ENERGY TRANSFER AND CHEMISTRY OF CARBON MONOXIDE
IN VIBRATIONAL MODE NON-EQUILIBRIUM

DISSERTATION

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

By

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The Ohio State University
2005

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ABSTRACT

Chemical reactions with vibrationally excited carbon monoxide show a marked enhancement over thermal reaction rates. These reactions were studied experimentally, in the gas phase, and on selected surfaces. In addition, vibrational energy transfer between CO (carbon monoxide) and N\(_2\) (nitrogen) in cryogenic liquids was studied. For these experiments, energy was partitioned into the vibrational modes of the reactant CO, by absorption of the infrared radiation from a carbon monoxide laser. The product, CO\(_2\) (carbon dioxide) from reactions of the vibrationally excited CO molecules was measured for varying vibrational energy loading conditions. Systematic variation of the vibrational mode energy loading was achieved by adding varying amounts of helium, which provides a channel for fast vibrational relaxation of the higher vibrational levels. The specific rate for the gas phase Boudouard disproportionation reaction CO + CO \(\rightarrow\) CO\(_2\) + C, was measured for the vibrationally excited CO reactant, at relatively low gas kinetic temperatures. An activation energy near 6.0 eV (140 kcal/mole) was inferred. Quantitative measurements in the gas phase reaction yield a specific kinetic rate on the order of \(k_{\text{overall}} = 1.0 \times 10^{-18} \text{[cm}^3/\text{sec]}\), for an energy loading of the CO vibrational mode of 0.260 eV/molecule, at a translational/rotational mode temperature of 1050 K. For these conditions the vibrational states were in a strongly vibration-to-vibration pumped distribution to at least \(v = 35\) being populated. With this same total vibrational mode
energy loading, the rate decreases dramatically as higher vibrational quantum levels are quenched by the helium addition. The rate also increases with increasing energy loading. These results are used to determine the validity of a rate based on a transition state theory describing the vibrational quantum state dependence of the chemical kinetic reaction rate. Results are in agreement with state dependence predictions of the theory. The magnitudes of the vibrational state dependence of the specific rates for the Boudouard disproportionation reaction are inferred.

In other phases of this research, qualitative observations of the vibrationally activated chemistry of the CO on surfaces (primarily copper oxide) have shown a production of CO$_2$, at surface temperatures below 200 °C. At these temperatures, thermal equilibrium reactions on the same surface show no CO$_2$ production. Extreme vibrational mode power loading was also created in cryogenic (87K) liquid CO and argon, and vibration-to-vibration pumping of N$_2$ is observed. An infrared fundamental band spectrum from vibrationally excited N$_2$ has been observed for the first time in emission.
Dedicated to my Family
ACKNOWLEDGMENTS

I wish to acknowledge my advisor, Professor William Rich, for his time and advice given to me which helped shape this thesis. Without his help this work would never have been finished. I also wish to thank him for guidance during my research.

I also wish to thank the other professors on my PhD committee: Dr. Subramaniam, Dr Adamovich, and Dr. Lempert who have supported me both in the classroom and in my research by lending me books and instruments that enabled me to continue and expand my research. I would also like to thank them for their input into my research; their ideas helped me tremendously. I would also like to thank Dr Umit Ozkan for her assistance on the surface phase portion of this thesis. She generously gave her time, input, and use of her excellent laboratory equipment that was used for this research.

I also wish to thank the Dr. Peter Palm and Dr. Elke Plonjes for their help in laboratory. Dr. Palm was very helpful when we were setting up the liquid experiments. They have had much experience in a lab that they generously shared. I especially wish to thank Dr. Urban and the University of Bonn for the carbon monoxide laser that was graciously sent to me to use after my third tube broke.

I would also like to thank those who work in the mechanical engineering department: Bob Frank, Joe West, Gary Gardner, Keith Rogers, Tom Merrick, Prem Rose Kumar, Grace Hines and the late Mary Richards, who machined mounts, advised
me in computer programming, built electronic circuits, and helped me with the endless paperwork. I also wish to thank the NETL group for their support, help and advice in the lab as we all work on our projects.

I especially wish to thank Allen White for allowing me to bend his ear about my doubts and fears while I was working. Without his support, I would not have finished this degree.

Finally, the support of the Air Force Office of Scientific Research Space Power and Propulsion Program, Dr. Mitat Birkan, Program Manager, and the support of the Ralph W. Kurtz Endowment are gratefully appreciated.
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1. Katherine Essenhigh and Umit Ozkan, and J. William Rich, “Surface reaction of
gas phase vibrationally excited carbon monoxide at low temperatures” AIAA paper


FIELDS OF STUDY

Major Field: Mechanical Engineering
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CHAPTER 1

INTRODUCTION

This research is a study of the effects on the chemical rate of reaction for situations where a large fraction of energy of the system is partitioned into the vibrational mode of a reactant, while the energy of the translational and rotational modes is kept low. Specifically, studies focus on reactions of vibrationally excited CO (carbon monoxide) in gas phase and surface environments. In addition, these projects were expanded to include studies of energy transfer between mixtures of diatomics in the cryogenic liquid phase. Knowledge of these processes is important in the modeling of energy transfer and vibrationally activated chemistry in different areas such as: High enthalpy flows, in the positive column of a glow discharge, reactive flows where there are low energy electrons, and in the upper atmosphere. Experimental data collected for this thesis shows evidence of vibrationally activated chemistry, specifically, in the Boudouard disproportionation reaction of carbon monoxide, and an overall kinetic rate for gas phase Boudouard reaction was measured.

Experiments were conducted in non-equilibrium environments, where energy is directed into the vibrational modes of the reactants. However, the translational and rotational modes remain at or near room temperature. Previous studies have shown vibrationally activated chemistry to occur with an enhanced rate; however, these studies
are limited to conditions where only the first vibrational energy level of the reactant was populated. In the experiments to be presented for this thesis, the first forty vibrational levels of the reactant CO are populated, at moderate pressures of a few Torr in a diluent of approximately 100 Torr. These systems, that are studied, have the conditions where the vibrational modes of the molecules are in disequilibrium with the other modes. An environment is created that enables us to study the effects of energy stored in many vibrational states of a single mode. The description of vibrational energy storage will be presented in the following Chapter, 2, as well as the basis for vibrationally activated chemistry in the gas phase as well as on surfaces.

