the CO vibrational mode, and vibrational levels approximately up to v=40 become strongly overpopulated. The CO vibrational distribution function (VDF) is determined by infrared (IR) emission spectroscopic diagnostics. The translational-rotational modes are in Boltzmann equilibrium at temperatures in the range 600-800 K. These temperatures are determined from rotationally resolved IR spectra. Such relatively low temperatures are maintained by the heat capacity
effect of the Ar-He diluent and by the convective cooling effect of the gas flow. Ionization, induced by the CO vibrational excitation and presumably occurring by the mechanism of Eq. (2.1), is studied by using the Thomson discharge [24] in the cell, supported by the laser beam. A preliminary report of ionization studies with this experimental approach was given recently as part of Refs. [13,25].

2.2 Experimental procedure

The apparatus used in the present experiments is quite similar to that described in Ref. [13]. Figure 2.1 gives a schematic of the experimental equipment used in these studies. Radiation from the CO gas laser (1) is focused into the flowing-gas absorption cell (6). Extensive details of the CO pump laser construction and operation are given in Refs. [12,13]. Briefly, the laser is an electrically excited, slow-flow, CO gas laser. The active discharge tube is 1 meter long and 2.5 cm in diameter. Power is supplied by a regulated d.c. power supply. The ends of the discharge tube are sealed by CaF$_2$ windows at Brewster's angle; external 2.5 cm diameter laser mirrors are used. The walls of the tube are cooled by a liquid-nitrogen bath. In the present experiments the laser operates in cw regime. Table 2.1 gives the typical laser gas partial pressures, discharge current, and output power for the present experiments.

The laser operates with broad bandwidth reflectivity mirrors, and, typically, the beam consists of approximately 20 vibrational-
Figure 2.1 Schematic of the experimental setup: 1, infrared CO laser; 2, d.c. power supply; 3, microammeter; 4, gas supply and gas mixing manifold; 5, impurity trap; 6, cell; 7, exhaust pump; 8, infrared spectrometer; 9, laser power meter
Table 2.1. Typical laser conditions

<table>
<thead>
<tr>
<th>Species</th>
<th>Partial pressure (Torr)</th>
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<tbody>
<tr>
<td>He</td>
<td>6.00</td>
</tr>
<tr>
<td>N₂</td>
<td>0.50</td>
</tr>
<tr>
<td>CO</td>
<td>0.03</td>
</tr>
</tbody>
</table>

| Discharge current | 30 mA |
| Laser power      | 14.0 W |

rotational lines on the CO 5-micron infrared fundamental band, extending from the v = 3 → 2 component to v = 12 → 11. Figure 2.2 gives a typical laser output spectrum. The laser is optimized to run on low-lying vibrational transitions, which is essential to start V-V pumping of the cold (T-300K) CO. The usual procedure for starting the experiment is to operate the laser at relatively low powers (approximately 3 W), for which there is considerable v = 3→2 output on low rotational lines (~0.6 W). The up-pumping starts by spontaneous fluctuations of the laser lines to the band v = 2→1 or by intra-cavity chopping (Refs. [12,13]). After substantial absorption occurs in the CO, the laser power is increased to 14 W, with about 1 W on the v →3→2 band, and the system is allowed to reach steady state. The amplitude stability of the steady state
Figure 2.2 Typical CO laser spectrum
broadband power is within ±3%. The laser beam is focused into the cell by a 30 cm focal length mirror. The reflecting angle is kept small to reduce astigmatism. The focusing area is approximately 1 mm².

The absorption cell, shown in Fig. 2.3, is a six-arm stainless steel tubing cross. Inside diameter of the tubing is 4 cm, and the ends of the cross arms along the pump beam axis are closed by CaF₂ windows. The total length of the cell, window to window, along the laser beam axis is 15 cm. The sidearms perpendicular to the laser beam have been shortened to increase the aperture for emission spectroscopy.

A mixture of CO, Ar and He is admitted into the cell through a 6 mm diameter port on the side of one arm; the gas mixture is exhausted through a similar port on the opposite cell arm. The cell gases are premixed before entering the cell.

The gas trapping system ((5) of the schematic of Fig. 2.1) is based on the findings of Center [26], who developed it to remove strongly electron-attaching iron pentacarbonyl Fe(CO)₅ from bottled CO. The iron and nickel carbonyls Fe(CO)₅ and Ni(CO)₄, being strong attachers, are also capable of producing Fe and Ni atoms. The trap consists of a 15 cm long copper tube, 12 mm in diameter, filled with a 5 Å molecular sieve material (zeolite). The trap is operated at room temperature and can be by-passed. Gases used were Matheson CP grade CO (99.5% min), prepurified grade Ar (99.98%) and high purity grade He (99.995%). Some preliminary tests were made with UHP CO (99.9%) and with trapped gases processed with a liquid-nitrogen-cooled trap preceding the molecular-sieve-containing trap. No significant differences were observed in these tests from the results reported here.
Figure 2.3 Cell with probe
The gas flow and the cell pressure can be varied by means of flowmeters and by a throttling valve before the pump. The gas flow through the cell is quite slow - less that 0.03 g/sec in all cases for the measurements reported here. It is estimated that the local gas flow velocity does not exceed 10 cm/sec in the region of the current measurement, which insures that the gas residence time is long enough to achieve steady-state CO vibrational distribution. On the other hand, any further throttling of the gas flow makes convective cooling ineffective, which leads to a significant temperature increase in the cell. The vibration-translation (V-T) relaxation rates also increase with temperature, so the vibrational nonequilibrium under very slow-flow or non-flowing conditions is not as strong.

The pressures of CO, Ar and He in the cell can be varied over a wide range; for the present studies the CO partial pressure was constant $P_{CO} = 3$ Torr, with the Ar-He mixture pressure being $P_{Ar-He} = 97$ Torr. The He partial pressure has been changed from zero to 97 Torr.

With the gases flowing through the cell under these conditions, the vibrational mode of the CO in the cell readily absorbs some of the pump laser energy into the lower CO vibrational states, $v \leq 12$.

Higher CO vibrational states, $v > 12$, are populated by collision induced vibration-to-vibration energy exchange (see Refs. [6,13]). One result of this V-V pumping is immediately seen in the absorption cell: there is an intense blue light emission visible, centered at the focal point of the laser beam. For the experiments described here, the glow starts approximately 4 cm before the focus and extends to the exit
window, thus spreading for about 10 cm. The diameter of this luminous region varies with cell and laser conditions; it is approximately 2-3 mm for the present measurements. This blue emission is due to visible band components of the C\textsubscript{2} Swan system, d\textsuperscript{3}\Pi\textsubscript{g} \rightarrow a\textsuperscript{3}\Pi\textsubscript{u}. The C\textsubscript{2} is generated by chemical reaction of the V-V pumped CO. It has been observed in previous work using this excitation technique (Refs. [9,13]).

The infrared radiation from the cell is observed perpendicular to the laser beam. The IR signal is focused onto the entrance slit of a 0.34 m scanning IR monochromator ((8) of the schematic of Fig. 2.1), by a two-mirror arrangement. It is analyzed by grating blazed for 4 μm and observed with an InSb detector. All the spectra are stored in and processed by an IBM PC 486 computer.

Under these excitation conditions, ionization occurs in the cell gases, presumably by the mechanism of Eq. (2.1). For the ionization measurements, two parallel plate brass electrodes are placed in the absorption cell. Figure 2.3 shows a detail of this arrangement. The plates are 2cm x 1cm with the long axis parallel to the laser beam. For the measurements reported here, the plates are separated by 1 cm. The axis of the pump laser beam is centered in the space between the plates. Insulated leads connect the plates to the exterior of the cell, as shown in Fig. 2.1.

The plates are connected to a regulated d.c. power supply (2), which can deliver an output voltage of up to 3000 V. In series with the supply is a microammeter (3) which can record the steady state current to within 10 nanoamperes.
Finally, the transmitted laser power is measured by a power meter, (9) of Fig. 2.1, positioned in the laser beam after the cell. Comparing the transmitted power under steady-state pumping conditions and after the CO is removed from the cell, one obtains the absorbed power. The incident power can be easily changed by using a beamsplitter, without changing the laser beam diameter and the laser spectrum. The absorbed power has been varied from 1.7 to 5 W for typical cell conditions as described above.

2.3 Results and discussion

2.3.1 Infrared measurements

Figure 2.4 shows three typical infrared emission spectra, generated by the V-V pumped CO in the cell, when operating under the conditions described above, at three different helium pressures. The first overtone, $\Delta v=2$, emission bands of CO, ranging from 2.3 to 4.4 $\mu$m wavelength, are shown under low resolution. The approximate centers of some of the radiating vibrational transitions are shown. As can be seen, vibrational states to $v \approx 40$ are populated and radiating. The abrupt signal rise at $\lambda \approx 4.4 \mu m$ is due to overlapping with the fundamental, $\Delta v=1$, spectrum. The signal at $\lambda < 2.3 \mu m$ is generated by the second overtone, $\Delta v=3$, radiation.

The observed IR radiation signal intensity $I(\lambda)$ is a superposition of the first and the second CO overtones (the latter - in
Figure 2.4 CO first overtone emission spectra at different He pressures.

P=100 Torr
1 - CO:Ar=3:97
2 - CO:He:Ar=3:12:85
3 - CO:He=3:97
the two first orders of the grating). In this case \( I(\lambda) \) can be expressed in terms of absolute intensities of the overtones \( I_{\text{abs}}^I(\lambda) \) and \( I_{\text{abs}}^{II}(\lambda) \), and the total InSb detector and 4 \( \mu m \) monochromator grating response function \( \Phi(\lambda)\Psi_\alpha(\lambda) \):

\[
I(\lambda) = \left[ I_{\text{abs}}^I(\lambda) + I_{\text{abs}}^{II}(\lambda) \right] \Phi(\lambda)\Psi_i(\lambda) + I_{\text{abs}}^{II}(\lambda/2)\Phi(\lambda/2)\Psi_{II}(\lambda/2) \tag{2.3}
\]

Here \( \Phi(\lambda) \) is the detector sensitivity, and \( \Psi_i(\lambda) \) and \( \Psi_{II}(\lambda) \) are the grating response functions in the first and in the second order, respectively. The product of \( \Phi(\lambda) \) and \( \Psi_\alpha(\lambda) \) was determined from a black-body source calibration of the spectrometer.

With known response functions, Eq. (2.3) allows comparison of the experimental CO spectrum and the computer-generated spectrum, based on a synthetic carbon monoxide VDF. Thus, the vibrational distribution functions of CO in the optical cell were inferred, as has previously been done by Rich and Bergman [9]. The procedure was first suggested by Horn and Oettinger [27]. Details of the method we followed are described in Ref. [13]. CO molecular spectroscopic constants were taken from Huber and Herzberg [28]; Einstein coefficients for CO spontaneous radiation were obtained from Chackerian and Tipping [29]. Fig. 2.5 shows the typical agreement obtained between the experimental and the synthetic spectra. Note that the periodic structure of these spectra at 3.8 \( \mu m < \lambda < 4.4 \mu m \) is second overtone/second order signal, and it is not attributed to the radiation from the high vibrational levels \( v>35 \). The same remark is also true for the curves 2,3 in Fig. 2.4.
Figure 2.5 Comparison of experimental and synthetic CO vibrational spectra
Figure 2.6 Comparison of experimental and synthetic CO rotational spectra
The rotational temperature of the cell gases $T_r$ was obtained from comparison of the experimental rotationally resolved CO fundamental spectrum on vibrational transitions $1\rightarrow 0$ and $2\rightarrow 1$ with the appropriate synthetic spectrum (see Fig. 2.6). The relative error in $T_r$ was estimated to be about 25%, both because of the strong self-absorption and because of the non-uniform temperature profile across the cell. There is no doubt, however, that the inferred $T_r$ for all measured regimes is in the range $T=600-800$ K. This result is also confirmed by our earlier rotationally resolved spectra of the $C_2$ Swan emission $d^3\Pi_u \rightarrow a^3\Pi_u$ in the cell (see Ref. [13]). It was shown that the $C_2$ rotational mode is in Boltzmann equilibrium. The inferred $C_2$ rotational temperature for similar cell conditions was in the same range, $T=600-800$ K, as that obtained from the present infrared measurements.

Figure 2.7 presents the CO vibrational distribution functions inferred from the experimental spectra. One can see that high vibrational levels of CO, up to $v=30-40$, are overpopulated. The rate constant of V-T relaxation CO-He is much higher than that of CO-Ar or CO-CO, and thus the total V-T rate increases with the helium concentration ($0 \leq n_{He}/n \leq 0.97$). Therefore by adding helium to the CO-Ar mixture, we succeeded in changing the plateau fall-off level $v^*$, where the V-T relaxation rate is equal to the local V-V rate, decreasing the plateau length. Note that the relative populations at $v<v^*$ did not significantly change, so we just cut the "tail" of the VDF, as has earlier been done in Ref. [8]. It should be pointed out that fine control of the plateau length can be obtained by this means. The distributions shown in Fig. 2.7 represent only some of the VDF's
Figure 2.7 Inferred CO vibrational distribution functions at different He pressures
measured. Measurable, reproducible plateau lengths are obtained for every 3% change in the $n_{He}/n$ ratio. The rotational temperature of the gas mixture remains nearly unaffected by the helium concentration change, as was found from the rotational spectra. Obviously, the effect of the higher helium thermal conductivity is compensated by the higher V-T energy transfer rate.

We note, however, that the shape of the CO VDF differs from that predicted by theory. Simple estimates show that the lower level populations should follow the Treanor distribution with some vibrational temperature $T_v$ since the nonresonant V-V exchange for these levels is much faster than the laser pumping or the V-T relaxation. But the best Treanor fit for levels $v\leq5$, at $T=700K$, $T_v=3200K$ gives a strongly underestimated plateau population at levels $v\geq10$ (see the lower dashed curve in Fig. 2.7). On the other hand, the Treanor distribution corresponding to the inferred plateau, $T=700K$, $T_v=3900K$ (the upper dashed curve in Fig. 2.7), does not fit to populations of levels $v<10$. A similar effect, but not so strong, was observed by Martin et al in Ref. [30], also in CO optical pumping experiments.

This anomaly can be qualitatively explained by the spatial nonuniformity of the cell gas. The infrared signal is collected from the entire optical path across the cell, while the energy is absorbed only in the near-axis area. The relaxation rates of the high CO vibrational levels are much faster than those of the low levels. This means that the molecules which contribute to the longer wavelength part of the infrared spectrum (which corresponds to the plateau region of the VDF), are concentrated near the optical axis. At the same time, the shorter
wavelength part of the spectrum (the Treanor region of the VDF) is a superposition of the signals both from the central and from the peripheral areas of the cell. Obviously, this decreases the effective vibrational temperature of the inferred Treanor-like population. The major contribution to these two parts of the distribution function comes from different cell regions. This spatial nonuniformity brings substantial error in the determination of absolute populations of the high CO vibrational levels, because the VDF should be normalized to unity. The effect can be reduced only by decreasing the cell diameter. In the experiments of Ref. [30] the effect was reduced by removing partially-relaxed CO from the cell by Ar flow, which decreased the optical path to several mm.