Experiments focus on the measurements and observations of the production of carbon dioxide produced by vibrationally excited carbon monoxide for different environments. The first environment is the gas phase environment, where CO$_2$ (carbon dioxide) production was measured for different degrees of vibrational excitation in the CO reactant. The experimental setup and results are presented in Chapter 3. The second set of experiments is the study of CO$_2$ production on surfaces with vibrationally excited CO reacting with pre-absorbed oxygen. The production of CO$_2$ is correlated with temperature measurements of the surface and with the degree of vibrational excitation. The details of these experiments and results are presented in Chapter 4. The final set of experiments take place in liquid CO/argon mixtures where translational temperatures are very low, 87 K. These experiments focused primarily on the study of energy exchanges, and the experimental setup and results are presented in Chapter 5. A discussion of the experiments, and correlation with existing theory is presented in the final Chapter, 6.
CHAPTER 2

NON-EQUILIBRIUM SYSTEMS:
VIBRATIONAL ENERGY STORAGE, TRANSFER AND CHEMISTRY

Thermal non-equilibrium environments can be found in many different engineering applications such as in high enthalpy flows, low-pressure electric discharges, and in optical pumping experiments in which lasers are used to excited selected internal modes of molecules. Studies of non-equilibrium environments yield information regarding the fundamentals of internal energy exchanges in molecular collisions. Such information can be applied to many different engineering applications with the specific objective of improving the operating performance of many heat engines, including lasers, for example. Not all of these widely varying applications will be discussed here. However, a general discussion of the thermal equilibrium and of the vibrational mode non-equilibrium will be presented. This vibrational non-equilibrium condition characterizes the environment studied in this dissertation. These non-equilibrium environments, in contrast to thermal equilibrium environments, create conditions that allow for the studying of vibrationally activated chemistry and energy transfer.
2.1 THERMAL EQUILIBRIUM CONDITIONS

Thermal equilibrium environments are characterized by a specific statistical distribution of the total energy in the system among the modes of the molecules, known as the Maxwell-Boltzmann statistics. These modes include translational, rotational, vibrational, and for some molecules, electronic, as well as in interactions between the molecules. The energy of the system is stored in these different modes, and the total energy for the system can be written as [1]:

\[ E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} + E_{\text{interactions}} \]

Equation 2.1

Each term on the right hand sides represents the fraction of the total energy stored in that particular mode. Energy equations for each of the terms, on the right hand side, in Equation 2.1 can be written, and are well known [2,3,4]: The translational and interaction terms are represented by energy expressions derived from classical mechanics. While the internal energy terms, rotational, vibrational and electronic, are derived from quantum mechanics, beginning with classical potentials, and results are energy expressions as a function of a specific energy level, generally referred to as \( i \). The distribution of the internal energy of a system is governed by Maxwell-Boltzmann statistics [1], and is represented by:
\[
\frac{n_i}{N} = \frac{g_i \exp\left(-\frac{\varepsilon_i}{kT}\right)}{Q_{\text{int}}}
\]

Equation 2.2

Where \(i\) represents the \(i^{\text{th}}\) level of the particular energy mode, \(k\) is Boltzmann’s constant, \(T\) is the kinetic temperature, \(\varepsilon_i\) is the energy for the internal modes, \(g_i\) is the degeneracy for the given energy, and \(Q\) is the partition function which is a constant for a given temperature, \(T\). The left hand side represents the fraction of molecules in the \(i^{\text{th}}\) energy level, where \(n_i\) is the number of molecules in energy level \(i\), and \(N\) is the total number of molecules.

The thermal equilibrium vibrational distribution of diatomics is described by Equation 2.2 with the appropriate energy expression for \(\varepsilon_i\). The vibrational energy for a diatomic molecule in vibrational level \(v\), is written as:

\[
E_{\text{vib}} = \omega_v \text{hc}(v + \frac{1}{2}) - \omega_e \chi_e \text{hc}(v + \frac{1}{2})^2
\]

Equation 2.3

Where \(h\) and \(c\) are respectively Planck's constant and the speed of light, and \(\omega_v\) and \(\omega_e \chi_e\) are spectroscopic constants. The factor \(\omega_v\) is related to the linear restoring force constant, \(k\), for a harmonic oscillator, and \(\omega_e \chi_e\) represents the anharmonicity of the diatomic. The vibrational energy level is represented as \(v\) and takes integer values of \(v = 0, 1, 2\ldots\). The anharmonic term in Equation 2.3 is not large factor except for higher vibrational energy
levels, v. For most moderate temperatures $T \sim 300 – 2000$ K, one may neglect the anharmonic term for thermal equilibrium situations. In such cases, the vibrational energy, represented by Equation 2.3, with the anharmonic term omitted, is substituted into the energy in Equation 2.2, which yields the thermal equilibrium distribution for vibrational energy modes, with $g_i$ taken as equal to one. The resulting equation is written as:

$$n_v = \frac{\exp\left(-\frac{\omega_c \hbar c (v + 1)}{kT}\right)}{Q_{\text{vib}}}$$

Equation 2.4

Where $Q_{\text{vib}}$ is the vibrational partition function and all the other terms have been previously discussed. Since the argument in the exponent is linear with $v$, the vibrational level, then the natural log of Equation 2.4 yields a logarithmic population distribution function that is linear with vibrational energy level, $v$. Typically only the first few vibrational energy levels, $v \sim 0-5$, have any significant populations, however, this is not necessarily the case for vibrational non-equilibrium systems used for the experiments of this thesis.

2.2 NON-EQUILIBRIUM CONDITIONS

Non-equilibrium systems are characterized by a non-Boltzmann distribution of the energy states within at least one mode, or by a departure of one or more modes, at some temperature $T_1$, from the other modes at temperature $T_2$. Experimental work to be
presented in this thesis was performed in non-equilibrium environments with energy stored in the vibrational modes of selected diatomic molecules, while translational and rotational modes are in a Boltzmann distribution at a low temperature. Many different processes occur in these systems, which can be generally classified as either radiative or collisional, which will be further detailed in this section. Previous research conducted on these systems has focused primarily on energy transfer processes between molecules during collisions, but there is now additional research into chemical reaction channels. While it has been known that chemistry occurs in these non-equilibrium systems, the details of the mechanisms and vibrational energy level dependencies have been difficult to determine. For example, the production of carbon dioxide from two carbon monoxide molecules has been known to proceed via electronically excited states. However, there is growing evidence of vibrationally activated chemistry occurring in these low temperature environments, which is further researched in this thesis. One of the major issues addressed is the dependence of the rate of chemical reaction on the level of vibrational excitation.