2.3.2 Ionization measurements

In these optical pumping experiments we have measured the electric current induced between two plane electrodes placed in the cell. It should be mentioned that the voltage applied to the electrodes was usually considerably lower than the breakdown voltage $U_b$; the voltage-current characteristics were measured for $U < U_b$ at different helium partial pressures (see Fig. 2.8). The typical value of the measured current was several microamperes. Obviously, a non-self-sustained electric discharge, supported by the laser beam, is ignited in the cell. The theory of this type of discharge was developed by Thomson as early as in 1928 [24]. It assumes that ionization by electron impact
Figure 2.8 Experimental and theoretical voltage-current characteristics of the Thomson discharge.
is negligible, because of the low energy of electrons. Then, the production of charge in the interelectrode region can be described by the ionization rate $q_1$, which is independent of the electron density.

The Thomson theory gives simple analytical relations for the current-voltage (I-U) characteristic of the discharge $I(U)$, the saturation voltage and current $U_s$ and $I_s$, the electric field and the charge species distributions (see Appendix). The I-U characteristics are different for two specific cases of distributed ionization ($q_1=$const in the entire discharge area) and concentrated ionization, when the external ionization layer width $d$ is much smaller than the interelectrode distance $L$. In the first case the induced current is proportional to the square root of the applied voltage:

$$I = \left(4 \mu_+ \varepsilon_0 e^3 q_1^3\right)^{1/4} \cdot S \cdot U^{1/2}, \quad (2.4)$$

where $\mu_+$ is the ion mobility, and $S$ is the electrode surface area. For the concentrated source, placed on the symmetry axis of the discharge, the current is proportional to the square of the voltage:

$$I = \frac{9 \mu_+ \varepsilon_0 S}{L^3} U^2, \quad (2.5)$$

where $L$ is the interelectrode distance. Note that in the case of the concentrated ionization source, which we are especially interested in, the I-U characteristic given by Eq. (2.5) is independent of the ionization rate $q_1$. Also, if the ionization source is shifted from the symmetry axis by a distance $\delta \ll L$, ($\delta > 0$ toward the positive electrode), the Eq. (2.5) becomes
which means that the alignment symmetry (and therefore the applicability of Eq. (2.5)) can be controlled by switching the voltage polarity.

It can be seen from Fig. 2.8 that the shape of the experimental I-U characteristics reasonably corresponds to the theoretical curve $I-U^2$ for the Thomson discharge supported by a concentrated ionization source (see Eq. 2.5). This supports the conclusion that the ionization of the cell gases occurs in the central area of the cell surrounding the laser beam. Furthermore, it is possible to show that if the ionization rate is not equal to zero in the vicinity of the electrodes, then

$$\lim_{U \to 0} \frac{dI}{dU} = \infty, \quad (2.7)$$

as is the case, for example, for the distributed ionization source (see Eq. (2.4)). Therefore, since the observed U-I characteristics do not reveal a noticeable sharp current increase at low voltages, one can conclude that surface ionization is negligible in the present experiments.

Further evidence supporting a gas-phase ionization process was obtained in the experiment by using a quartz tube. The laser beam was surrounded by the tube which allowed the UV radiation from the CO excited electronic states to pass, while the near-axis region was completely isolated from the electrodes. No current was measured in this
case (see Ref. [13]), which shows that the photoelectric effect on the electrodes is also negligible. Also, no current can be measured in an Ar-He mixture or when the pump laser is turned off.

It also can be seen that at some voltage \( U_s \) the slope of the current curve substantially decreases, although the current nevertheless continues to grow linearly. This part of the I-U characteristics is associated with saturation. The fact that the current is not completely saturated is explained by the finite size of the electrodes.

If we assume that the ionization in the plasma is catalyzed by the laser radiation, and the ionization rate \( q_i \) follows the laser beam power distribution (Gaussian profile), then we can write

\[
q_i(x) = q_i(0) \exp \left[ -\left( \frac{x-L/2}{0.5d} \right)^2 \right], \tag{2.8}
\]

where \( d \) is the characteristic profile width \((d \ll L)\). For this distribution of \( q_i \) the saturation current and voltage are given by the following relationships:

\[
I_s = eq_i(0)d \frac{\pi^{1/2}}{2} S, \tag{2.9}
\]

\[
U_s = \left[ \frac{eq_i(0)d}{\mu \varepsilon_0} \right]^{1/2} \frac{\pi^{1/4}}{3^{1/2}} \frac{L^{3/2}}{2} \tag{2.10}
\]

As can be seen, these equations do not contain rate constants of any collisional process in the plasma, except the external ionization rate. Therefore, the product \( q_i(0)d \) can be unambiguously inferred from the experimental values of \( I_s \) and \( U_s \).
For the present situation of CO optical pumping by resonance absorption of CO-laser radiation, when one can neglect multiphoton ionization (the estimated power density is far too weak), the ionization occurs in collisions of two heavy particles, and we can write

\[ q_1 = \kappa_1 n_{\text{CO}}^2, \quad (2.11) \]

where \( n_{\text{CO}} \) is the concentration of CO molecules, and \( \kappa_1 \) is the reduced ionization rate. To express \( \kappa_1 \) in terms of the ionization rate constant \( k_1 \) and relative concentrations of colliding molecules, one has to make an additional assumption on the process mechanism.

It is clear from Fig. 2.8, that the experimental I-U characteristics for different He concentrations at \( U < U_s \) are very close, while the saturation voltages and currents are substantially different. This is also in good agreement with the theoretical prediction that for the concentrated ionization source the I-U characteristic is independent of the ionization rate \( q_1 \) (see Eq. (2.5)). Obviously, \( q_1 \), determined by relations (2.9, 2.10), varies for different regimes in Fig. 2.8.

Recent time-resolved measurements, where the Q-switched CO laser was used to pump CO in the cell, have shown that the measured current pulse occurs with some delay after the laser pulse. On the other hand, the current pulse is synchronized with the CO \( v=22 \rightarrow 20 \) IR pulse, emitted from the cell (see Ref. [13]). Finally, the present experiments in the CO-Ar-He mixture with different helium concentrations confirm that a definite correlation exists between vibrational excitation and ionization. An analysis of Figs. 2.7 and 2.8 shows that the lower the
population of high CO vibrational levels, the lower is the saturation current. These measurements were carried out at constant laser power, total pressure of the CO-Ar-He mixture, and CO partial pressure.

The sum of these arguments leads to the following conclusions: i) the observed ionization, stimulated by the CO laser, occurs in the gas phase, in the narrow near-axis area of the cell, occupied by the laser beam; and ii) it is induced by highly vibrationally excited CO molecules, which are also concentrated near the optical axis.

Generally, ionization is allowed when the total energy of reactants is high enough to overcome the ionization potential of one of them. The previous discussion leaves us with two possible mechanisms of ionization:

\[
\text{CO}(v) + I \rightarrow \ldots \rightarrow \text{CO} + I^+ + e, \quad E_v \geq E_I(I) \quad (2.12)
\]

\[
\text{CO}(v) + \text{CO}(w) \rightarrow \ldots \rightarrow \text{CO}^+ + \text{CO} + e, \quad E_v + E_w \geq E_{I}(\text{CO}) \quad (2.13)
\]

where I is some easily ionizable impurity, \(E_v\) is the energy of the \(v^{th}\) CO vibrational level, \(E_I(I)\) and \(E_I(\text{CO})\) are the ionization potentials of the I and CO molecules, respectively. Dots in the reaction equations (2.12) and (2.13) mean that the detailed mechanism of the ionization is still uncertain. For example, it is not clear how metastable \(\text{CO}(a^3\Pi)\) molecules, which can be also created in the collision of vibrationally excited \(\text{CO}(X^3\Sigma,v)\) molecules (see Farrenq et al, Ref. [31]), affect the ionization. The metastables could be an intermediate stage of the process.
The present phenomenological approach cannot resolve questions about the importance of intermediates in the vibrationally-induced ionization of CO. However, it is possible to make a choice between the first-order mechanism (2.12) and the second-order reaction (2.13). The reduced ionization rate \( \kappa_1 \) (see Eq. (2.11)) in these two cases can be written as follows:

\[
\kappa_1 = (k_1 f_I) \sum f_v, \quad E_v = E_1(I)
\]  

(2.14)

\[
\kappa_1 = k_1 \sum f_v f_w, \quad E_v + E_w > E_1(CO)
\]  

(2.15)

where \( k_1 \) is the ionization rate constant, \( f_I \) is the impurity fraction in the mixture \( (f_I = n_I/n_{CO}) \), and \( f_v \) is the relative population of the CO \( v^{th} \) vibrational level.

Since the saturation voltage and current of the Thomson discharge are functions of the reduced ionization rate \( \kappa_1 \) (see Eqs. (2.9-2.11)), and the CO VDF in Eqs. (2.14-2.15) is known from the infrared measurements, it is possible to determine the ionization rate constant \( k_1 \) (or the product \( k_1 f_I \) for the first-order mechanism) from the experimental values of the saturation current \( I_s \).

Figure 2.9 gives the dependence of the saturation current, determined in the junction point of the parabolic and the linear parts of the I-U characteristics in Fig. 2.8, as well as the dependence of the first order and the second order sums in Eqs. (2.14) and (2.15).
Figure 2.9 Saturation current and number of "active CO molecules" dependence on the He pressure
on the helium concentration. The first order sum \( S_1 \) was calculated for several different threshold energies \( E_1(I) \), which would correspond to different ionization potentials of impurities. One can see that the second-order sum \( S_2 \) reasonably corresponds to the current curve. On the other hand, it is clear, that the first order sum is also in reasonable agreement with the current curve if the impurity ionization potential is about 7 eV (\( v \approx 35 \)), which is characteristic for some metal atoms (Fe - 7.90 eV, Ni - 7.64 eV, Cu - 7.73 eV). These metals can be present in the cell because the cell gases are stored in steel cylinders, and copper tubes are also used in the experimental setup. Besides that, such impurities as chemical reactions products \( \text{CO}_2 \), \( \text{C}_2 \text{O} \), \( \text{C}_2 \), \( \text{C}_3 \text{O}_2 \) and their polymers are always present in the vibrationally excited CO because of chemical reactions (see Rich and Bergman, Ref. [9]). On the other hand, we can definitely exclude impurities whose ionization potentials are lower or much higher than ~7 eV.

If we assume that ionization does occur in collisions of two vibrationally excited CO molecules, then the ionization rate constant inferred from the infrared spectra and the saturation current measurements is \( k_l = (6 \pm 2) \times 10^{-15} \text{cm}^3/\text{s} \). Otherwise, if the first-order mechanism is assumed, one gets the product \( k_l f_I \sim 10^{-17} \text{cm}^3/\text{s} \), which in the gas-kinetic limit for the ionization rate constant (\( k_l < 10^{-10} \text{cm}^3/\text{s} \)) gives \( f_I = n_I/n_{\text{CO}} > 10^{-7} \), or for the present cell conditions, \( N_I > 10^{10} \text{cm}^{-3} \). It is disappointing that the possible influence of ionizable
impurities cannot be eliminated on the basis of the preceding estimates on the lower bound of their concentrations. However, the trapping system described previously is specific for eliminating Fe(CO)$_5$ and also has been observed to remove Ni(CO)$_4$ from similar cell experiments of Ref. [32] (with the trap atomic Ni lines disappeared from the cell radiation spectrum). Such metal carbonyls are definitely present when the gases are untrapped, and form a ready source of Fe and Ni atoms when in the presence of vibrationally pumped CO. Their concentrations are significantly reduced when the trap is used. We observed that when the trap is in use, both the populations in the $v>20$ plateau and the electric current are slightly increased.

This result is inconsistent with such species being the source of impurity ionization. The observed increase in the $v>20$ concentrations when the trap is used is an expected consequence of the reduced V-T rates, as the fast-relaxing metal atoms are eliminated. The increase in current is consistent with the slightly higher plateau populations, if ionization occurs in collisions of two vibrationally excited CO molecules. On the other hand, the current would decrease significantly when the trap was used if impurity metal ionization were a major source of electrons. We conclude that the ionization is indeed due to the mechanism of Eq. (2.1).

The electron concentration and the ionization fraction in the field-free case can be estimated on the assumption that the dominant channel of electron loss is CO dissociative recombination ($\beta$$\sim$$10^{-7}$ cm$^3$/s, [26]). This gives the electron concentration to be $n_e$$\sim$$10^{10}$ cm$^{-3}$, with an ionization fraction about $y_e = n_e/n \sim 10^{-8}$. 
Equations (2.9, 2.10) allow determination of only the product $q_1(0)d$. We therefore require an independent determination of the characteristic width, $d$. Since the ionization is localized in the region of substantial concentration of highly excited CO molecules $CO(v\approx25)$, $d$ can be found from the experimentally determined width of the visible blue glow ($C_2$ Swan band radiation observed in the cell). The $C_2$ molecules are produced in chemical reactions which are started by a vibrationally stimulated reaction

$$\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}_2 + C \quad (2.17)$$

with an activation energy corresponding to CO vibrational level $v\approx25$. One can neglect diffusion of the excited $C_2$ at the present cell pressures (~100 Torr), and thus the glow diameter approximately corresponds to the ionization region width $d$. This parameter can be easily estimated visually within an accuracy of ~50%, and it is usually 2-3 mm for the present conditions. Taking into account the uncertainty in the rotational temperature of ~25%, we get an accuracy in $\kappa_1$ of a factor of 2.

The accuracy of the inferred ionization rate constant $k_1$ depends on the accuracy of determination of the VDF. Due to the spatial nonhomogeneity effect, discussed above, the uncertainty in the inference of populations of zero and the first vibrational levels can reach a factor of 2. The combination of uncertainties in the $\kappa_1$ and VDF determinations gives the overall range for the inferred rate constant $k_1=(8\pm5)\times10^{-15} \text{ cm}^3/\text{s}$. This uncertainty can be substantially diminished.
by changing the cell design, thus reducing the nonuniformity of the flow across the cell, and this work is being done. This result for $k_i$ corresponds to within an order of magnitude to that obtained by Polak et al [20] for associative ionization of nitrogen:

$$k_i = 1.9 \cdot 10^{-15} \exp(-1160/T) \text{ cm}^3/\text{s}$$

(2.18)

### 2.3.3 Vibration-to-electron coupling measurements

To better understand how the electrons can affect the CO VDF, we also carried out a series of experiments where the relative populations of different vibrational levels of carbon monoxide were measured twice - with and without the electric field. Here we used an interesting property of the Thomson discharge, that is a strong difference of the electron and ion concentrations, due to their different mobilities (see Fig. 2.10 and Appendix). One can easily show (see Appendix, Eqs. (A1-A4)) that in the saturation regime

$$\frac{n_{e\text{ max}}}{n_{i\text{ max}}} = \left( \frac{\mu_e}{\mu_i} \right)^{1/2} \ll 1$$

(2.19)

In other words, the electron concentration $n_e$ in the saturation regime is much lower that the concentration of ions, $n_i$. Since in the absence of the electric field $n_e = n_i$ (see Fig. 2.10), $n_e$ can obviously be reduced by orders of magnitude just by increasing the applied voltage, without changing the energy loading in the plasma by the external source.
Figure 2.10 Charged species distributions in the Thomson discharge in the absence of the field and in the saturation regime.