2.2.1 Vibrational Energy Storage and Energy Transfer

Vibrational non-equilibrium environments are complex systems where the energy of the system diffuses through the different molecular modes at different rates. We are considering systems that are prepared initially by placing large amounts of energy into specific vibrational modes. Generally, energy delivered into a specific mode of the
system is distributed among the modes of the molecules through inelastic molecular collisions. Energy is exchanged during these collisions causing the system to approach an equilibrium state. However, these exchange processes proceed at different rates due to the varying efficiencies of the energy transfer. Typically, the most efficient energy transfer is the T-T (translation-to-translation) energy transfer, which only takes a few collisions for the energy to be Boltzmann distributed among the translational modes [5]. Similarly, R-R (rotation-to-rotation) energy exchanges are also fast achieving equilibrium within 5 to 10 collisions [5] for nitrogen and oxygen, and within only a few more for CO [5]. The anomaly is hydrogen, where experimental results show 100 to 200 collisions to equilibrate [5]. While the R-R energy exchange is slower than T-T energy exchanges, both are considered fast when compared to V-V (vibration-to-vibration). For this work, it is assumed that the T-T and R-R energy exchanges have been equilibrated. Other energy exchange processes, specifically the V-V exchanges are slower, taking on the order of several hundreds of collisions before equilibrium is attained [5]. In comparison to the V-V energy exchanges, the V-T (vibration-to-translation) and V-R (vibration-to-rotation) energy exchanges are even slower, especially at low (room) temperatures. These two exchanges are often grouped together, V-TR. The slow V-TR rates together with the comparatively faster V-V rates allow energy to diffuse through the vibrational energy modes before losses occur by V-TR exchanges.

A system is considered to be in vibrational non-equilibrium if either of the following two situations occurs: One, the vibrational mode distribution is in a Boltzmann distribution according to Equation 2.4 but the temperature parameter, $T$, is not equal to
the temperatures of the translational and rotational modes, i.e. the different modes do not share the same temperature. Two, the vibrational distribution cannot be represented by a single temperature characteristic of the usual equilibrium relation described Equation 2.4, and thus is highly non-Boltzmann. This second situation is the one of interest in the present research. We are specifically interested in the case where the vibrational mode is high, and the translational and rotational mode energies are low. These systems are characterized by their non-Boltzmann distribution in the vibrational modes, showing marked departure from the normal dependence on vibrational energy as given by Equation 2.4. Vibrational distribution functions in these cases illustrate the phenomena called vibrational up-pumping or ladder climbing of the vibrational energy during collisions.

The up-pumping is controlled by vibrational energy exchange (V-V) collisions. The following figure illustrates the energy exchange process in such V-V up-pumping conditions.
Figure 2.1: Illustration of energy vibrational spacings in anharmonic oscillators for vibrational energy level, W, greater than vibrational energy level, V.

Figure 2.1 depicts the vibrational energy levels of two diatomic molecules, A and B in levels V and W respectively, before a collision. It is assumed that vibrational level W is higher than vibrational level V. It is important to note that diatomics are not harmonic oscillators, for which all the vibrational energy spacings would be equal. Rather, the diatomics are anharmonic, and the spacings between adjacent levels decrease with increasing vibrational energy levels. Consider molecule A colliding with molecule B, and exchanging a quantum of vibrational energy by the V-V process. Molecule B, being in a higher vibrational level, has less energy to overcome if it is promoted to the next vibrational level, rather than molecule A being promoted to the next vibrational energy level, which has the larger energy gap. The excess energy, $\Delta E$, shown in the figure,
would be transferred into the translational and rotational modes. Energy transfer upward into B at the expense of A, is favored. This biasing of energy transfer can also be proven through detailed balancing, which balances out the number of molecules moving into and out of a vibrational energy level. From this balancing, a relationship between the rates of moving up and down a vibrational level is determined and is [6]:

\[ P_{v,v-1}^{w,w+1} = \exp \left( \frac{\Delta E}{k_B T} \right) P_{v,v+1}^{w,w-1} \]

Equation 2.5

Where \( P_{v,v-1}^{w,w+1} \) is the rate of the molecule B going from level \( w \) to \( w+1 \) while molecule A moves down a vibrational energy level, \( v \) to \( v-1 \). Similarly, \( P_{v,v+1}^{w,w-1} \) represents the rate of molecule B going down from level \( w \) to \( w-1 \) while molecule A moves up a vibrational energy level, \( v \) to \( v+1 \). Boltzmann’s constant is referred to as \( k_B \) and \( T \) is the gas thermal temperature. The \( \Delta E \) is the energy difference between the two molecules as is shown in the above figure, also referred to as the resonant energy defect which is written as

\[ \Delta E = E(V)-E(V-1) - E(W+1) + E(w) \]

Equation 2.6

Equation 2.5 shows that the rate of the molecule, B, in the higher vibrational energy level, W, being promoted to the next higher vibrational level, with the lower energy molecule A moves down a level, exceeds the rate for the reverse process. Thus, energy
in the vibrational modes of anharmonic oscillators preferentially moves to higher vibrational levels. This are the conditions for vibrational up-pumping.

Each of the different inelastic collisional energy transfer processes, VV, VT, and VE are represented by rates, which can differ by orders of magnitude. Two other mechanisms are the SRD (spontaneous radiative decay) and CHEM (chemical processes) [7,8,9]. In general, the rate of change in population of the $v^{th}$ vibrational energy level of molecular species $i$ is balanced by the different processes that can affect the vibrational level of an anharmonic oscillator. The rate equation, also known as the master equation for a given vibrational level $v$ can be written as [10,11]:

$$\frac{dn_{v,i}}{dt} = VV^v_i + VT^v_i + VE^v_i + SRD^v_i + CHEM^v_i$$

Equation 2.7

Where $n_{v,i}$ is the population of the $i^{th}$ species in the $v^{th}$ vibrational level. The right hand side of the equation represents all the different processes that can affect the population and these processes are also functions of $n_{v,i}$. More sophisticated models now include a radial diffusion term to account for spatial variations [9]. Thus, an additional term for special dependency appears in the equation. The specific terms that appear on the right hand side of the equation are presented in Appendix A. These are expressions for the rates of energy exchanges, which represent the physics occurring during an inelastic collision. There is enormous literature on the dynamical theory of inelastic collision
processes of this type; the books by Yardley [26] and Capittelli [43] provide reviews of some of this literature.

To examine the vibrational up pumping or ladder climbing, Equation 2.7 above is rewritten to contain only the VV term for one species and is written as [6]:

\[
\frac{dn_v}{dt} = \sum_w p_{v+1,w}^{w-1,w} \left[ n_{v+1}n_{w-1} - e^{(E_{v+1} + E_{w-1} - E_w - E_{v+1}) k_B T} n_v n_w \right] - \sum_w p_{v,w+1}^{w-1,w} \left[ n_v n_w - e^{(E_v + E_{w+1} - E_{w+1} - E_w) k_B T} n_{v+1}n_{w-1} \right]
\]

Equation 2.8

Where \( n_v \) and \( n_w \) are the populations of the \( v \)th and \( w \)th vibrational levels, \( p_{v+1,w}^{w-1,w} \) is, as was described in Equation 2.5 the rate for molecule A gaining a vibrational quantum of energy and molecule B losing a vibrational quantum. For steady-state conditions, \( \frac{dn_v}{dt} = 0 \), it can be shown by direct substitution, see Treanor, Rich & Rehm [6], that:

\[
n_v = n_v e^{-\gamma} \exp\left(-\frac{E_v}{k_B T}\right)
\]

Equation 2.9

Where \( \gamma \) is an arbitrary constant, and is usually represented as:

\[
\gamma = \left( \frac{E_1}{k_B \theta_i} \right) - \frac{E_1}{k_B T}
\]