$P = 100 \text{ torr, CO:Ar} = 3:97, \quad d/L = 0.25; \quad q_1(0) = 10^{-21} \text{ cm}^3/\text{s}$ (see Eqs. (2.8), A2-A4). $L$ - interelectrode distance
Moreover, in the saturation regime the remaining electrons do not contribute to the energy loading, because the estimated electric field power \( P_e \sim U I \sim 1 \text{ mW} \), which is much lower than the absorbed laser power \( P_l > 1 \text{ W} \). For this reason, the removal of the electrons is the only direct result of the applied voltage. The influence of ions can be neglected because the electron-to-vibration (e-V) energy transfer cross-sections in CO are of the order of the atomic cross-section (see Ref. [33]) and therefore the appropriate rate constants can considerably exceed the gas-kinetic limit.

Figure 2.11 represents the results of these measurements. It is clear that the electron removal (field ON in Fig. 2.11) increases the populations of high vibrational levels, \( v \geq 15 \). The effect is not very dramatic, about 10% variation at the beginning of the plateau region, increasing with the vibrational quantum number to attain 70% variation at \( v = 30 \). On the other hand, the populations of the levels below \( v = 10 \) decrease when the electrons are eliminated from the discharge area. Here again the effect does not exceed 10% variation. The qualitative change in the VDF is shown in Fig. 2.12, where the effect is strongly exaggerated for illustrative purposes.

The following approximate analysis can interpret qualitatively the observed dependence of the CO VDF on the electron concentration. The interaction of the CO molecules with electrons can be expressed by the reaction

\[
\begin{align*}
\text{CO}(v) + e & \quad \overset{k_e}{\longleftrightarrow} \quad \text{CO}(v+\Delta v) + e, \\
\text{on} & \quad \overset{k_s}{\rightarrow} \quad \text{CO}(v+\Delta v) + 2e,
\end{align*}
\]

(2.20)
Figure 2.11 Electric field influence on different CO vibrational level populations
Figure 2.12 Qualitative demonstration of the $V \rightarrow e \rightarrow V - \Delta V$ effect (strongly exaggerated). $\epsilon$ - electron energy, $T_e$ - electron temperature.
where the forward process is the vibrational excitation by electron impact, and the reverse one is the effect of superelastic collisions. Let us approximately assume that the electron energy distribution function (EEDF) is Maxwellian, so that we can write

$$k_e = k_s \exp \left( \frac{-\Delta E_{v+\Delta v,v}}{T_e} \right), \quad (2.21)$$

where $\Delta E_{v+\Delta v,v} = E_{v+\Delta v} - E_v$ is the difference in energies of vibrational levels $v+\Delta v$ and $v$, and $T_e$ is electron temperature. The CO VDF can be represented as follows:

$$f_v \sim \exp(-E_v / T_{vlb}^v), \quad (2.22)$$

where $T_{vlb}^v$ is the "local" vibrational temperature. This temperature obviously increases with vibrational quantum number, because the measured VDF at the high $v$'s has much higher values than the corresponding Boltzmann distribution at $T_{vlb}^v$.

Now, one can easily show that the detailed balance for the process (2.20) is attained at $T_e = T_{vlb}^v$. If the electron temperature exceeds the local vibrational temperature, the vibrational excitation by electron impact is a dominant process. On the other hand, for the high vibrational temperatures the superelastic collisions prevail. Since $T_{vlb}^v$ strongly increases with $v$, it means that the lower CO levels are populated by electron collisions, while for the very high $v$'s the effect is quite opposite (see Fig. 2.12). In other words, the influence of this vibrational-electron interaction is as was observed in our experiments, where $T_{vlb}^v \sim 3-4$ kK.
This analysis gives a simple estimate of the electron temperature from the measured VDF, from which the value $T_e \sim 6$ kK is obtained (see straight line in Fig. 2.12). Since the perturbation of the VDF is the strongest in the absence of the field, it means that the electrons acquire energy from the high vibrational levels (otherwise they would be quickly thermalized) and return it to the lower levels ($V \to e \to V-\Delta V$ process).

The effect of the acceleration of the remaining electrons, when the field is on, on the VDF should be considered as completely negligible. The typical value of the reduced electric field between the electrodes is $E/N < 40$ Td, which implies the electron temperature to be $T_e \sim 1$ eV (see Ref. [34]). This means that the concentration of the high-energy electrons ($e \approx 5$ eV), which are able to excite higher vibrational levels $v\sim 20$, is still low, $n_e^* \sim 10^{-2} n_e$. Taking into account the fact that $n_e$ drops by approximately 3 orders of magnitude, when the field is on (see Fig. 2.10), one has $n_e^* \sim 10^5$ cm$^{-3}$ for typical experimental conditions, when $n_{CO} \sim 10^{17}$ cm$^{-3}$. Now one can see that the excitation of the higher CO levels by the high-energy electrons is insignificant compared to the resonant $V-V$ exchange:

$$k_{eV} n_e^* n_{eCO} \ll k_{Vv} n_v^2 f_v^2$$  \hspace{1cm} (2.23)

Here $k_{eV} \sim 10^{-8}$ cm$^3$/s [34] - rate constant of vibrational excitation by electron impact, $k_{Vv} \sim 10^{-10}$ cm$^3$/s [35] - rate constant of the resonant $V-V$ exchange at $v \sim 20$, and $f_v \sim 10^{-3}$ - relative population of level $v \sim 20$ in our experiments. Electron impact ionization of highly excited CO molecules can be neglected for the same reason.
More detailed interpretation of the effect can be obtained by a self-consistent solution of the master equation for the CO VDF and the Boltzmann equation for the EEDF. Some results in this direction are already obtained (see, for example, work of Capitelli et al [34]), but a complete kinetic model for this problem still requires the cross-sections of the process (2.20) for the high v's.

Finally, we want to emphasize that the using of the Thomson discharge in an optical pumping experiment allows direct observation of the e-V energy transfer effects, arbitrarily changing the electron concentration, which is definitely impossible in self-sustained electric discharge systems.

2.4 Conclusions

Ionization occurring in collisions of two excited CO molecules is investigated in steady-state conditions of optical pumping. This mechanism appears to be the same "associative ionization" process studied in vibrationally excited N₂ by Polak, Sergeev and Slovetskii [20], and in N₂ and in CO by Achasov et al [21]. The present experiments allow the study of this process by using a non-self-sustained discharge (Thomson discharge), supported by a CO laser beam. The ionization rate constant k₁ is inferred from CO VDF measurements and the experimental saturation current of the discharge. A specific ionization rate constant of k₁=(8±5)x10⁻¹⁵ cm³/s is measured, which reasonably corresponds to the result of Ref. [20], obtained for nitrogen.
The influence of low-energy electrons on the CO vibrational distribution function is also investigated, by varying the discharge voltage, which allows elimination of the electrons from the discharge area. The effect of energy transfer from higher to lower vibrational levels of CO via collisions with electrons (\(V \rightarrow e \rightarrow V-\Delta V\) process) is observed for the first time.

The experimental technique used in the present work permits further studies of ionization and e-V processes in strongly excited, translationally cold gases. The detailed interpretation of the observed effects requires further theoretical study of elementary processes of interaction of highly excited molecules and electrons.
CHAPTER III
STUDIES OF VIBRATIONAL AND ELECTRONIC EXCITATION
OF NITRIC OXIDE

3.1 Introduction

As has been said in Chapter I, nonequilibrium molecular vibrational-mode energy distributions have been widely studied for various species [1-5]. For some diatomic molecules, such as \( \text{N}_2 \) and especially CO, which have very slow rates of V-T relaxation, there exist extensive experimental and theoretical data on this subject (see Refs. [1-5] and references therein).

Vibrational energy transfer in nitric oxide (NO) is much less studied, although it reveals some interesting features making it very attractive for investigation. First, this process has a very fast V-T self-relaxation rate; the rate constant, \( P_{v,v-1} \), of the process

\[
\text{NO}(v) + \text{NO} \rightarrow \text{NO}(v-1) + \text{NO},
\]

for \( v=1 \) and \( T=300 \) K, is \( P_{10} = 2.5 \text{ ms}^{-1} \cdot \text{Torr}^{-1} \) (see Ref. [36]), and is about 5 orders of magnitude faster than that of CO and \( \text{N}_2 \). Second, \( P_{10} \) has an anomalously weak temperature dependence with a minimum between
300 and 500 K (see a review of experimental data in Ref. [37]). Finally, recent measurements of the NO V-T rates using the stimulated emission pumping (SEP) technique by Yang, Kim and Wodtke [38] also show an unusual dependence of $P_{v,v-1}$ on the vibrational quantum number. Detailed state-resolved experimental data on NO V-V rates are still not available, except for the rate constant of the process

$$\text{NO}(v) + \text{NO}(w) \rightarrow \text{NO}(v+1) + \text{NO}(w-1), \quad (3.2)$$

measured in Ref. [39] for $v=w=1$ at room temperature, $Q_{10}^{12}=124 \text{ ms}^{-1} \cdot \text{Torr}^{-1}$.

Despite its fast V-T relaxation, NO does allow anharmonic vibration-vibration (V-V) pumping [6,7], such as has been experimentally found for $\text{N}_2$ [40,41] and CO [8]. This nonequilibrium V-V pumping of NO has been observed in a glow discharge in NO/He and NO/$\text{N}_2$ at $T=250-350$ K [15], and also in CO laser optical pumping experiments [16,42,43] at $T=300-400$ K, where the $v=0+1$ vibrational transition of NO was excited by a CO laser. Strongly nonequilibrium vibrational distribution functions (VDF) of NO have been measured up to level $v=15$ in Ref. [15] and up to $v=14$ in Ref. [43]. In addition, the NO $\beta$ and $\gamma$ bands, as well as the continuum spectrum of the NO$_2$ recombination in the reaction

$$\text{O} + \text{NO} \rightarrow \text{NO}_2 + \hbar \nu \quad (3.3)$$

were observed in Ref. [16]. Finally, new interesting results obtained in a NO/He radiofrequency afterglow, Ref. [44] show well-pronounced vibrational bands in the first overtone NO infrared spectra up to $v=17$, ...
at translational/rotational temperature $T=250-300\,\text{K}$, which indicates strong V-V pumping.

The present optical pumping experiment allows detailed investigation of NO vibrational and electronic energy transfer, as well as of vibrationally-induced chemical reactions. Its main advantage over glow discharge excitation methods is that vibrational levels above $v=1$ are populated by the processes of V-V exchange only.

This work presents the results of our experiments on NO optical pumping and a theoretical discussion of the different energy transfer processes involved. Also, new experimental data on V-T relaxation of NO as well as possibilities for further V-T/V-V rate measurements are reviewed, in light of the present results.

### 3.2 Experimental procedure

The schematic of the experimental equipment used in these studies is shown in Fig. 3.1. Radiation from the CO gas laser (1) is focused into the flowing-gas absorption cell (5). A liquid nitrogen cooled flowing-gas CO laser with a 140 cm active length and a 20% transmitting mirror (2) is operated single-line using a gold-coated grating (3) with 290 grooves/mm. The central 20 mm ID glass laser tube with precooling coils is held in an insulated stainless-steel reservoir that contains the liquid nitrogen bath. A 2-arm glow discharge is ignited in the tube. The laser delivers up to 8 W on the CO fundamental line $P(11) 8 \rightarrow 7$, $\lambda=5214\,\text{nm}$, which has a very close resonance with the
Figure 3.1 The experimental setup. 1, CO laser; 2, laser mirror; 3, grating; 4, focusing mirror; 5, absorption cell; 6, monochromator; 7, InSb infrared detector; 8, photomultiplier; 9, lock-in amplifier; 10, computer; 11, powermeter
Table 3.1. Laser parameters optimized for P(11) 8→7

<table>
<thead>
<tr>
<th>Partial pressures (Torr)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>12.5</td>
<td></td>
</tr>
</tbody>
</table>

| Gas velocity | 5 m/s |
| Temperature  | 120 K  |
| Discharge current | 30 mA |
| Discharge voltage | 13 kV |

NO line 1/2R(12.5) 1 ← 0. The energy displacement between these lines is 6.8×10⁻³ cm⁻¹ from the mean of the NO A-doublet, Ref. [45] (split by 9.5×10⁻³ cm⁻¹, Ref. [46]), and the laser line lies within the Doppler width of the lower-frequency A-component, Ref. [16]. The laser parameters, optimized for the maximum power at this line, are listed in Table 3.1. In the present experiments the laser is operated in the cw regime.

The laser mirror and the grating holder are mounted on an optical table to improve the passive stability. No active stabilization
is used. The achieved single-line stability is ±8% over 3 hours. Short time fluctuations are much smaller and not critical for the measurements.

The laser beam is focused into the pumping cell by a gold-coated mirror (4) of 30 cm focal length. The reflecting angle is kept small at 15° to reduce astigmatism. The focusing area is approximately 0.1 mm², which gives a power density of ~10 kW/cm². The complete beam path is purged with dry nitrogen to avoid atmospheric water absorption.

An aluminum optical cell with 8 mm ID and an absorption length of 8 cm is used. It is sealed with CaF₂ windows. A high gas velocity through the cell reduces the concentration of possible chemical products and also holds down the gas temperature which tends to be increased by the exothermic up-pumping process. To avoid back flows and turbulence in the pumped region, the gas inlet of the cell is designed with a smooth entry section. The gas mixture enters and leaves the cell through four symmetrical 6 mm tubing ports; it is flowing towards the laser beam. Except for the cell itself, all the tubing is stainless steel to avoid corrosion. The cell gas velocity reaches 7.2 m/s in the observed pumping region at a mass flow rate of 110 mg/s. This gives a residence time of \( t_r \sim 10 \text{ ms} \).

The gases used are Matheson CP grade NO (99.9%) and Ar (99.9%). The pressures of NO and Ar in the cell can be varied over a wide range; for the present studies the NO partial pressure was in the range from 0.5 to 3 Torr, with the NO-Ar mixture pressure being \( P_{\text{NO-Ar}} = 90 \) Torr. The absorbed laser power is determined by measuring the transmitted power behind the cell with and without NO. It changes from 1
W to 5.3 W for the range of gas pressures listed above, approximately linearly increasing with the NO partial pressure.

The fluorescence light from the cell is collected perpendicular to the laser beam. It is analyzed with a 1/3 m monochromator (6 of Fig. 3.1) and an InSb detector (7) in the infrared or with a 1/2 m monochromator and a photomultiplier (8) in the UV and visible. In both cases, a mechanical chopper at a frequency of 227 Hz is used. A lock-in amplifier (9) records the signal; it is connected to a PC 486 (10) for data acquisition and processing.

3.3 Results

In these experiments, the absorption conditions are optimized to get maximum ultraviolet signal from the cell. The strongest UV emission is achieved with a mixture of 1.1 Torr of NO diluted in argon at a total pressure of 90 Torr. At a given NO partial pressure, the argon pressure shows a wider optimum range; the UV signal is not very sensitive to it. Measurements with NO pressures from 0.5 to 3 Torr are analyzed while the total pressure is kept constant, P=90 Torr. Table 3.2 lists three selected cases of conditions.