Equation 2.10
The quantity $\theta_1^*$ is an effective vibrational temperature determined by the populations of the first two vibrational energy levels given by $\theta_1^* = E_1/\ln(n_1/n_0)$. The quantity $E_1$ is the energy difference between vibrational levels one and zero ($E_1 = \hbar \nu$, where $\nu$ is the fundamental oscillation frequency of the molecular vibration). $E_1/k_B$ is the characteristic vibrational temperature and is 3120 K [8] for CO. $\theta_1^*$ (or $\gamma$) is a measure of the energy in the vibrational mode for these non-equilibrium systems. The distribution, Equation 2.9, is the distribution maintained in steady state in the absence of all by V-V processes. As such, it is a theoretical limit, but one meriting examination. As the gas kinetic temperature or translational temperature, $T$, tends toward the vibrational temperature, $\theta_1^*$, the quantity $\gamma$ tends to zero, and the population distribution in Equation 2.9 tends toward Boltzmann. Due to the anharmonic nature of the diatomic, $E_v$ in Equation 2.9 above is quadratic in $v$. The resulting distribution for nitrogen, for various gas kinetic temperatures and the vibrational temperature parameter, $\theta_1^*$, selected to be 3000K is shown in the following figure.
Figure 2.2: Calculated plots for various translation temperatures of the analytical vibrational distribution with no losses for N$_2$, and $\theta^*_1 = 3000$ K [6].

This figure shows the theoretical vibrational populations distribution for N$_2$, and $\theta^*_1 = 3000$ K [6] as a function of vibrational quantum level, $v = r$ in the figure. Each plot was generated for different translational temperatures and shows that at higher vibrational quantum numbers the populations increase. The figure also shows that as the translational temperature increases, the populations at the higher vibrational levels begin to decrease, and the plot becomes more Boltzmann-like. It must be emphasized that the V-V distribution of Figure 2.2 is not fully realized in actual experimental environments. In conditions where vibrational energy is high, and gas kinetic (translational/rotational) temperatures are low, i.e. where $\theta^*_1 >> T$, such as in glow discharges and laser-pumped
gases, the vibrational distribution functions are indeed strikingly non-Boltzmann, and high upper level populations occur. However, the total population inversions of Figure 2.2 are not seen. This is because additional processes are present that have rates comparable to the V-V exchange rates. Most importantly, at high vibrational levels, rate of V-T/R and V-E become comparable to those of the V-V up-pumping process. Critically, the V-T/R rates increase dramatically with temperature, so that as gas kinetic temperature increases, V-T/R quenching rates become comparable to the V-V rates at even lower vibrational quantum levels. For this reason, with increasing temperature, the up-pumping process occurs at decreasing vibrational quantum levels. The net result is that actual vibrational population distribution functions (the “VDF”s) follow the predition of Equation 2.9 and Figure 2.2 only up to the minimum of the distribution (the “Teanor minimum”). Beyond this point, the distribution decreases slowly in a more or less gently-sloping “plateau”. It should be noted that, beyond the analytical solution of Equation 2.9, various researchers have developed analytical approximations for these VDF’s modified by the presence of V-T/R rates, notably the works of Gordiets [12], Lam[13], and Likalter [14].

Experimentally the vibrationally non-equilibrium systems was first reported in the early 1960’s when lasing on vibrational lines was observed by Patel and Kerl [8]. The laser gain medium was the positive column of an electric discharge in CO gases. Rich and Thompson [15] were the first to measure of the populations of the vibrational energy levels in these vibrational non-equilibrium systems. A side window allowed for the passage of the spontaneous emission from the vibrationally excited CO in the positive
column of the CO/He gas mixtures in a high-power laser. The vibrational distribution was inferred from the measured intensity of the CO fundamental. The following figure shows this distribution.

![Graph showing vibrational distribution](image)

**Figure 2.3:** Emission from the carbon monoxide fundamental, taken from the sidelight of a positive column [15].

Plotted on this graph are the results from the measured CO fundamental intensity spectra, as well as various Boltzmann (linear relations) plots at different temperatures. Clearly, the plotted vibrational distribution shows that the vibrationally excited CO is not in thermal equilibrium; and the distribution is non-linear as is noted that the measurements deviate from the Boltzmann relation. It should be noted that the populations of the higher
vibrational energy levels decrease rapidly. This should be compared to theoretical
distributions with no losses showing populations of the higher energy levels increasing.

2.2.2 Overview of Experiments in Optically Pumped Carbon Monoxide gas mixtures

Experiments with optically pumping of CO in nitrogen and argon gas mixtures
where CO absorbs the carbon monoxide laser radiation were first conducted by Rich and
Bergman [16]. In these experiments, the environments do not have free high-energy
electrons, providing a simpler system to study, though there is evidence of some low
ergy electrons [17,18,19]. The vibrational population distribution of the CO was
measured from the CO overtone spectra, which clearly showed a non-Boltzmann
distribution, validating the vibrational ladder climbing theories. Due to the decrease in
populations of the higher vibrational energy levels, the other right hand side terms in
Equation 2.7, such as the VT, VE and Chemistry terms are important to include for
accurate modeling. In addition, Rich and Bergman [16] found evidence of electronically
excited $C_2(A^3\Pi_g \rightarrow X^3\Pi_u)$ (Swan Band), and a strong ultra violet emission from the
$CN(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$. This is very important because it is direct evidence of gas phase
vibrationally activated chemistry occurring at low temperatures.

Additional CO optically pumped experiments have been done in different
environments where translational temperatures are kept cold, such as in cryogenically
cool liquids, with diatomics in a solid argon cryogenic matrices [20], and with diatomics
condensed on sodium chloride crystals [21]. For these experiments, the translational
temperatures are very cold, so the rate of transfer of vibrational energy to translational energies is slow. This allows for higher vibrational excitation, the vibrational temperatures are higher, which means higher populations at higher vibrational energy levels. Ewing et al. [22,23] have conducted experiments in high-density cryogenically cool liquid phases, where CO is dissolved in liquid argon, at 87 Kelvin. A carbon monoxide laser is used to vibrationally excite the CO in the liquid phase, and the emission from the CO overtone is measured. In these experiments, the CO vibrationally up pumped to levels, v=40, just as in the gas phase; the populations among the higher vibrational levels remain high, though they decrease rapidly after levels V = 35. Vibrational up pumping in CO has also been shown to occur in an argon matrix [24], as well as on surfaces [25]. While last two experiments investigate coupling of vibrational energy to phonons in the solids, they are interesting to study the VV, VT and VE energy transfers involving long-range interactions. An interesting phenomenon observed in the CO in the argon matrix was that emission from a forbidden transition CO(a^3\Pi \rightarrow X^1\Sigma^+) was observed. While this is the case for the liquid experiments, where there are higher densities yet collisions follow gas mechanisms, the corresponding VDF’s still rapidly fall in populations for vibrational levels v=35 and higher [22,23]. This could imply that there is energy transfer into an electronic state. However, in these liquid experiments, emission from the CO electronic states was looked for, but no signal was observed, which could be due to the optical thickness in the liquid mixtures.
2.2.3 Energy Transfer Rates in Vibrationally Excited Carbon Monoxide Gas Mixtures