Figure 3.2 shows infrared emission spectra, generated by the optically pumped NO in the cell, for the three pumping conditions of Table 3.2. The first overtone, \( \Delta v=2 \), emission of NO bands is shown under low resolution and ranges from 2.6 to approximately 3.5 \( \mu \)m wavelength. The approximate centers of some of the vibrational transitions are
Figure 3.2 The first overtone infrared NO spectra; solid lines - experimental spectra, dashed line - synthetic spectrum.
Table 3.2. Experimental regimes

<table>
<thead>
<tr>
<th>Case</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_{NO} \text{, Torr})</td>
<td>0.5</td>
<td>1.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Absorbed power, W</td>
<td>1.1</td>
<td>2.4</td>
<td>5.2</td>
</tr>
</tbody>
</table>

shown. Overlapping P and R-branches of different vibrational bands create the wavy structure of the signal. As can be seen, vibrational levels up to \(v=15\) are populated and radiating. Note that above level \(v=15\) there is still measurable infrared signal, but the signal-to-noise ratio here becomes worse, which makes the analysis of the spectrum difficult. The NO spectra shown are normalized to the same intensity at 2.8 µm and demonstrate that the intensity distribution is remarkably similar over the measured range of NO partial pressures.

The dashed line in Fig. 3.2 corresponds to a computer-generated synthetic spectrum, calculated for different NO vibrational distribution functions (VDF) until the best fit with the experimental curve of case II was obtained. Details of this standard procedure of inference of the NO VDF from partially-resolved IR emission spectra can be found in Refs. [15,27]. The spectrometer sensitivity used in this method is determined by a blackbody calibration. The most serious problem in the calculation of the synthetic spectrum is that there are
no experimental measurements of the Einstein coefficients for spontaneous radiation of NO at high vibrational levels, \( v > 8 \). Figure 3.3 shows the results of \textit{ab initio} calculations of the Einstein coefficients by Billingsley [47], for \( \Delta v = 1 \) (curve 1) and \( \Delta v = 2 \) (curve 2). Curve 1', for \( \Delta v = 1 \), is recommended in [48] up to \( v = 13 \), and uses the Billingsley scaling with a more reliable experimental value for \( A_{10} \) of \( 13.4 \text{ s}^{-1} \). Curve 2', for \( \Delta v = 2 \), is obtained in [48] from combining the direct measurements of ratios \( A_{v,v-2}/A_{v,v-1} \) (for \( v = 2-13 \)) with curve 1'. Here we present the best fit, extrapolated up to \( v = 15 \). The accuracy of these measurements, used in the present chapter, decreases from \( \pm 6\% \) for \( v = 2 \) to \( \pm 20\% \) for \( v = 13 \). The uncertainty in the inferred VDF is determined by this accuracy, since the population distributions are inversely proportional to the Einstein coefficients. The synthetic spectra are not very sensitive to rotational temperature variations within this accuracy. Another possible uncertainty is due to spatially inhomogeneous pumping conditions in the cell.

We believe the NO VDF in the cell attains steady-state at our experimental conditions, \( P_{\text{NO}} = 0.5-3 \text{ Torr}, t_r \sim 10 \text{ ms} \). It has been shown in [16] that the IR radiation of the optically pumped NO reaches steady-state after \( \sim 5 \text{ ms} \) at \( P_{\text{NO}} = 0.15 \text{ Torr} \), and after \( \sim 2 \text{ ms} \) at \( P_{\text{NO}} = 0.59 \text{ Torr} \), for a similar laser power density.

Figure 3.4 presents the NO VDF obtained from the infrared spectrum of Fig. 3.2. It is obvious that the vibrational levels up to \( v = 15 \) are strongly overpopulated compared to a Boltzmann distribution at \( T = 700 \text{ K} \), which is a typical temperature in our experiments (see below). The VDF measured in earlier optical pumping experiments [43], at lower
Figure 3.3 Einstein coefficients for NO infrared spontaneous radiation; 1,2 - [47], 1',2' - [48]; 1,1' - Δv=1, 2,2' - Δv=2
Figure 3.4 The experimental NO vibrational distribution functions (points); 1, 2, Treanor distributions for $T_v = 2500K$, $T=300K$, and $T_v = 2500K$, $T=700K$, respectively; 3, Boltzmann distribution, $T=700K$
temperature $T=300$ K, is also shown. By fitting the VDF’s to the Treanor distribution (see Ref. [7], Eq. (1.3)) we obtained the vibrational temperature of the first level, $T_v = 2500$K (see Eq. (1.4)).

We also analyzed the visible/ultraviolet emission between 200 and 400 nm due to the γ and β bands of NO, emitted from the electronically excited states $A^2Σ^+$ and $B^2Π$, respectively. A spectrum for the pumping conditions of case II is shown in Fig. 3.5. The β-bands extend into the violet and blue regions and make the center of the pumped region visible to the eye. One can see a visible glow of about 1 mm in diameter and over 3-4 cm in length. Identification of different bands (some of them are indicated in Fig. 3.5) shows that only progressions $v'=0, 1$ and 2 can be found in these spectra. For the cases I and III, the ultraviolet emission of β and γ bands is still present, but it is much weaker. The same transitions are observed as in case II, and the intensity ratios are very similar.

The electronic spectra are also used for the inference of the rotational temperature $T_r$, necessary for correct analysis of the obtained results. Figure 3.6 shows a comparison of the experimental contour of the vibrational γ band 0,2 (case II) with the low resolution synthetic spectrum of this band for $T_r = 500$, 700, and 900K. One can see that the agreement at 700K is quite reasonable. Repeating this procedure for several non-overlapping bands, we infer the temperature $T_r = 700 ± 100$ K for all three cases of Table 3.2. Simple estimates show that the characteristic time of rotational relaxation at these conditions, $-10^{-8}$ s, is much shorter than the radiative lifetime of $A^2Σ^+$ and $B^2Π$ states.
Figure 3.5 The visible/ultraviolet NO spectrum
Figure 3.6 The experimental profile of the NO 0,2 $\gamma$ band (points); the synthetic profile at different temperatures (lines)
(-0.1-0.4 μs and 3 μs, respectively, Ref. [49]) and the residence time, 
-10 ms. This allows assuming translation-rotation equilibrium, \( T = T_r \).

### 3.4 Discussion

#### 3.4.1 Vibrational excitation

First of all, the experimental results show that vibrationally excited NO molecules (at least up to level \( v=15 \)), as well as electronically excited molecules in \( A^2Σ^+ \) and \( B^2Π \) states, are produced in the cell. Note that the cell is irradiated by a single CO laser line, which excites only the vibrational transition \( \text{NO}(X^2Π, v=0 \rightarrow 1) \). This may be compared to the energy of the vibrational level \( v=0 \) of the \( B^2Π \) state, which corresponds to \( v=35 \) of the ground electronic state. The measured translational temperature \( T=700K \) is too low to account for this excitation by an equilibrium thermal population. Also, the laser power density in the focal area does not exceed a value of \(-10 \text{ kW/cm}^2\), which makes multiphoton excitation processes completely negligible. Therefore, the only possible explanation of the high vibrational excitation observed is the anharmonic V-V pumping of nitric oxide \([6,7]\). Basically, this mechanism involves single-quantum transitions, at least at the lower vibrational levels.

The NO VDF, measured in our experiments (see Fig. 3.4), reasonably corresponds to the Treanor distribution (see Eqs. (1.3-1.5) at \( T=700K \) and \( T_v=2500K \) up to \( v_v=15 \). This confirms (see Ref. [7]) that
the VDF in this region is controlled by the V-V processes. The VDF, measured in Ref. [43] at a lower temperature, T=300K, reveals a similar structure. The Treanor curve at T=300 K, v \geq v_o=7 lies much higher than the experimental VDF, which shows a significant influence of V-T relaxation.

As has been discussed in Ref. [15], the substantial V-V pumping of NO occurs because the V-V rates, at least among the lowest vibrational states, exceed the V-T relaxation rate, for example, $Q_{12}^{10}/P_{10} \sim 50$.

There remains a question, whether the vibrational levels at high v's are populated in far-from-resonance V-V exchange processes,

$$\text{NO}(v) + \text{NO}(1) \rightarrow \text{NO}(v+1) + \text{NO}(0), \quad (3.4)$$

or whether the near-resonant V-V exchange,

$$\text{NO}(v) + \text{NO}(v) \rightarrow \text{NO}(v+1) + \text{NO}(v-1), \quad (3.5)$$

dominate. Recent measurements of the V-T rates in NO [38] have shown that at T=300 K the non-resonant V-V influence is negligible already at v=8, where the energy defect of the process (3.4) becomes significant. Nevertheless, the V-V pumping effect at room temperature does exist even at v=14 (see Fig. 3.4). Thus, it becomes obvious that at T=300 K the nonequilibrium VDF at v=8 is created by near-resonant V-V exchange (3.5). Note that the NO V-T relaxation rate only slightly rises with temperature; for example, the rate constant of the process (3.1) for v=1, increases approximately 20% from T=300 to 700 K (see Ref. [37]). In
addition, the VDF's at these two different temperatures look very similar. Therefore, it is reasonable to conclude near-resonant V-V exchange is also a dominant process at $T=700K$, at least up to $v=15$.

For the conditions of the present experiment, the analytical diffusion theory of vibrational relaxation of diatomic molecules [1,50] predicts a gently decreasing plateau in the VDF above the Treanor minimum $v_0$ (this is the so-called strong excitation regime):

$$f_v = \frac{\Gamma}{v+1} \frac{P_{10}^T}{Q_{10}^{12AE}} \frac{\delta_{vn}^3 \exp(\delta_{vt} v)}{v+1} \approx \frac{\Gamma}{v+1} \left( P_{10}^T < Q_{10}^{12AE} \right) \quad (3.6)$$

Here $\Gamma$ is a constant to be found by matching the distributions of (1.3) and (3.6) at $v=v_0$, $\delta_{vt}$ and $\delta_{vv}$ are parameters of the SSH [51] theory of V-T and V-V exchange, respectively:

$$P_{v+1,v} = (v+1) \cdot P_{10}^T \cdot \exp(\delta_{vt} v) \quad (3.7)$$

$$Q_{v+1,v}^{w+1} = (v+1) \cdot (w+1) \cdot Q_{10}^{12AE} \cdot \exp(-\delta_{vv} \cdot |v-w|) \cdot \left[ \frac{3}{2} - \frac{1}{2} \exp(-\delta_{vv} \cdot |v-w|) \right] \quad (3.8)$$

$$\delta_{vt} = \delta_{vv} = \left( \frac{1}{\alpha} \right) \cdot \left( \mu/T \right)^{0.5} \cdot \Delta E \quad (3.9)$$

Qualitatively, this theory may be applied to the NO VDF. One can see that the VDF's in Fig. 3.4 at $v>8$ decrease much steeper than $-1/(v+1)$. However, in the case of NO the ratio $P_{10}^T/Q_{10}^{12AE} \sim 0.02$ is not so small as for $N_2$ and CO; for this reason the second term in Eq. (3.6) becomes significant to give an exponential fall-off to the VDF. Also, numerical calculations for the conditions of the experiments [43], using master
equation analysis [6], are shown in Fig. 3.7. Here $\delta_{VT}$ and $\delta_{VV}$ were taken from Ref. [16], rather than determined by the SSH-theory relations, Eqs. (3.7-3.9). In Ref. [16], these two parameters were found by measuring the rise and decay time of the overall IR signal from the optically pumped NO (see discussion in Section 4 of Ref. [16]). The distribution function, created by all the V-V processes, follows the experimental VDF rather closely. At the same time (see Fig. 3.7), it is clear that non-resonant V-V are important only below $v \leq 7$. Note that V-V and V-T rates of Ref. [16] cannot be used for the simulation of the present experiments at $T = 700K$, because they give an unrealistic temperature dependence.

3.4.2 Electronic excitation

The mechanism for creation of the molecules in electronically-excited states observed is not so unambiguous as the ground state V-V, V-T processes. There exist three major possibilities:

a) collision-induced resonant vibration-to-electronic (V-E) energy transfer, following the V-V pumping of NO($X^2\Pi$) up to level $v$-35 as suggested in Ref. [16] (a similar process was experimentally observed in carbon monoxide, Ref. [31]):

$$
\text{NO}(X^2\Pi, v=35) + M \rightarrow \begin{cases} 
\text{NO}(S^2\Pi, v=0) + M \\
\text{NO}(A^2\Pi, v=0) + M 
\end{cases} \quad (3.10)
$$
Figure 3.7 Comparison of the master equation calculation with the experiment of Ref. [43]
b) recombination of N and O atoms:

\[
N + O + M \rightarrow NO(A,B) + M \quad (3.11)
\]

c) energy pooling in the process

\[
NO(X,v) + NO(X,w) \rightarrow (NO)_2^\pm \rightarrow NO(A,B) + NO(X,v-\Delta v), \quad (3.12)
\]

and

\[
E_v + E_w \geq E_A, E_B \quad (3.13)
\]

Here \( E_v, E_w \) are energies of vibrationally excited molecules in the X-state; \( E_A, E_B \) are energies of excitation of A and B states, respectively.

Note that the last two mechanisms (b and c) do not require the excitation of NO up to very high vibrational levels, \( v \approx 35 \).

The major mechanism of production of the atomic species in the cell is a vibrationally induced chemical reaction

\[
\begin{align*}
NO(v) + NO(w) & \rightarrow N_2O + O \\
& \rightarrow N_2 + O_2 \\
& \rightarrow NO_2 + N
\end{align*}
\quad (3.14)
\]

The activation energies of the three channels of the reaction (3.14) are \( E_1 \approx E_2 \approx 33 \text{ kK} \) and \( E_3 \approx 39 \text{ kK} \), respectively (see Ref. [52]), which correspond to NO vibrational levels \( v \approx 15 \) and \( v \approx 17 \). Given the levels of NO vibrational excitation observed, such atom production is possible in the cell. However, the formation of NO(A,B) in the recombination reaction (3.11) is very unlikely. If recombination occurs in the cell,
the continuum fluorescence in reaction (3.3), much faster than (3.11),
would appear, which we did not observe. We conclude that the residence
time ~10 ms is too short to produce enough atomic species for any
observable recombination to occur in reactions (3.3,3.11), following the
vibrationally-induced reaction (3.14). The recombination continuum was
observed previously, but only in a non-flowing cell [16], and in a slow-
flowing cell with residence time ~ 0.2 sec [43].

In addition, we did not identify any electronic transitions
A,v' → X,v" (v',v" γ) and B,v' → X,v" (v',v" β) with v'>2. Some of
these transitions have substantial Franck-Condon (FC) factors f(v',v")
in the range of λ= 200-400 μm [49], comparable with the FC factors for
the observed bands. For example, the γ transition 5,10 (λ=263 nm, Ref.
[53]) has a FC factor f(5,10)=0.210, while for the γ transition 0,3
(λ=259 nm) it is f(0,3)=0.147. Similarly, in β bands f(3,10)=0.0393
(λ=323 nm), while f(0,8)=0.0384 (λ=320 nm). One can conclude that the
relative populations of NO(A,B,v>2) are small compared with those of
v=0-2, which mitigates against a purely recombination mechanism of
NO(A,B) formation.