Much of the research performed on non-equilibrium systems have been to investigate the validity of energy exchange theories, by comparing them to experimentally measured rates. Early experiments measuring rates were ultrasonic absorption and dispersion experiments; where adiabatic compression of the gases caused the temperature to increase [26]. The energy is then dispersed among the different modes of the molecules at different rates. The vibrational contribution to the specific heat for the gas mixture is dependent on the frequency of the ultrasonic wave, which gives information regarding the timescale for vibrational relaxation. Shock tube studies have also yielded information about vibrational relaxation times, where usually fluorescence from a diatomic was followed after the shock passed, increasing the temperature of the gas mixture [26]. These research projects have been attempts to determine the processes that occur during collisions, but have been confined to vibrational relaxation times. Essentially the overall V-T/R rates are inferred. The earlier work was not usually vibrational state resolved. More sophisticated experiments [7,9,18,27] have yielded more detailed information into other energy transfer processes, and their subsequent rates.

There are many processes occurring in the optically pumped CO/Ar mixtures, which were described earlier in Equation 2.7. The V-V rates, for CO are on the order of $10^{-12}$ cm$^3$/sec and increasing beyond $10^{-10}$ cm$^3$/sec with increasing vibrational quantum number [8,7]. These rates are faster than the V-T rates for comparable vibrational states, which for CO in He range from $10^{-18}$ cm$^3$/sec at low vibrational quantum number to $10^{-14}$ cm$^3$/sec for higher vibrational quantum numbers at low temperatures of 100 Kelvin [27].
These rates increase approximately an order of magnitude for each 100 degrees Kelvin increase in temperature. The V-T rates with helium as the diluent are the upper bound, while V-T rates for other diluents such as argon are even slower.

Helium is often added to the gas mixture to deliberately affect the populations of the upper vibrational energy levels, since the V-T rates of helium are fast. The following figure shows VDF’s inferred from CO overtone spectra taken from an optically pumped CO/Ar/He gas mixtures.

![Figure 2.4: Carbon monoxide vibrational distribution functions for various helium partial pressures [17,28].](image)

The figure shows the helium concentration varying from 0 to 97 Torr, while the CO remains constant at 3 Torr and argon made up the balance from 97 Torr to 0 Torr. The tail of the VDF, at high vibrational quantum numbers v>20 shown in Figure 2.4, corresponds to decreasing populations with increasing helium concentrations. This is due
to the effective relaxation of helium. This is an effective method that changes the vibrational distribution that has the overall effect of lowering the energy loading per molecule.

Energy transfer between two dissimilar molecules is also a process that is important in systems of diatomic mixtures where vibrational energy may be exchanged between them. Considering a mixture of only two diatomics, for simplicity, Equation 2.9 and Equation 2.10, which are the equations describing the analytical form of the vibrational distribution, can be written for each constituent in the mixture. Following the work of Treanor et al. [6], the equations for $\gamma$ for each diatomic may be written and are, for molecule A:

$$\gamma = \frac{E_i^A}{k_B \theta_B} - \frac{E_i^A}{k_B T}$$

Equation 2.11

And for the second diatomic, molecule B,

$$\gamma = \frac{E_i^B}{k_B \theta_B} - \frac{E_i^B}{k_B T}$$

Equation 2.12

Equating the $\gamma$, which are the same due to the same amount of vibrational energy into the system, and rearranging, the equation becomes:
\[
\frac{E_i^A}{\Theta_A} - \frac{E_i^B}{\Theta_B} = -\frac{E_i^B}{T} + \frac{E_i^A}{T}
\]

Equation 2.13

This equation shows if the characteristic vibrational energies, \(E_i^A > E_i^B\), then the vibrational temperatures, \(\Theta_A\) and \(\Theta_B\), will adjust so that the energy transfers into molecule B, the diatomic with the lower characteristic vibrational energy \([8,29]\). This is the basis for isotope separation where the vibrational energy is transferred into the heavier isotope \([30,22,23,31]\). This preferential energy loading into the heavier isotope has also been shown to occur in UV photolysis of CO to products such CO2, C2O and C3O2 etc., which were found to be enriched in the heavier isotope \([32]\).

Much more difficult to quantify are the VE (vibration-to-electronic) energy exchanges. The details of the mechanisms are not well understood, partly because there are some electronic states, such as the CO\((\alpha^3\Pi)\) a spin forbidden state, which do not readily radiate back to the ground state, and thus is difficult to determine its populated distribution. The CO potential energy for the first three lowest lying electronic states is illustrated in the following figure.
Figure 2.5: Potential energy of carbon monoxide, showing three electronic states [33].

Figure 2.5 shows the vibrational energy levels within the ground state potential energy for the diatomic CO as well as the first two lowest electronic states. From the figure, it can be seen that the first excited electronic state, CO(a^3Π) is nearly iso-energetic with vibrational levels 27 and up, while the CO(A^1Π) is nearly iso-energetic with vibrational levels 40 and up. Fluorescence from the CO(A^1Π) state indicates that there is energy transfer into this state. DeLeon and Rich [34] observed UV emission from the CO(A^1Π → X^1Σ^+(v=7)) transition, which was followed in time and was correlated to
measurements of the populations of selected vibrational levels. These time traces are shown in the following figure:

Figure 2.6: Time traces showing the populations of different vibrational energy levels, \( v=11,17,29,\text{and }35 \), and the electronically excited CO(A\(^1\Pi\)) as a function of time[34].

The time traces show emission from the CO(A\(^1\Pi \rightarrow X^1\Sigma^+ (v=7)\)) only when higher vibrational levels of the ground state of CO(X\(^1\Sigma^+)\) are populated above \( v = 35 \) [34]. However, the details of the mechanisms of the energy transfer are still not clear, for example two different mechanisms have been postulated: The first mechanism is the excitation by the collision of two vibrationally excited molecules, while the second is excitation by collisions with electrons [18,19,35].

Vibration-to-electron energy exchanges are difficult to quantify, due to difficulties in measuring the populations of these states. While it is known that the CO(A\(^1\Pi\)) state is
populated in vibrational non-equilibrium CO mixtures [34], the population of the CO(a^3Π) is more difficult to measure. However, examining experimental VDF’s, shown earlier, show a marked decrease in the vibrational population distribution at higher vibrational energy levels. Specifically the CO VDF has not been measured in levels above v=40, or 8 ev. This is just below the lowest vibrational energy level in the electronically excited CO(A^1Π) state. More specifically there is the evidence of a depletion of population at vibrational energy level V = 26 [36]. While experimentally populations for levels forty and higher cannot be measured from the overtone, due to interference by the fundamental, the numerical calculated VDF’s show that populations do decrease rapidly [9]. One possible reason for the decrease has been hypothesized to be a conversion into the CO(A^1Π) state which was known to be populated because of the measured 4^{th} positive bands [16]. VE transfer to the CO(a^3Π) state beginning at energy levels v=27 has been hypothesized, and has been considered to be a contribution to the energy loss causing the tail behavior [16,37]. However, because the CO(a^3Π−X^1Σ^+) state is a spin forbidden transition, and radiation is not observed. Thus it is difficult to determine accurately the mechanisms for the V-E energy transfer. Most recently optically pumped experiments conducted by Porshnev et al. [38] have postulated a kinetic rate for the V-E energy transfer from the ground state to the CO(a^3Π) to be 10^{-13} cm^3/sec.

The CO(a^3Π) state has been investigated by other means; additional experiments have been conducted by directly exciting ground state CO with UV (ultraviolet radiation) [32] or by electric discharges [39]. These experiments produced information about some
The CO($a^3\Pi$) state could be directly populated by UV radiation from an iodine lamp, and, as has already been mentioned, chemical products were studied [32]. Dunn et. al. [32] measured the products with time and measured a kinetic rate of $(1.2-1.4)\times10^{-12}$ [cm$^3$/sec]. These kinetic rates were also verified by Ivanov et al. [40], who measured the CO$_2$ produced in an electric discharge and measured a kinetic rate of $(1.4\pm0.6)\times10^{-12}$ [cm$^3$/sec]. Additional work by Ionik et. al. [39] studied the quenching of the CO($a^3\Pi$), excited by UV radiation, and measured a quenching rate of $0.8\times10^{-10}$ cm$^3$/sec [39]; These authors also measured the vibrational distribution of the quenched CO and their results show a distribution in vibrational levels between 8 and 12. The quenching of CO($a^3\Pi$) to vibrationally excited ground state CO was also measured by Dunn et al. [32], and they report a rate of $10^{-10}$ [cm$^3$/sec]. These rate are summarized in the following table:

<table>
<thead>
<tr>
<th>Authors with Ref. No.</th>
<th>Process</th>
<th>Experimental conditions</th>
<th>Reported kinetic rate [cm$^3$/sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ivanov et al. [40]</td>
<td>CO$_2$ production via CO($a^3\Pi$) state</td>
<td>Electric discharge</td>
<td>$(1.4\pm0.6)\times10^{-12}$</td>
</tr>
<tr>
<td>Dunn et. al. [32]</td>
<td></td>
<td>UV absorption</td>
<td>$(1.2-1.4)\times10^{-12}$</td>
</tr>
<tr>
<td>Ionik et. al. [39]</td>
<td>Quenching of the CO($a^3\Pi$) state</td>
<td>UV absorption</td>
<td>$0.8\times10^{-10}$</td>
</tr>
<tr>
<td>Dunn et al. [32]</td>
<td></td>
<td>UV absorption</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>Porshnev et al. [38]</td>
<td>Population of the CO($a^3\Pi$) state by two vibrationally excited CO molecules</td>
<td>Optically pumped Rate is determined by numerical fitting</td>
<td>$10^{-13}$</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of kinetic rates governing the population of the CO($a^3\Pi$) state.
This table summarizes the different major processes that are involved in the population of the CO($a^3\Pi$) state. There are three major processes that are considered: The two processes that cause the population of the CO($a^3\Pi$) state to decrease are the CO$_2$ production and quenching. The process that populates the CO($a^3\Pi$) state is by two vibrationally excited molecules, which may also involve mediation by free electrons [18].

2.3 VIBRATIONALLY ACTIVATED CHEMISTRY

Vibrationally activated chemistry in the gas phase has been studied for several simple systems [41], usually between an atom and a diatomic. In these cases, energy is delivered into the vibrational mode of the diatomic, and the enhancement of the reaction rate is measured. Below is a figure depicting such a chemical reaction between a diatomic and an atom [41].
Figure 2.7: The chemical pathway for the reaction of an atomic, A, and a diatomic, BC going to the diatomic, AB, and atomic, C [41].

This figures shows the energy pathway in this hypothetical exothermic reaction, beginning with the reactants, A and BC, on the left. Following the reaction coordinate, moving to the right, the reactants must overcome the activation energy, labeled $E_a$ before moving on to the products. This figure also shows the first vibrational level of the diatomic, which is to be excited by $h\nu$ radiation from a laser, and is higher than the activation energy. It is important to realize that one must consider the total energy in system, which implies that the products may also be vibrationally excited, as well as electronically excited. There are many different reactions that follow this pattern, $A + BC \rightarrow AB + C$, [41,42], and experiments show that their rates increase due to vibrational excitation. Two such reactions are:

$O + H_2 \rightarrow OH + H$
Reaction 2.1,

for which an increase by four orders of magnitude at 300 K was measured [42] and:

\[ \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H} \]

Reaction 2.2,

for which an increase by three orders of magnitude 300 K was measured [42]. However, predictability in the kinetic rates, as well as understanding the dynamics of these reactions is still elusive.

More difficult to understand are the reactions between two diatomics, because some of these reactions did not react to products. One such reaction is [41]

\[ \text{HD}(v=5) + \text{HD} \rightarrow \text{H}_2 + \text{D}_2. \]

Reaction 2.3

In this case, both of the bonds in the HD would need to be broken. Another reaction that was not enhanced with vibrational excitation is [41]

\[ \text{OH}(v) + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]

Reaction 2.4

It was noted that vibrational energy in the OH bond, was deactivated by the CO; the vibrational energy was transferred into the heavier molecule. However, there is
experimental evidence of some reactions between diatomics of being enhanced by vibrational excitation. Such as in the reaction [41]

\[ \text{OH}(v) + \text{H}_2(v') \rightarrow \text{H}_2\text{O} + \text{H} \]

Reaction 2.5

In these reactions, it has been shown that vibrational energy in either of the two diatomics increases the reaction rate. In addition, of the two enhanced reactions the rate of the reaction is the fastest if the vibrational energy is in the molecule with the bond to be broken, i.e. the \( \text{H}_2 \) bond. It is has also experimentally been observed that vibrational activated chemistry is taking place with the reaction [16]

\[ \text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}_2 + \text{C} \]

Reaction 2.6

This is of course the Boudouard or disproportionation reaction. The free carbon produced reacts very quickly to produce \( \text{C}_2 \). There are not many theories predicting the kinetic rates for these vibrationally activated reactions. However, one theory is based on transition state theory, where two \( \text{CO} \) molecules collide, and the vibrational energy quickly redistributes through out the dimer. The equation that represents this mechanism is as follows [43]
\[ k_{vw}^{CO_2} = Z(T) \left( \frac{h \omega_{CO}(v+w)-E_a}{h \omega_{CO}(v+w)} \right) \left( \frac{\omega_{CO}^2}{\omega_{CO}^2} \right) \theta \]

Equation 2.14

Where the \( \omega \)'s are the main frequency of the specified molecule, and \( \theta \) is a step function.