Energy pooling (3.12) cannot be excluded on the basis of these
experimental results. This process may occur if the total energy of
colliding molecules exceeds the excitation energy of A^2Σ or B^2Π states,
(which also makes possible the (NO)^* transition complex formation in
reaction (3.12), since its activation energy is lower, Ref. [38]). In
addition, the transition complex lifetime should be much greater than
its period of vibration, to make possible the vibrational energy
redistribution. The importance of this mechanism compared to resonant V-
E could be determined by measuring the rise time for populations of different vibrational levels of the NO(X^\text{\Pi}) state, together with the rise time for the NO(A,B) population, using pulsed CO laser optical pumping.

3.4.3 V-T and V-V rates measurements

The experimental data and the discussion presented above show that anharmonic V-V pumping of NO is possible despite its fast rate of V-T relaxation. In particular, at high vibrational levels \( v \geq 8 \), only near-resonant V-V exchange can compete with the V-T processes. The importance of this effect depends on the relative populations of the high vibrational levels and should be carefully checked in experiments involving vibrationally excited NO. For example, we consider the recent work by Yang, Kim and Wodtke [38], where NO V-T rates were measured using stimulated emission pumping (SEP), at \( v = 8-22 \). In these experiments, one particular rotational level of NO was excited by a tunable narrowband ArF excimer laser (PUMP):

\[
\text{NO}(X^\text{\Pi}, v=0, J) \rightarrow \text{NO}(B^\text{\Pi}, v'=7, J') \quad (3.15)
\]

Then a high vibrational level of the X-state was prepared using a XeCl excimer pumped dye laser (DUMP):

\[
\text{NO}(B^\text{\Pi}, v'=7, J') \rightarrow \text{NO}(X^\text{\Pi}, v''=8-22, J'') \quad (3.16)
\]

The decay of the population of level \( v'' \) was observed using laser induced
fluorescence. The measurements were made at room temperature, with two different isotopes, $^{14}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{18}\text{O}$. The rotational levels, available for the PUMP transition (3.15), with the ArF laser, used in Ref. [38] ($\omega = 51815\pm175$ cm$^{-1}$), are $J=24.5-32.5$ for $^{14}\text{N}^{16}\text{O}$ and $J=15.5-23.5$ for $^{15}\text{N}^{18}\text{O}$. Simple estimates (see also Ref. [54]) show that, if both PUMP and DUMP pulses are saturated, the vibrational level $v''$ is prepared with a maximum relative population of $f_{v''} \sim 3 \cdot 10^{-4}$ and $f_{v''} \sim 3 \cdot 10^{-3}$, for light and heavy isotopes, respectively. Since the present work shows that the effect of near-resonant $V-V$ processes (3.5) on relaxation at $v\sim10-15$ is very strong for $f_{v''} > 10^{-4}$ (see Fig. 3.4), the measured relaxation rate $k(v'')$ should represent the combined action of both the $V-T$ and the near-resonant $V-V$ energy transfer.

The possible influence of near resonance $V-V$ energy transfer was not discussed in Ref. [38]; it was not explicitly specified whether the laser pulses were saturated. Thus, the initial population of the level $v''$, as well as the possible influence of this $V-V$ energy transfer, is uncertain. It appears, however, that the experiments of Ref. [38], using the heavy isotope $^{15}\text{N}^{18}\text{O}$, indicate that the measurements are not affected by $V-V$ transfer. In the saturation regime the population of $^{15}\text{N}^{18}\text{O}(v'')$ is about 10 times higher than that of $^{14}\text{N}^{16}\text{O}(v'')$. Since the rate of the near-resonant $V-V$ exchange non-linearly depends on $f_{v''}$, this would give a much higher $k(v'')$ for the heavy isotope. However, the measured $k(v'')$ for $^{15}\text{N}^{18}\text{O}$ is $\sim 10-20\%$ lower than that for $^{14}\text{N}^{16}\text{O}$. The only explanation, consistent with our measurements, is that the laser transitions in Ref. [38] were far from saturation, which made $f_{v''}$ low enough to avoid the faster relaxation due to near-resonant $V-V$. This
made possible reliable measurements of the V-T rate constants. Nevertheless, there is no doubt that the same experimental setup of Ref. [38] can be used for independent determination of the V-V rates, if it is operated in the saturation regime. It appears [54] that the lasers used in the experiments [38] are capable of producing sufficient pulse powers for saturation.

Some phenomenological measurements of the NO V-T and V-V rates, using time-resolved optical pumping, were made in Ref. [16]. In these experiments, the IR radiation from the cell was not state-resolved, and only the overall signal intensity was monitored. This work used the functional dependence (3.7,3.8) of the rates on the quantum number, where \( P_{10} \) and \( Q_{10}^{12} \) were measured in Refs. [36,39]. \( \delta_{VT} \) and \( \delta_{VV} \) were considered as merely adjustable parameters, and the relations (3.7,3.8) are therefore not the results of SSH-theory, but only convenient parametrizations. The rate constants were determined by fitting the rise and decay of the IR signal, calculated using a master equation analysis [6], to the experimental curves. Of course, this procedure is reasonable for inference of the rates only at low quantum numbers, presumably \( v \leq 10-15 \), because the IR radiation from upper states in these experiments is very weak, and the extrapolation to higher \( v \)'s, as well as to higher temperatures, has no firm basis. Figure 3.8 shows a comparison of these inferred V-T rates [16] to the direct measurements of Ref. [38]. One can see good agreement in the range of applicability of the procedure of Ref. [16].

A more reliable and explicit method of inference of both the V-T and V-V rate constants would be a state- and time-resolved
Figure 3.8 Comparison of the NO V-T rates measured by optical pumping, Ref. [16] and by SEP, Ref. [38] (the point for v=1 is the result of Ref. [36])
experiment with NO optical pumping, which would allow separate determination of the V-T, near-resonant V-V and non-resonant V-V rates. Again, this method would allow measurements at low v's, v≤10-15, while the SEP technique cannot be used at v<8 because of strong Franck-Condon pumping [38].

The theoretical explanation of anomalously fast NO vibrational relaxation is still uncertain. An explanation given in Ref.[38] uses the basic arguments of adiabatic theory, developed in the 1960's (e.g. see Ref. [55]). This theory takes into account the strong attraction between two NO molecules. It reasonably explains the absolute value of $P_{10}$ and its temperature dependence, but it would give a much stronger dependence of $P_{v,v-1}$ on v, then was actually found in Ref.[38]. On the other hand, non-adiabatic theory [3,56], predicting very weak quantum number dependence, gives no explanation of the $P_{10}(T)$ rise at low temperatures T<300 K. Obviously, this problem requires further experimental studies and theoretical analysis.

3.5. Conclusions

Vibrational and electronic excitation of nitric oxide has been investigated in optical pumping experiments. It is shown that the mechanism of vibrational excitation is nonequilibrium V-V pumping, in particular near-resonant V-V exchange on high vibrational levels, 8 ≤ v ≤ 15. This result shows the importance of the V-V processes even for fast relaxing diatomic molecules. Electronically excited NO
molecules in $A^2\Sigma$ and $B^2\Pi$ states can be created both by resonant $V$-$E$ energy transfer, following $V$-$V$ pumping up to $v$=35, and in an energy pooling process (3.12). The relative influence of chemical reactions appears to be small due to short residence time of the gas mixture in the cell.

Recent measurements of NO $V$-$T$ rates are analyzed. It is suggested that direct $V$-$V$ rate measurements at high $v$'s, $v$$\approx$10, can be made using the SEP technique with pulse intensities giving saturation. Also, state and time-resolved infrared measurements in optical pumping are suggested as an efficient method of determination of the NO $V$-$T$ and $V$-$V$ rates at low $v$'s, $v$$\approx$10-15.
CHAPTER IV
SPATIAL NONHOMOGENEITY EFFECTS
IN NONEQUILIBRIUM VIBRATIONAL KINETICS

4.1 Introduction

An analytical theory of vibrational relaxation of anharmonic oscillators, based on the modified SSH [51,57] and Sharma-Brau [58] theories of the V-T and V-V rates, as well as many numerical models, have been developed in 60's and 70's (see Ref. [1] and references therein). These theoretical models considered only the motion of molecules in the space of vibrational energy (such motion occurs by excitation of vibrations, V-T and V-V exchange, radiation, chemical reactions and so on). However, in a real nonequilibrium gas flow, there is always a presence of some spatial nonhomogeneity in parameters such as gas velocity, temperature, vibrational energy, and concentrations of chemical species. This nonhomogeneity produces diffusion fluxes of mass, of momentum, and of the different modes of molecular energy. If the diffusion flux is comparable or greater than the flux of vibrational quanta in the vibrational energy space due to energy exchange in inelastic collisions, it may well affect the vibrational kinetic processes in a gas. Therefore, correct interpretation of the
nonequilibrium effects in gas flows requires simultaneous consideration of kinetics and diffusion.

One type of experimental evidence of the correlation between spatial nonhomogeneity and vibrational kinetics can be seen from a comparison of vibrational distribution functions (VDF) of CO, measured in different experiments, with the well-known theoretical predictions. The VDF is a direct measurement of the populations of each vibrational quantum state existing in the gas. Figure 4.1 shows four different measurements of the CO VDF (points): (a) by Farrenq et al [31], in a CO-N₂-He glow discharge; (b,c,d) by Rich et al [8], by Adamovich et al [14], and by Martin et al [30], respectively, in an optically pumped CO-Ar-He gas flow. Curves in all four graphs show the Treanor distribution (see Eq. (1.3)). All Treanor distributions are plotted at T and T\* inferred from the experiments. One can see that in cases (a) and (b) the decreasing branch of the Treanor distribution, from v=0 to its minimum at v=v₀ (see Eq. (1.5)), closely fits the experimental distribution function. The gently sloping plateau in the VDF starts from the Treanor minimum, where the distribution has the value

\[ f_{TR} = \exp(-v^2\Delta E/T) \sim \exp(-E^2_{1}/4\Delta E T^2_v) \]  \hspace{1cm} (4.1)

as is predicted by the analytical theory of anharmonic oscillators in the "strong" excitation regime, when the near-resonance V-V exchange

\[ AB(v) + AB(w-1) \leftrightarrow AB(v-1) + AB(w), \ v-w \gg 1 \]  \hspace{1cm} (4.2)
Figure 4.1 Measured vibrational distribution functions of CO (points) and Treanor distributions (curves): a, CO-N<sub>2</sub>-He glow discharge, Ref. [31]; b, c, d, CO-Ar-He optical pumping, Refs. [8, 14, 30], respectively.
dominates (see Refs. [1,50,59]). These two cases (a,b) represent the experiments wherein spatial nonhomogeneity is not very significant: in case (a) [31], the infrared signal was collected along the axially uniform positive column of a glow discharge, and in case (b) [8], an unfocused gas dynamic laser beam with a uniform power distribution across the beam filled the entire optical absorption cell, with no substantial spatial gradients being present.

However, cases (c,d) demonstrate a considerable deviation from the predicted behavior. Here the well-pronounced plateau starts much earlier than the Treanor minimum, and the plateau height, given by the theory in Ref. [1], \(f_{\text{plateau}}/f_{\text{TR}}\) is much lower (up to an order of magnitude) than in the experiment. In addition, numerical simulation using the one-dimensional master equation (see Ref. [13]) shows that the measured VDF cannot be fitted by the calculated curve for any conceivable V-V and V-T rates. Note that the measurements (c,d) have been made in a strongly nonhomogeneous environment, where CO in an absorption cell was excited by a focused CO laser beam. A similar effect has been reported in measurements by De Benedictis and Cramarossa [60] in a decaying CO-N\(_2\) RF afterglow. The anomaly observed in these cases is obviously due to the spatial nonhomogeneity.

So far, little attempt has been made to simulate the coupling of the spatial gradients and vibrational energy transfer at strong vibrational nonequilibrium. One may mention papers by Osgood, Sackett and Javan [61], where the "vibrational temperature" diffusion has been experimentally observed and discussed; by Likalter and Naidis [59], who investigated the influence of diffusion on the VDF; by Dobkin and Son
[62], where they studied the influence of the V-V and V-T processes on the heat conductivity; and a book by Rusanov and Fridman [4], where some issues of nonhomogeneous vibrational kinetics have been discussed qualitatively.

The present chapter addresses the following aspects of nonequilibrium vibrational kinetics in nonhomogeneous gas flows: transport coefficient dependence on vibrational excitation; mutual interaction of the vibrational energy diffusion and the VDF; the influence of the non-local diagnostics by emission or absorption spectroscopy on the observed signal and its interpretation. Finally, the problem of developing a kinetic model, which takes into account the relevant kinetic processes and the diffusion, will be also discussed.

4.2 Results and discussion

4.2.1 Vibrational excitation and transport coefficients

A thorough analysis of the influence of the vibrational energy exchange, as an inelastic process, on the heat conductivity and on the translational and vibrational energy fluxes, has been made by Dobkin and Son [62], on the basis of the Wang Chang - Uhlenbeck kinetic equations. It was concluded that at low and moderate temperatures, $100 < T < 700K$, in diatomic gases such as $N_2$, $O_2$, CO, NO etc., where the rate constant $Q_{10}$ of the V-V exchange
\[ AB(1) + AB(0) \rightarrow AB(0) + AB(1) \]  

is much smaller than the gas dynamic collision frequency \( Z \) (at \( T<1000K \), \( Q_{10}/Z < 10^{-2} \) for CO, and \( <10^{-4} \) for \( N_2 \)), the effect is negligible. In other words, both translational and vibrational mode energies diffuse with approximately the same diffusion coefficient \( D \), given by the Chapman-Enskog theory, and the two energy fluxes can be written as follows:

\[ q_{tr} = -\rho D V T = -\lambda VT \]  
\[ q_{vib} = -\rho D V E = -\rho D y T E V f \]  

where \( \lambda = \rho c D \),

\[ E_v = (R_0/\mu) \omega_v^e \left[ 1 - \delta(v+1) \right] \]  

\( \delta = \omega_e^e/\omega_v^e \), and \( y_\alpha = N_\alpha/N < 1 \) is the mole fraction of vibrationally excited species \( \alpha \) (\( N_2 \), CO, NO etc.) in an inert diluent, such as Ar or He. The authors then expressed the vibrational energy flux in terms of translational and vibrational temperature gradients, rather than the gradient of vibrational energy in Eq. (4.4),

\[ q_{vib} = -\lambda_{VT} VT - \lambda_{VV} VT \]  

where

\[ \lambda_{VT} = \rho D y_\alpha \sum E_v \frac{\delta f_v}{\delta T} \]  
\[ \lambda_{VV} = \rho D y_\alpha \sum E_v \frac{\delta f_v}{\delta T} \]
They found that $\lambda_{\nu T}$ and $\lambda_{\nu v}$ for anharmonic oscillators in the "strong" excitation regime can exceed the usual thermal conductivity coefficient $\lambda$ by two orders of magnitude. We note that this merely reflects the strong nonlinear dependence of vibrational energy $E_{\nu b}$ on $T$ and $T_v$, but by no means the influence of vibrational energy transfer in the inelastic collisions on the vibrational mode energy diffusion. This also shows that the use of the expression $q_{\nu b} = -\lambda VT_v$ for the vibrational energy flux at strong vibrational nonequilibrium would be totally erroneous.