The term, \( E_a \), is the activation energy for the process, \( h \) is Planck’s constant, \( c \) is the speed of light, and \( v \) and \( w \) are the vibrational energy levels of the two carbon monoxides. The factor, \( Z(T) \), is the gas kinetic collision frequency as a function of temperature, \( T \), and is expressed as [9]:

\[ Z(T) \approx 3 \times 10^{-10} \left( \frac{T}{300} \right)^{1/2} \text{[cm}^3/\text{sec]} \]

Equation 2.15

Equation 2.14 illustrates that \( k_{vw}^{CO_2} \) approaches the gas kinetic collision frequency as the sum of the energy of the vibrational levels \( V \) and \( W \) exceeds the activation energy. For one particular configuration, the carbon of one of the diatomics is stretched so far that it dissociates, leaving \( CO_2 \) and free C.

The Boudouard reaction is the reaction of two CO molecules colliding to produce \( CO_2 \) and free C. This reaction has been known to occur on surfaces at high temperatures. Specifically, in this reaction, one of the carbon monoxide reactants is absorbed onto the surface, and reacts with a gas phase CO as it approaches the bound diatomic [44]. In these surface reactions, the temperatures are high and the activation barrier is reduced. However, the activation energy, in the gas phase, has not been directly measured, and the
best estimate is based on the reactions of CO($a^3\Pi$) with CO to yield CO$_2$ as described earlier, which gives an activation energy of $6 \text{ ev}$ [32,39]. This activation energy is much lower than the expected dissociation energy of $11 \text{ ev}$. There have, however, been efforts to observe direct dissociation of CO in the gas phase.

As we have noted in the previous section, CO has a deep potential well, with dissociation energy, of $11.09 \text{ ev}$, which corresponds to approximately $129,000 \text{ K}$, which makes it difficult to dissociate directly by Reaction 2.7 below. CO is, indeed, the strongest bound diatomic. Early shock tube experiments, were performed at very high temperatures ranging from $7000 \text{ K} – 15000 \text{ K}$, in various amounts of CO. These experiments were attempts to measure the rate of the direct thermal dissociation of CO, i.e. the reaction:

$$\text{CO} + \text{M} \rightarrow \text{C} + \text{O} + \text{M}$$

Reaction 2.7

Appleton et al., see Ref. [45], conducted experiments with 2% CO diluted in Ar. Their experimental results obtained an activation energy of $\sim 8 \text{ ev}$, lower than the originally assumed $11 \text{ ev}$. Another key feature of the shock tubes experiments is an observation of an induction time in experiments by Faribairn [46]. The induction time is several times that of the characteristic vibrational relaxation times. In these experiments, the reactant CO and products C$_2$ and C were followed, and emission from the CO fundamental at $4.6 \mu\text{m}$ found to be constant for five to ten vibrational relaxation times [46]. The author
concluded that the dissociation of CO was not a simple one step process, and considered a transition into one of the electronic states, the CO($a^3\Pi$); which lies in the 6ev to 8 ev range. As in the earlier experiment, the CO was diluted in argon, and the temperature ranged from 6000 to 11000 K. Later experiments were performed in pure CO mixtures [47], which reported much higher kinetic rates, by a factor of 10, and one group reported no incubation time [47]. A summary of the experimental data is presented in the figure below taken from Ref. [48].

![Figure 2.8: Reaction rate data for various experiments performed in shock tube data. Dashed lines are for experiments in pure CO [48].](image)

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This graph shows the experimental kinetic rates, where the values range from $10^{13}$ cm$^3$/mole-sec to $10^6$ cm$^3$/mole-sec, which corresponds approximately to $k = 1.66 \times 10^{-11}$ cm$^3$/sec to $1.66 \times 10^{-18}$ cm$^3$/sec. Arrhenius fits to the experimental data yield extreme inverse temperatures dependencies in the pre-exponential factor. This has been considered to be non-physical and are indicative that other mechanisms are present rather then single CO collision events [47]. The most extreme inverse-temperature pre-exponential factor fit is in the fitting expression of Hanson [47]:

$$k = 8 \times 10^{38} \ T^{-5.5} \ exp(-1.20 \times 10^5/T) \ [\text{cm}^3/\text{mole*sec}],$$

where $T$ is the temperature in Kelvin. However, the exponent $n = -5.5$ for the temperature in the pre-exponential factor is differs greatly form simple collision theory, which gives $n = -0.5$. Hanson noted that fitting an Arrhenius equation to the data without a pre-exponential temperature dependency was with an activation energy of 7.2 ev [45]. Similarly Appleton et al. [45] also calculated an Arrhenius representation to the data excluding the pre-exponential temperature and was able to fit the data with and activation energy of 8.48 ev.

In reviewing these thermal “dissociation” experiments, and reviewing previous work on vibrational up-pumping of CO, it is questionable if any of the shock tube data measures the direct dissociation rate (processes described by Reaction 2.7) without being compromised by the gas-phase Boudouard disproportionation process (Reaction 2.6). All work in V-V pumped CO systems, whether in electric discharges [15,49] or in optically pumped CO, Rich and Bergman [16], and Deleon and Rich [34], show that the CO cannot
be vibrationally excited to levels above $V \approx 40 (~8 \text{ ev})$. Though there are approximately an additional 40 bound vibrational states with energies extending above $v=40$, up to the 11.09 ev dissociation energy, these states have not been observed to be populated. Indeed in Deleon and Rich, and Plonjes et al. [34,18] it is seen that if CO is excited to $V \approx 40$, rapid energy transfer into the CO($A^1\Pi$) excited electronic state occurs. CO($A^1\Pi$) decays rapidly by the CO 4$^\text{th}$ positive (CO($A^1\Pi \rightarrow X^1\Sigma^+$) transitions (lifetime ~ 10 nsec [34]), and this fast channel appears to effectively preclude higher level CO vibrational excitation. In addition, the gas phase Boudouard process, and energy transfer into CO($a^3\Pi$), has been observed where the CO($X^1\Sigma^+$) is excited to levels as low as $V \approx 25 (~6.0 \text{ ev})$. The work in this dissertation reinforces the thesis that free carbon production in high enthalpy CO is not due to direct dissociation of the ground state, but of very high vibrational levels. This issue is treated at length in this dissertation.