The results by Dobkin and Son can be also obtained by the less formal, but more illustrative method of comparison of the characteristic time for elastic collisions, $\tau_{TT} \sim 1/(NZ)$, with the time for VDF change due to the V-V processes, $\tau_{VV}$. For low vibrational levels, it is enough to note that one has a small parameter, which is the ratio of $\tau_{TT}$ and the characteristic time of non-resonance V-V exchange

$$AB(v) + AB(w-1) \leftrightarrow AB(v-1) + AB(w), \ w \gg v-1 \quad (4.8)$$

$$\tau_{VV}^N \sim 1/(NQ_{10}^\alpha), \ such \ as$$

$$\frac{\tau_{TT}}{\tau_{VV}^N} \sim Q_{10}^\alpha /Z \ll 1, \quad (4.9)$$

which makes impossible any diffusion-vibration coupling. This informal comparison particularly gives insight into the case of large inelastic transition probabilities. We can understand, qualitatively, why even near-resonance V-V exchange at high vibrational levels, where V-V rates may become equal to or greater than the gas kinetic frequency (see Ref.
[11]), still has no effect on the transport coefficients. For the higher levels (plateau region in the "strong" excitation regime), the characteristic time of the VDF change is determined by the simultaneous action of the two fast energy transfer processes (forward and reverse processes of Eq. (4.2)). This results in the slow vibrational quanta flow upward along the vibrational energy axis (see Refs. [1,50,59]). The flux of quanta $\phi_0$, in cm$^3$/sec, is given by

$$\phi_0 = \frac{6\xi_0^{S} \Delta E}{T_0^{S} \nu_0^{2}} (\nu_0 + 1)^2 f_{TR}^{2} = \phi_0^*(\nu_0 + 1)^2 f_{TR}^{2}$$

(4.10)

where $\nu$ (also in cm$^3$/s) is the vibrational quanta diffusion coefficient, and

$$\xi = 1 + \frac{\delta_{vv}^{3}}{12 \Delta_{vv}} \left( \frac{\pi}{\Delta_{vv}} \right)^{1/2} Q_{10}^{L}/Q_{10}^{S}$$

(4.11)

In Eqs. (4.10, 4.11), $Q_{10}^{S}$, $Q_{10}^{L}$, $\delta_{vv}$, and $\Delta_{vv}$ are parameters in the expression for the V-V rates (see Eqs. (4.2, 4.8)):

$$Q_{v+1,v}^{w,w+1} = (v+1)(w+1) \left[ \frac{Q_{10}^{S} e^{-\delta_{vv}}}{v-w} \right]^{3} \frac{1}{2} e^{-\delta_{vv}} \left( \begin{array}{c}
3 & 1 & -\delta_{vv} \\
2 & 2 & -2
\end{array} \right) +$$

$$+ \frac{Q_{10}^{L} e^{-\Delta_{vv}}}{v-w} (v-w)^2,$$

(4.12)

where $Q_{10}^{S}$ and $Q_{10}^{L}$ are the rates of the process (4.3) calculated taking into account only short-range repulsive forces and long-range multipole
interaction, respectively. Then the characteristic time for VDF change due to the V-V processes is

$$\tau_{\text{VV}}^R = \frac{y_0 \sum E \phi_y}{E_1 \phi_y N_y^2} \leq \frac{1}{\phi_y N_y}$$  \hspace{1cm} (4.13)$$

which is much greater than the time of near-resonance V-V exchange, $-1/(Q_{10} N_y^2 v^2)$. For typical experimental conditions in strongly V-V pumped CO, at $T$-100-800K, $T_0$-2000-4000K, one has $v_0$-5-10, $f_{\text{TR}}$-10^{-2}-10^{-3}, $\delta_{\text{VV}}$-6.0-$T^{-1/2}$-0.2-0.3, $Q_{10}$-10^{-12} cm^3/s, $\xi$=1-10, and the ratio $\tau_{\text{TT}}/\tau_{\text{VV}}^R$-$10^{-5}$-$10^{-7}$. This means that the VDF is actually frozen in the elastic collision time scale, despite the fact that the V-V exchange may occur at nearly the gas kinetic rate. This again excludes the possibility of the diffusion-vibration coupling.

Note that Eq. (4.10) is not valid in the "moderate" excitation regime, when non-resonant V-V exchange with the lower levels is faster than the near-resonant processes. However, in this case one obviously has $\tau_{\text{VV}}^R \approx \tau_{\text{VV}}^N$, and we come back to Eq. (4.9). Finally, the V-T relaxation in most diatomic gases at moderate temperatures is so slow (except very high levels) that $\tau_{\text{VT}}$ is always much greater than $\tau_{\text{TT}}$.

Thus, one may say that diffusion of the vibrationally excited diatomic molecules may be described using a common diffusion coefficient D for all vibrational levels. The only dependence of D on the vibrational energy is due to the change of the elastic collision cross-section with vibrational state, which is a weak dependence. A strong effect of vibrational energy transfer on the transport coefficient only exists for molecules having a large dipole moment, and therefore having
large $Q_{10} - Z$ (such as $CO_2$ and $N_2O$), and this case requires detailed calculations using the approach of Ref. [62].

4.2.2 Diffusion and vibrational distribution function

It is easy to show that for the Treanor part of the VDF the influence of diffusion is always small except for the very low pressures; comparing the characteristic times for diffusion over a radius $R$, $\tau_{\text{diff}} = R^2/D$, and the nonresonant $V-V$ exchange, $\tau_{V^N}$, one has

$$R \sim \left( \frac{D}{Q_{10}^{01} N y_\alpha} \right)^{1/2} \sim \left( \frac{D_0 N_0}{Q_{10}^{01} N_0^2 y_\alpha} \right)^{1/2}, \quad (4.14)$$

where the subscript $0$ refers to a "normal pressure", $P=1$ atm. For example, for pure CO at $T=300K$ this correction is important only if $R \lesssim 10^{15}/N$ cm, or $R \lesssim 1$ mm even at 1 Torr total pressure.

An analysis of the diffusion flux influence on the plateau part of the VDF for the "strong" excitation regime was first made by Likalter and Naidis [59]. The VDF perturbation by diffusion was calculated as a first-order correction to the analytical solution for the "homogeneous" VDF (see Ref. [1]),

$$f_v = \frac{N_v}{N} = \frac{\Gamma}{\nu+1} - \frac{P_{10} T}{\xi Q_{10}^{01} y_\alpha} \left[ \frac{3}{12 \Delta E \delta_v} \delta_{VT}^{v} \right]^{\nu+1} - \frac{A_{10} T}{\xi Q_{10}^{01} y_\alpha} \left[ \frac{3}{12 \Delta E \delta_v} \delta_{VT}^{v} \right]^{\nu+1} \quad (4.15)$$

Here $P_{10}$, $\delta_{VT}$, and $A_{10}$ are parameters in the expressions for the $V-T$ and spontaneous radiation rates,
\[ P_{v+1,v} = P_{10} (v+1) \exp(\delta_{VT}) ; \quad A_{v+1,v} = A_{10} (v+1), \quad (4.16) \]

and \( \Gamma \) is to be found from matching of the distributions (1.3) and (4.15) at the Treanor minimum \( v_0 \) (see Eq. (1.5)), \( \Gamma \approx f_{TR} (v+1) \) at \( P_{10}, A_{10} \approx Q_{10} \). In Eq. (4.15), the first term in the right hand side describes the plateau in the VDF, created by the nearly constant flow of quanta \( \phi_0 \) (see Eq. (4.10)) due to near-resonant V-V exchange, and the other two terms describe the plateau cutoff due to the V-T relaxation and radiation, respectively. According to Ref. [59], diffusion adds the following correction to the right hand side of Eq. (4.15):

\[ \text{Diff} \approx \frac{L(v) - L(v_0)}{v+1} \frac{D}{2\phi_0 N^2 y_0} \frac{d^2(\Gamma N)}{dx^2}, \quad (4.17) \]

where

\[ L(v) = v \left[ \ln(v_1/v) + 1 \right], \quad (4.18) \]

and \( v_1 \) is the coordinate of the VDF cutoff due to some sink such as V-T relaxation, radiation, diffusion or chemical reactions. For a first estimate, \( v_1 \) can be found by equating \( f_{v_1} \) in Eq. (4.15) to 0. One finds that the diffusion correction becomes important when

\[ R \leq \left( \frac{\phi_0 D}{2}\right)^{1/2} \quad (4.19) \]

which for the typical conditions in nonequilibrium CO environments (see Section 2.1) gives \( R \leq (10^{16} - 10^{17})/N \text{ cm}, \) or \( R \sim 0.1-1 \text{ mm} \) at \( P \sim 100 \text{ Torr}. \)
This is a characteristic scale of spatial nonhomogeneity in focused laser beams [13] and in gas discharges with a contracted current channel [19]. Note that, if the condition (4.19) holds, the diffusion flux exceeds the vibrational quanta flow due to V-V exchange, \( \Phi_0 \). In the non-steady-state flows, this may strongly affect the rise and decay times for characterizing the population and depopulation of the high vibrational levels of diatomic species. Measurements of these characteristic times have been previously used for the inference of the V-V and V-T rates in time-resolved optical pumping experiments in CO [11,63] and in NO [16]. Equation (4.19) indicates that the time-resolved data can be adequately used for this purpose only if the inequality is reversed, which can happen only at high pressures.

Strong vibrational excitation may also lead to the occurrence of different vibrationally-stimulated chemical reactions with high activation energies (see Refs. [1,4]), which, in turn, may affect the VDF. For a chemical reaction faster than resonance V-V exchange, i.e., reactions for which

\[
A \gg Q_{10} v_a^2 f_a^2,
\]

where \( A \) is the pre-exponential factor in the chemical reaction rate expression, \( k = A \cdot \exp(-E_a/T) \), and \( v_a \sim E_a/\omega_e \) is the vibrational energy activation level, the plateau distribution was found by Macheret [64]:

\[
f = \frac{\Gamma}{\nu} \left( \frac{\nu - \nu}{\nu_a - \nu_0} \right)^{1/2}
\]

(4.21)
The solution (4.21), which is independent of the nature of the chemical reaction and of its rate, should replace the first term in the right-hand side of Eq. (4.15). It is important, for example, to use this correction for simulation of the VDF in the presence of the fast collisional near-resonant vibration-to-electronic (V-E) energy transfer, such as

\[ \text{CO}(X^3\Sigma, v=40) + M \rightarrow \text{CO}(A^1\Pi) + M, \quad (4.22) \]

which has an estimated rate of \( k_{VE} \approx 10^{-12} \text{ cm}^3/\text{s} \) [11,12]. The process (4.22) is presumably responsible for the experimentally measured [8,14,30,31] fall-off of the CO VDF at level v=40. In fact, there are no experimental measurements where CO has been found to be pumped higher than this level, even at cryogenic temperatures, when the V-T relaxation rates dramatically drop (see Fig. 4.1(a) and Ref. [31]). Another process which may possibly lead to the VDF cutoff at v=40, is the two-quantum near-resonant V-V exchange, such as

\[ \text{CO}(v=0) + \text{CO}(v=41) \rightarrow \text{CO}(v=1) + \text{CO}(v=39), \quad \Delta E \approx 70 \text{ K}, \quad (4.23) \]

which has been theoretically discussed in Refs. [65,66]. Note that for the process (4.23) to influence the VDF, its rate should also be \( \approx 10^{-12} \text{ cm}^3/\text{s} \), or comparable to that of the exact resonance one quantum process (4.2), \( Q_{10} \approx 2 \times 10^{-12} \text{ cm}^3/\text{s} \), which seems unlikely.

If one takes into account the plateau shape of Eq. (4.21) instead of \( \Gamma/(v+1) \) in Eq. (4.15), the diffusion correction (4.17) remains valid, but with a different quantum number function \( L(v) \):
Figure 4.2 Vibrational quantum number function $L(v)$ in the diffusion correction, Eq. (4.17), for different plateau solutions

$v_0 = 10$
$v_1 = v_a = 42$
Equation (4.24) has been obtained here by integration of the master equation with a diffusion term in the regime of the "strong" excitation (see also Ref. [1]). Figure 4.2 plots the function \( L(v) \) obtained by Likalter and Naidis [59], Eq. (4.18) and by us, Eq. (4.24), for a typical Treanor number \( v_0 = 10 \) and plateau cutoff level \( v^a = v^a = 42 \). One can see that the present diffusion correction (4.17, 4.24) is by about a factor of 2 smaller than what has been obtained in Ref. [59]. The reason is that the number of available vibrational quanta per molecule decreases with vibrational quantum number due to V-E sink, which also reduces the diffusion flux.

Thus, the approximate analytical solution of the master equation (Eqs. (1.3,4.15) with corrections given by Eqs. (4.17,4.21)) may be used for simulation and analysis of the quasi-steady-state vibrational distribution functions of diatomic molecules, created by the V-V and V-T relaxation, diffusion, and fast V-E energy transfer.

4.2.3 Spatial integration

As has been shown in Section 4.2.2, the perturbation of the Treanor distribution by diffusion is a minor effect in cases of practical interest. However, the experimental data (see Fig. 4.1) show

\[
L(v) - L(v_0) = \frac{1}{\sqrt{\frac{v}{v_0} - \frac{v}{v_0}}} \int_{v_0}^{v} \left[ -2(v_a - v')^{1/2} + \sqrt{\frac{v}{v_0}} \ln \frac{\sqrt{v} - \sqrt{v - v'}}{\sqrt{\frac{v}{v_0}} + \sqrt{\frac{v}{v_0} - v'}} \right] dv'
\]
that the observed perturbation is much stronger. Note that in an actual experimental setup, the collected signal comes from an extended volume in space, and one observes only the integrated signal intensity,

\[
I_v = \int_{y_1}^{y_2} A_v N(x) f_v(y) dy = A_v f_v(y) \int_{y_1}^{y_2} N(y) dy \quad (4.25)
\]

In Eq. (4.25), \(A_v\) is the Einstein coefficient, \(N(y)\) and \(f_v(y)\) are the total concentration of molecules and the relative population of the level \(v\) at point \(y\), respectively, and \(f_v\) is the inferred "observed" population. Note that even if in the experiment the optics are focused at some particular point in space, Eq. (4.25) is still valid, since the decrease of the radiating volume towards the focal point is exactly compensated by its greater steradiancy.

For the VDF of diatomic molecules, neglecting the influence of the V-T relaxation, radiation and diffusion, this gives (see Eqs. (1.3, 4.15))

\[
f_v = \int_{y_1}^{y_2} \frac{f_0(y)}{T(y)} \exp \left[ -\frac{E(v)}{T_v(y)} + \frac{\Delta E(v-1)}{T(y)} \right] dy \quad (4.26)
\]

for the Treanor part of the VDF and

\[
f_v = \frac{1}{v+1} \left( \frac{v-a}{v-v_0} \right)^{1/2} \int_{y_1}^{y_2} [v_0(y)+1] \cdot \exp \left[ -v_0^2(y) \Delta E/T \right] dy \quad (4.27)
\]
for the plateau. The observed rotational population of the vibrational band $1\rightarrow 0$,

$$ f_{J,1} = \int_{y_1}^{y_2} \frac{B_1}{T(y)} (2J+1) \exp \left[ - \frac{B_1(J+1)}{T(y)} \right] f_0(y) \exp \left[ - \frac{E_1}{T(y)} \right] dy, \quad (4.28) $$

can be used for the inference of the common "rotational/translational" temperature $T_{r,1}$, which gives the best fit between the measured rotational spectrum of the thermally nonhomogeneous gas volume, $f_{J,1}$, and the single rotational temperature synthetic spectrum

$$ f_{J,1} = \frac{B_1}{T_{r,1}} (2J+1) \exp \left[ - \frac{B_1 J(J+1)}{T_{r,1}} \right], \quad (4.29) $$

Now we show that in spatially nonhomogeneous media the integration substantially perturbs the Treanor part of the VDF. If one fits the measured VDF by the theoretical "local" distribution function, then for $v=1$ one obtains

$$ \tilde{f}_{\nu} \exp \left[ - \frac{E_1}{T_{\nu}} \right], \quad (4.30) $$

while for any vibrational level in the plateau one has
\[
\tilde{f}_v \approx \frac{1}{v+1} \left( \frac{v-a}{v-a_0} \right)^{1/2} \left[ \frac{1}{2x_e T_v^*} + \frac{1}{2x_e T_{r,1}^*} \right] \exp \left[ -\frac{E_{1 r,1}}{4x_e T_{v}^*} \right] \quad (4.31)
\]

In the simplest case when \( T(x) = T_{r,1} = \text{const} \), which can be realized if \( v_a \ll 1 \), when the gas heating is not substantial due to thermal inertia provided by an inert diluent, and assuming that \( T_v \) changes linearly,

\[
T_v(y) = T_{v1} + \frac{T_{v2} - T_{v1}}{x_2 - x_1} y, \quad (4.32)
\]

we calculate the effective vibrational temperature of the first level, \( T_v^* \), and that of the plateau, \( T_v^{**} \), as a function of the minimum and maximum vibrational temperatures \( T_{v1}, T_{v2} \), and \( T \) (see Fig. 4.3). One can see that \( T_v^{**} \) is always greater than \( T_v^* \), and the difference \( T_v^{**} - T_v^* \) increases with the spatial nonhomogeneity \( \Delta T_v \) and temperature. In other words, the observed plateau in the VDF corresponds to higher \( T_v \) than the lower vibrational levels (see Fig. 4.4), as has been previously reported and qualitatively explained in Ref. [14]. It has been noted that the signal corresponding to the plateau part of the VDF comes from the most excited part of the gas volume with very high \( T_v \) which is localized near the excitation source. At the same time, there is a considerable contribution of the signal from the much less excited region to the Treanor part of the VDF, which decreases its "observed" vibrational temperature, \( T_v^* \). A simple estimate of the ratio of the two characteristic distances at which the population of some plateau level \( v_p \), and the population of the level \( v=1 \), drop e times, gives
Figure 4.3 Effective vibrational temperatures of the first level, $T'_v$, and of the plateau, $T''_v$, Eqs. (4.30, 4.31) as functions of the spatial nonhomogeneity $\Delta T_v = T_{v2} - T_{v1}$ and temperature.
Figure 4.4 Integrated VDF (solid line) and Treanor distributions with two effective vibrational temperatures (dashed lines)
for the typical CO experiments. This estimate also shows that in the measured VDF, the plateau population in the most excited region is underestimated by several times, compared to the population of the Treanor part of the VDF, due to normalization on the same space area, $L(v=1)$. This may bring a substantial uncertainty in the inference of kinetic rates from the steady-state VDF measurements, which has been done in Ref. [14] for the rate of vibrationally-induced ionization in CO.

4.2.4 Two-dimensional kinetic model of vibrationally nonequilibrium gas flows

An analysis of the influence of diffusion and non-local diagnostics on the VDF measurements, made in Sections 4.2.2-4.2.3, shows that the correct interpretation of experimental results requires two-dimensional kinetic modeling. The complete kinetic model for the simulation of spatially nonhomogeneous, vibrationally nonequilibrium gas flows has to include the following equations:

- gas mixture equations of motion;

- translational energy equation with terms describing the presence of direct heating sources and energy exchange between the translational and vibrational modes;
- a system of the partial differential kinetic equations for the population of each vibrational level of each diatomic species (master equation with diffusion):

\[
\frac{1}{N} \frac{dN}{dt} + \frac{df}{dT} = \text{div} \left( D \cdot \text{grad}(f_v) \right) + (\text{Exc})_v + (V-T)_v + (V-V)_v + (V-V')_v + (V-E)_v + (\text{Chem})_v, \quad v = 0, v_{\text{max}}
\] (4.34)

where \((\text{Exc})_v\), \((\text{Rad})_v\), \((\text{Chem})_v\) and \((V-V')_v\) are the terms responsible for the excitation of vibrations, infrared radiation, chemical reactions and the vibrational energy transfer between the excited species, respectively.

The solution of such a large number of equations \((N_{v_{\text{max}}} \sim 50)\) requires extensive computer resources and this has not been attempted here. Future. Even if one neglects diffusion on the right-hand side of Eq. (4.34), one has \(-N_v\) ordinary differential equations, where \(N_g\) is the total number of the grid nodes, which is also unacceptable. However, if the vibrational kinetics are uncoupled from the gas flow field, that is if the characteristic time for the VDF to reach the steady-state, \(\tau_{v_{\text{v'}}}\), is much less than the residence gas dynamic time, \(\tau_{\text{GD}}\), the problem may be reduced to the solution of vibrational and translational mode energy balance equations. In this quasi-steady-state case, the system of equations (4.34) can be replaced by just one equation for the average vibrational energy per molecule of each diatomic species, \(E_{v_{\text{vib}}} = \sum E_{v} f_v\), where \(E_v\) is given by Eq. (4.5). For now, we confine ourselves by the
case of just one diatomic species in an inert diluent, and therefore do
not consider V-V' exchange, which can be incorporated later (see Ref.
[1]). This energy equation may be obtained directly from Eq. (4.34) and
the continuity equation. In the boundary layer approximation one has

\[ \rho u \frac{\partial E_{\text{vib}}}{\partial x} + \rho \nu \frac{\partial E_{\text{vib}}}{\partial y} = - \left( \nu \rho D \frac{\partial E_{\text{vib}}}{\partial y} \right) + \sum v (E_{\text{Exc}})_v - (Vib)^- \]  

(4.35)

Here \( u \) and \( \nu \) are gas velocity components, \( i=0,1 \) for the planar and
cylindrical geometries, respectively, and \( (Vib)^- \) is the vibrational
energy loss in V-T, V-V, V-E processes, radiation and diffusion. For the
two practically important cases of vibrational excitation by a laser
beam and by electron impact, the excitation term can be written as

\[ (E_{\text{Exc}})_v = T_{v+1,v} f_{v+1} - T_{v,v+1} f_v + T_{v-1,v} f_{v-1} - T_{v,v-1} f_v , \]  

(4.36)

where, for example,

\[ T_{v,v+1} = \sum_j \frac{A_v B_v}{8 \pi c k T} \left( \frac{c}{\nu} \right)^3 I_{\nu} \theta S_j \exp \left( - \frac{B_v (j+1)}{T} \right) f_v , \]  

(4.37)

and

\[ \sum v (E_{\text{Exc}})_v \equiv \eta_{\text{vib}} \cdot iE/N = e \gamma e \nu E^2 , \]  

(4.38)

respectively. In Eqs. (4.37, 4.38), \( A_v \) is Einstein coefficient, \( B_v \) is
the rotational constant, \( \nu \) is the laser line frequency, \( I_{\nu} \) is the laser
power density on this line in \( \text{W/cm}^2 \), \( \theta \) is the absorption line shape
factor, \( S_j \) is the Honl-London factor, \( i \) is the discharge current
density, $E$ is the electric field, $y_e$ is the ionization fraction, $\mu$ is the electron mobility, and $\eta_{\text{vib}}$ is the energy fraction of the discharge going into vibration.

In a discharge, one also has to supply equations for concentrations of charged species (electrons and ions), as well as the equation for the electric field (Poisson equation), which, for example, for the positive column of the glow discharge gives $E=\text{const}$. In addition, the direct heating of the gas by electron impact,

$$(\text{Dir.Heat.}) \equiv (1-\eta_{\text{vib}}) \cdot jE/N ,$$

has to be taken into account in the translational energy equation. Parameter $\eta_{\text{vib}}$ can be found from the solution of the Boltzmann equation for the electron energy distribution function (see Ref. [19]).

In the quasi-steady-state "strong" excitation regime, when the vibrational energy loss due to the V-T relaxation on the low levels is negligible, the term $(\text{Vib})^-$ in Eq. (4.35), can be expressed in terms of vibrational quanta flow $\Phi_0$:

$$(\text{Vib})^- \equiv \Phi_0 \cdot (R_0/\mu) \cdot E_1 \cdot (1-2x_v) \cdot Ny^2 \sim \text{const} \cdot \nu \cdot f_{\text{TR}}^2 (v^1_0 +1)^2 \cdot (1-2\delta v_0)$$

According to this result, first obtained by Gordiets and Mamedov [67], the total vibrational energy relaxation rate does not depend on the V-T, V-E, chemical reaction rates, diffusion, and is also independent of the VDF shape above the Treanor minimum $v_0$. The comparison of the Eq. (4.40) with the master equation numerical calculations, shows good agreement within 20%. For example, Fig. 4.5 shows the vibrational quanta diffusion
Figure 4.5 Vibrational quanta diffusion coefficient
coefficient \( v \), given by Eq. (4.10), and calculated using master equation (see Ref. [13]).

The vibrational distribution function \( f_v \), which still can be present in the excitation term of Eq. (4.34), is to be determined using the approximate analytical representation by Eqs. (1.3, 4.15, 4.17, 4.21) for the steady-state VDF, where \( T_v(x,y,z) \) becomes a parametric function to be found from the normalization conditions

\[
\sum f_v(T,T_v,x,y,z) = 1 ; \quad \sum E_v f_v(T,T_v,x,y,z) = E_{v,1b}(x,y,z) \quad (4.41)
\]

The translational energy equation at low Mach numbers can be written as

\[
\frac{\partial T}{\partial t} + \frac{\partial}{\partial x} \left( \rho c_p u \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \rho c_p v \frac{\partial T}{\partial y} \right) = \frac{1}{\gamma} \frac{\partial}{\partial y} \left( \gamma \lambda \frac{\partial T}{\partial y} \right) + (\text{Trans})^* + (\text{Dir. Heat.}) \quad (4.42)
\]

Here the term (Trans)* describes the gas heating in different relaxation processes. The local vibrational energy loss in relaxation, (Vib)*, is not necessarily equal to the local translational energy gain, (Trans)*. The vibrational energy can be lost from the volume by diffusion or by V-E energy transfer (if existent), followed by the fast radiative deactivation of the excited electronic state (V-E/radiation sink). For example, the radiative lifetime of the CO(A^1\Pi) state, prepared in the V-E process (4.22), is \( \tau_r \approx 10 \, \text{ns} \). The relative energy fractions removed from the vibrational mode by V-V, V-E/radiation, V-T energy transfer and by diffusion can be easily calculated by differentiation the energy flux along the vibrational axis, \( \Psi = \phi(v) \cdot E_{1} (1-2\delta v) \).
Here the first term in the right hand side describes the energy loss due
to the decrease of the vibrational quanta toward the high vibrational
levels (V-V exchange), while the second term is the energy loss due to
decrease of the number of quanta per molecule (diffusion and/or V-E
transfer). Taking into account the vibrational quanta flow change
towards the higher levels due to V-E energy transfer and diffusion, one
obtains (see also Eqs. (4.10, 4.17,4.21)),

\[
\phi(v) \equiv \nu \cdot f^2 v^2 \equiv \phi_{VE}(v) + \phi_d(v) =
\]

\[
\frac{\Phi_0}{\nu_{a}-v} \left[ L(v) - L(v_0) \right] \frac{D}{r^2 N^2 \gamma_\alpha} \frac{d^2(GN)}{dx^2}, \quad (4.44)
\]

where \(L(v)\) is given by Eq. (4.24). If V-E transfer is not present \((v_a \gg v, v_0)\), then the plateau in the VDF is truncated by V-T relaxation, and
the first term in Eq. (4.44) becomes equal to a constant \(\Phi_0\), while the
diffusion correction is given by Eq. (4.17).

For the plateau, controlled by V-T relaxation (see Eq. (4.15)),
integration of Eq. (4.43) gives the relative energy fractions going into
V-V, V-T processes and diffusion:

\[
\frac{1}{\Psi_0} \frac{d\Psi}{dv} = \frac{1}{\Phi_0 (1-2x_v)} \frac{d}{dv} \left[ \phi(v)(1-2\delta v) \right] =
\]

\[
- \frac{\phi(v)}{\Phi_0} \frac{2\delta}{1-2\delta v} - \frac{1}{\Phi_0} \frac{d\phi(v)}{dv} \frac{1-2\delta v}{1-2\delta v_0}, \quad (4.43)
\]
\[
(V-V) \equiv \frac{2\delta (v_1 - v_0)}{1 - 2\delta v_0} \quad (4.45)
\]

\[
(Diff) = \frac{D}{\Phi_0 \Gamma^2 \alpha N^2 \gamma} \frac{d^2(TN)}{dx^2} \frac{(v_1 - v_0) \left[ 1 - (v_1 + v_0) \right] - v_0 \ln \frac{1}{v_0} (1 - \delta v_0)}{2 (1 - 2\delta v_0)} \quad (4.46)
\]

\[
(V-T) = 1 - (V-V) - (Diff) \quad (4.47)
\]

For the plateau, controlled by V-E transfer (see Eq. (4.21)), when the V-T losses are negligible at any vibrational level, the energy dissipation in V-V processes becomes smaller than that given by Eq. (4.45), by a factor of 2. The V-E/radiation loss is

\[
(V-E) \equiv \frac{1-\delta (v_1 + v_0)}{1 - 2\delta v_0} \quad (4.48)
\]

The expression for vibrational energy loss in diffusion is too long, and we leave it here as an integral

\[
(Diff) = \frac{1}{\Phi_0 \Gamma^2 \alpha \gamma} \int_{v_0}^{v_a} \frac{d\Phi_d(v)}{d\Phi_d} (1 - 2\delta v) dv \quad (4.49)
\]

where \( \Phi_d(v) \) is given by Eq. (4.44) with \( L(v) \) from Eq. (4.24). In one-dimensional flow, a simple estimate for typical values of \( v_0 \leq 10, v_1 \leq 40, \delta - 6 \cdot 10^{-3} \), and for the plateau controlled by V-T relaxation, gives
(V-V)-40%, (V-T)-60%. For the case of the V-E transfer domination one has (V-V)-20%, (V-E)-80%. Of course, the energy fraction removed by V-E transfer, may strongly vary with pressure (or collisional deactivation time of the excited electronic state) and the optical density of a gas.

The two energy equations (4.35, 4.42) have to be supplemented by the momentum and continuity equations:

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = \frac{1}{y} \left( y \frac{\partial \alpha}{\partial y} \right) - \frac{dP}{dx} \quad (4.50)
\]

\[
\frac{\partial (puy')}{\partial x} + \frac{\partial (puy'^2)}{\partial y} = 0 \quad (4.51)
\]

The natural boundary conditions are

\[
\left. \frac{\partial u}{\partial y} \right|_{y=0} = \left. \frac{\partial T}{\partial y} \right|_{y=0} = \left. \frac{\partial E_{vib}}{\partial y} \right|_{y=0} = 0 \quad (4.52)
\]

\[
u_{wall} = v|_{r=0} = 0, \quad T_{wall} = T_w(x), \quad \gamma v_{wall} E_{vib} + D \frac{\partial E_{vib}}{\partial y} |_{wall} = 0
\]

where \( \gamma \) is the probability of heterogeneous vibrational relaxation on the wall, \( v_T \) is the average molecular velocity, and \( T_w(x) \) is determined by the cooling regime of the laser absorption cell or the discharge tube.

Thus, we obtain the complete system of equations (4.35, 4.42, 4.50, 4.51), where the VDF is given by Eqs. (1.3, 4.15, 4.17, 4.21), which allow simulation of two-dimensional, vibrationally nonequilibrium,
quasi-steady state gas flows in the boundary layer approximation. Note that, beside its affordability, this model has one additional important advantage, since it depends only on a few kinetic rates. We also note that the shape of the VDF, except the cutoff coordinate $v_1$, depends only on the oscillator matrix elements.

Finally, the model can be generalized for non-steady-state problems using the time-dependent analytical theory of anharmonic oscillators, developed in Refs. [68,50].

4.2.5 Results of calculations and discussion

First, the model developed in Section 4.2.4 has been tested in calculations of quasi 1-D CO-Ar-He flow in a laser absorption cell used in experiments of Rich et al [8] (see also Section 4.1). In these experiments, an absorption cell of 25 cm length and 0.95 cm in diameter was nearly filled by a 200W gas dynamic CO laser beam, directed along the flow axis, the gas flow velocity being 9.0-9.8 m/s at 1 atm total pressure. The quasi-steady-state condition was satisfied at $\tau_{gd} \sim 30$ ms and $\tau^R_{vv} \sim 1$ ms. No substantial spatial gradients were present because of the uniform laser power distribution across the beam, which removes diffusion effects.

Necessary kinetic data used in the model, such as $Q^S_{10}$, $Q^L_{10}$, $\delta_{vv}$, $\Delta_{vv}$ for CO-CO, $P_{10}$ and $\delta_{vt}$ for CO-CO, CO-Ar, and CO-He were taken from Ref. [13]. Note that the values of these parameters are not those recommended by SSH and Sharma-Brau theories; they have been inferred.
from the experiments of Refs. [8,11], where theoretical relations of Eqs. (4.12, 4.16) for V-V and V-T rates have been used only as convenient parametrizations.

Since at this high pressure the collisional deactivation time of the CO(A^1\Pi) state is \(\sim 0.1\) ns, while its radiative lifetime is \(\sim 10\) ns, it has been assumed that all the energy going into the singlet state came back to the vibrational mode of the CO ground electronic state in collisions.

Figure 4.6 presents the comparison of the model calculations of the VDF (curves) with the experimental data of Ref. [8] (points), at a distance of 4 cm from the cell inlet, for three different gas mixtures. One can see that the results are in good agreement. The vibrational temperature obtained in the calculations from the energy balance equations (4.35, 4.42), fits its experimental value, \(T_v = 2600\)K. The plateau slope, given by Eq. (4.21), is consistent with the assumption of the presence of a strong vibrational energy sink at the level v-40 of CO. The decrease in relative populations of the high levels with the increase of He concentration is due to the faster CO V-T relaxation on He atoms, which has also been reported in Ref. [14].

The absorbed laser power, obtained in the calculations, also agrees well with the experimental value of 40W (the experimental laser spectrum was one of the input parameters of the computer code). The calculated temperature increase of \(\Delta T \approx 60\)K at the outlet of the cell agrees with calculations using a 1-D master equation within 20%.

Next, the two-dimensional model has been used for the simulation of the glow discharge experiments of Ref. [31]. Here, a gas mixture
Figure 4.6 Experimental CO VDF's, Ref. [8] (points) and results of quasi-1-D model calculations (curves)
CO:N$_2$:He=0.2:0.7:5.2 at a total pressure of 6.1 Torr was flowing through a discharge tube of 120 cm length and 1.34 cm in diameter, cooled by liquid nitrogen. The 2-arm discharge voltage and current were $V=6.6$ kV and $I=14$ mA, respectively, at an interelectrode distance of $L/2=54$ cm, which gives a power loading of $Q=1.7$ W/cm in the positive column. At present, our two-dimensional kinetic model does not incorporate the simulation of a discharge. For this reason, the electron concentration distribution across the tube was taken to be the Shottky distribution

$$n_e(y) \sim J_0(2.4y/R),$$  \hspace{1cm} (4.53)

where $J_0$ is Bessel function, normalized to the total discharge current $I$. The distribution of Eq. (4.53) assumes the the ionization rate across the discharge tube is constant and that the loss of electrons is by diffusion, which is a reasonable approximation for low pressure glow discharges (see Ref. [19]). The electric field has been assumed to be constant in the entire discharge area, $E=V/(L/2)$. Finally, the discharge energy fraction going into vibrations was assumed to be $\eta_{vib} \approx 1$, which is a good approximation for CO:N$_2$:He mixtures at the reduced electric field $E/N \approx 1\cdot10^{-16}$ V·cm$^2$ (see Ref. [4]). These assumptions allowed simple calculation of the vibrational excitation term (4.38) in the vibrational energy equation (4.35).

We also assumed that nitrogen in the mixture does not contribute in the vibrational energy balance, despite its effective vibrational excitation by electron impact. In the steady-state, the vibrational temperatures of CO and N$_2$ are related as follows (see Ref. [7]):
\[
\frac{E^N_{1}}{T^N_{v}} - \frac{E^CO_{1}}{T^CO_{v}} = \frac{E^{N}_{1} - E^{CO}_{1}}{T},
\]  

which for experimental values of T=125K and T^CO=1975K gives \(T^N_{v} = 900K\).

Simple estimates then show that the vibrational energy stored in nitrogen is several orders of magnitude less than that in CO, and therefore it has been neglected. The V-V and V-T data for CO-CO and CO-He at T=100K were taken from experiments of Powell [69] and trajectory calculations by Billing [35].

At these experimental conditions the collisional and radiative lifetimes of CO(A^\text{II}) state are comparable. For this reason, it is not clear what part of the discharge energy is being lost by the ultraviolet radiation, and how much energy is going into the gas heating. We made two limiting calculations, assuming zero and 100% efficiency of the V-E/radiation mechanism.

Figure 4.7 shows the results of comparison of the experimental CO VDF of Ref. [31] (points) with the two-dimensional calculations (curves). Here the "observed" VDF and temperature were calculated using Eqs. (4.25, 4.28), with a substitution dy→ydy, since in the experiments [31] the IR signal has been collected along the discharge tube. The solid and the dashed curves correspond to the assumptions of zero and 100% energy loss by radiation, respectively. One can see that in both cases the agreement of the calculated VDF with the experiment is reasonable (both curves are close to each other since the vibrational energy relaxation rate is approximately the same). However, the calculated average temperature at zero radiative energy loss, T=123 K,
Figure 4.7 Experimental CO VDF, Ref. [31] (points) and the distribution function obtained from two-dimensional model (curves). Solid line, zero efficiency of the radiative energy loss; dashed line, 100% energy loss by V-E/radiation mechanism.
is much closer to its experimental value $T=125\pm3$ K, than the temperature, corresponding to the second assumption, $T=94$ K. Better understanding of the role of CO($a^1\Pi$) radiation in the energy balance of vibrationally excited CO requires additional experimental measurements of absolute intensities of the CO $4^{th}$ Positive emission bands in optical pumping experiments.

The "dimple" in the VDF at the level $v\approx25$, which may be seen more clearly in Ref. [31], is presumably due to the near-resonance V-E transfer

$$CO(X^1\Sigma,v\approx25) + M \leftrightarrow CO(a^3\Pi) + M, \quad (4.55)$$

which has not been considered by the model.

The influence of diffusion on the VDF has been found to be weak ($\approx10\%$), and therefore is not shown in Fig. 4.7. The reason is that at these discharge parameters, the spatial nonhomogeneity is not very strong, and, in addition, the radial profiles of $T$ and $T_v$ are similar (see Fig. 4.8), which leads to a weak change of the expression $\Gamma N$ in the diffusion correction of Eq. (4.17),

$$\Gamma N = \nu_f \frac{1}{\Gamma_0} \frac{T}{2x T_v} \exp(-E_1 T/4x T_v^2) \quad (4.56)$$

and makes the correction negligible.

Both quasi-1-D and 2-D calculations for the conditions of Refs. [8,31] have shown that the diffusion energy flux to the wall consists almost entirely of the translational energy, due to the small probability of vibrational excitation quenching on the wall $\gamma$. 
Figure 4.8 Calculated normalized radial profiles of temperature and vibrational temperature for the experimental conditions of Ref. [31]; no energy loss by radiation.
Measurements of vibrational quenching of $\text{H}_2$, $\text{D}_2$, and $\text{N}_2$ on quartz, steel, and aluminum give $\gamma \sim 6 \times 10^{-5} - 5 \times 10^{-3}$ at room temperature (see Ref. [70]). Variation of $\gamma$ in the range $10^{-2} - 10^{-4}$ did not substantially affect the energy balance, integrated VDF and temperature for both experimental conditions of Refs. [8,31].

The question of applicability of the two-dimensional kinetic model to the optical pumping experiments of Refs. [14,30] needs careful analysis. In Ref. [14], the CO-Ar-He mixture at a total pressure of $P=100$ Torr was flowing in a six-arm cross absorption cell of 35 mm inner diameter and 12 cm total length (see the details and the schematic of the cell in Refs. [13,14]). As one can see, the cell length is comparable to its diameter. In addition, the diameter of the focused laser beam, $d_b \leq 2.5$ mm, was much less than the cell diameter, to provide higher power density (the focal area size was estimated to be $d_f \sim 1$ mm).

In this situation, the gas flow in the near-axis region of the cell is a circular jet, which accelerates due to the axial pressure gradient

$$\frac{\partial P}{\partial x} = - \rho u^2 \left[ \frac{\partial T}{\partial x} - \frac{1}{A} \frac{\partial A}{\partial x} \right]$$

resulting from the fast intensive gas heating in vibrational relaxation processes. In Eq. (4.57), $A$ is the effective cross-section of the jet, $A-x/Re_x$ for the laminar jet. Since $A$ is much smaller than the cross-section of the cell, this axial gradient is not constant across the cell (or radial and axial velocity components are comparable), and the boundary layer approximation is not valid. Calculations performed using
the boundary layer flow code have shown that the model gives substantially underestimated values of the observed VDF's (up to an order of magnitude) and translational temperatures (up to two times) compared to the experiments. Qualitatively, this can be explained by the effect of suction of the ambient gas by the accelerating jet, which is created by the positive radial pressure gradient, \( \frac{\partial P}{\partial y} \sim -\frac{\partial P}{\partial x} \). This suction reduces the effect of diffusion towards the cell walls, and actually "locks" the energy in the near-axis area, which increases the integrated \( T \) and \( T_v \).

In experiments of Ref. [30], the CO-Ar-He mixture was injected in the cell from a 4 mm tube, perpendicular the focused laser beam axis, and extracted through a similar tube placed 8 mm downstream (see the cell schematic in Ref. [13]). Obviously, the characteristic size of the excitation region along the gas flow is comparable to its size across the jet, and therefore the axial and radial gradients of temperature and vibrational energy are also comparable. For this reason, again, the boundary layer approach cannot be used.

As one can see, the influence of the flow field on the spatial distributions of temperature and vibrational energy, and therefore on the measured \( T \) and \( VDF \), cannot be neglected. Simulation of the nonequilibrium gas flows, studied in Refs. [8,31] can be performed using the same approach described in Section 2.4, and the full two-dimensional Navier-Stokes equations. The kinetic model based on the Navier-Stokes flow code, is currently being developed.
4.3 Conclusions

The influence of spatial nonhomogeneity on the vibrational kinetics of anharmonic oscillators has been analyzed. It has been found that for the diatomic molecules with $Q_{10} / Z < 1$, vibrational energy relaxation has no effect on the heat conductivity of a gas, despite the very high probabilities of V-V processes at the high vibrational levels. Analytical correction for V-E transfer and diffusion influence on the VDF and on the gas heating rate in vibrational relaxation has been obtained. It has been shown that non-local diagnostics of spatially inhomogeneous, vibrationally nonequilibrium flows leads to a substantial deviation of the observed VDF from the theoretical predictions. A two-dimensional kinetic model based on the vibrational and translational mode energy balance equations, on an analytical VDF of the diatomic species and on a the boundary layer flow code, has been developed. The comparison of the model with the experiments has shown good agreement within the limits of the boundary layer approximation applicability. A more advanced model based on the same semi-analytical approach and a Navier-Stokes flow code, is being developed.
APPENDIX

THE THOMSON DISCHARGE (Ref. [24])
For Gaussian distribution of the external ionization source power, Eq. (2.6), the distributions of the ionic and the electronic currents are

\[
j_+ (x) = \frac{eq(0)d \pi^{1/2}}{4} \left[ \frac{\phi(L/d) + \phi(2x/d)}{\sqrt{1/2} \left( \frac{L}{d} \right) + \sqrt{1/2} \left( \frac{2x}{d} \right)} \right]
\]

\[
j_e (x) = \frac{eq(0)d \pi^{1/2}}{4} \left[ \frac{\phi(L/d) - \phi(2x/d)}{\sqrt{1/2} \left( \frac{L}{d} \right) - \sqrt{1/2} \left( \frac{2x}{d} \right)} \right]
\]

where

\[
\phi(x) = \frac{2}{\pi^{1/2}} \int_{0}^{x} e^{-\xi^2} d\xi,
\]

The electric field distribution is

\[
E(x) = \left[ \frac{eqd}{\mu_e e_0} \right]^{1/2} \left[ \frac{\pi^{1/2}}{2} x \left( \phi(L/d) + \phi(2x/d) \right) + \frac{d}{4} e^{-\frac{4x^2}{d^2}} \right]^{1/2}
\]

\[
+ \left[ \frac{eqd}{\mu_e e_0} \right]^{1/2} \left[ \frac{\pi^{1/2}}{2} x \left( -\phi(L/d) + \phi(2x/d) \right) + \frac{d}{4} e^{-\frac{4x^2}{d^2}} \right]^{1/2}
\]

Finally, the ion and the electron distributions (excluding the near-
electrode regions) are

\[
n_+^e(x) = \frac{j_+^e(x)}{e\mu_+^e(x)}, \quad n_e^e(x) = \frac{j_e^e(x)}{e\mu_e^e(x)}.
\]  \hspace{1cm} (A4)

The characteristic width of these near-electrode layers where the charge diffusion is significant, in the saturation regime is

\[
\frac{\Delta x_\alpha}{L} \sim \frac{D_\alpha}{\mu_\alpha E_L} = \frac{T_\alpha (eV)}{U_s} \sim 10^{-2} - 10^{-3}, \hspace{1cm} \text{(A5)}
\]

or \( \Delta x_\alpha \) is much smaller than \( L \).
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118


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