2.4 VIBRATIONALLY ACTIVATED HETEROGENEOUS REACTIONS

Less is known about the effects of vibrationally exciting the reactant when it proceeds to react on surfaces. There have been some studies [50,51] that have shown that some vibrational energy can be converted to kinetic energy, and promoting dissociation of the reactant. Mechanisms and kinetic rates with vibrationally excited molecules and surfaces have been studied for many different chemical [50] and physical [52] processes. The emerging result has been that excitation of the vibrational modes of molecules aid in promoting the reaction process. Some of the physical processes studied have shown increase in: sticking probability, dissociative chemisorption, and chemical rates of
reaction over surfaces. There is also evidence of non-equilibrium V-V energy exchange processes of the vibrational mode between molecules adsorbed on surfaces [53]. Experiments where these processes have been observed have been done in systems where the kinetic or thermal energy is kept low. Chemistry studied in this environment can yield much information regarding the mechanisms underlying surface chemistry.

Studies [50] focusing on the effect of vibrationally excited molecules interacting with surfaces, have demonstrated an increase in adsorption of molecules, and observed a lack of dependency on translational mode energy. The authors propose that the molecule is stretched due to the vibrational excitation, which then distorts the electron cloud, and could possibly affect chemical properties. To study this effect, vibrationally (v=13, and v=15) excited nitric oxide was created, and scattered from an oxygen-covered copper surface [50]. Scattered nitric oxide was monitored. The results showed that the vibrationally excited nitric oxide had an increase in the sticking coefficient by three orders of magnitude when compared to the ground state, independent of initial translational energy.

An additional mechanism that should not be overlooked, given the energy in the vibrationally excited diatomics, is dissociative chemisorption. The mechanisms for the methanation reaction over a nickel catalyst were studied at low pressures. This reaction depends on the dissociation of CO and cannot proceed, even though it was thermodynamically favored [54]. Additionally, it was reported that, at these low pressures, increasing the kinetic energy of carbon monoxide (done in molecular beam studies) did not increase the probability of dissociation. To develop a mechanism to
explain the problem, the dissociative chemisorption model originally proposed by Lennard-Jones was used. This is illustrated in the potential diagram shown below in Figure 2.9:

![Figure 2.9 Schematic diagram of the potential energy of dissociative chemisorption as a function of the distance between the center of mass of the molecule, AB, and the surface as a function of distance, d, [54].](image)

The diagram illustrates the interaction between the molecule AB and the surface as a function of distance, d, between them. The molecule physically adsorbs on the surface, represented by the smaller potential well, and the molecule remains in the shallow well if there is not enough available energy. However, if there is enough energy, then the reaction can proceed over the activation barrier, and the molecule undergoes dissociative chemisorption on the surface. A “chemical hammer” was later proposed as the catalyst for dissociation, where an inert gas atom collides with a physisorbed molecule, transfers
its energy, and causes dissociation [50]. Also reported was that the excitation of the low frequency vibrational mode of Ni-CO aided the dissociation rate [50,54]. The modeling of this mechanism assumed that the vibrational excitation occurs after physical adsorption by the collision of an inert molecule. However, others have proposed other mechanisms that study the mechanism of vibrationally excited molecules impinging on a surface.

The second common kinetic model for surface reaction is the Eley-Rideal mechanism. There is evidence for an Eley-Rideal type of mechanism between adsorbed CO on iron oxide surfaces and gas phase CO, which has been presented in [55]. Arguments using energy and geometry of surfaces have lead the authors to conclude that the Boudouard reaction takes place on FeO surfaces. Gas phase CO, labeled as C1O1, collides linearly with molecularly adsorbed CO, labeled as C2O2, as is shown in the following figure:

![Figure 2.10](image1)

Figure 2.10: A schematic of a gas phase CO molecule labeled as C1O1 colliding linearly with an adsorbed CO molecule [55], labeled as C2O2.

![Figure 2.11](image2)

Figure 2.11: A schematic showing the products, carbon dioxide, labeled C1O1O2, after the collision [55], leaving a carbon atom C2, on the surface.
As is seen in Figure 2.11, carbon dioxide desorbs leaving behind a carbon atom adsorbed to the surface. The authors also consider the possibility of gas phase CO reacting with the lattice oxygen and concluded that it would be energetically unfavorable.

A summary of the mechanisms and a single model representation can now be postulated: Two predominate mechanisms that guide surface reactions are the Langmuir-Hinshelwood and the Eley-Rideal. The Langmuir-Hinshelwood mechanism represents reactions that take place between adsorbates, while the Eley-Rideal mechanism represents reactions between gas phase reactants and adsorbed reactants. The focus will be on the analysis of surface reactions for the conversion of CO to CO$_2$ on oxidized surfaces. Additional mechanisms are included in the surface reaction model, because of the vibrational energy available in the molecules. These mechanisms are dissociative chemisorption and the Boudouard reaction. The oxidation of CO to CO$_2$ then can be written as follows:

$$O_2 \rightleftharpoons O_{2,ad} \rightarrow O_{ad} + O_{ad}$$  \hspace{1cm} \text{adsorption and dissociation of oxygen, with overall forward rate } k_1.  \hspace{1cm} \text{Reaction 2.8}

$$CO + * \rightleftharpoons CO_{ad}$$  \hspace{1cm} \text{with reaction rates, } k_{ad} \text{ and } k_{des} \text{ for adsorption and desorption of CO.}  \hspace{1cm} \text{Reaction 2.9}

$$CO_{ad} + * + M \rightleftharpoons C_a + O_{ad} + M$$  \hspace{1cm} \text{with reaction rate, } k_{f,3} \text{ and } k_{r,3} \text{ for the forward and reverse rates, a dissociative process, after being physisorbed, dissociative chemisorption, , where } M \text{ is any participating molecule.}  \hspace{1cm} \text{Reaction 2.10}
CO\textsubscript{ad} + O\textsubscript{ad} ⇌ CO\textsubscript{2} + 2\text{*} \quad \text{with reaction rate, } k_{f,4} \text{ and } k_{r,4} \text{ for the forward and reverse rates, a Langmuir-Hinshelwood type of reaction.}

Reaction 2.11

CO + O\textsubscript{ad} ⇌ CO\textsubscript{2} + \text{*} \quad \text{with reaction rate, } k_{f,5} \text{ and } k_{r,5} \text{ for the forward and reverse rates, a Eley-Rideal type of reaction.}

Reaction 2.12

CO\textsubscript{ad} + CO ⇌ CO\textsubscript{2} + C\text{ad} \quad \text{with reaction rate, } k_{f,6} \text{ and } k_{r,6} \text{ for the forward and reverse rates, the Boudouard reaction.}

Reaction 2.13

Here the nomenclature, ‘ad’, represents the molecule adsorbed to a site, ‘\text{*}’. In the present case, we have no gas phase O\textsubscript{2} and “Oad” is merely the concentration of chemisorbed oxygen with the metal, which is a constant parameter that can be varied. Reaction 2.8, Reaction 2.9, Reaction 2.11, and Reaction 2.12 are the typical mechanisms used to describe the oxidation of carbon monoxide to carbon dioxide [56]. The additional two reactions, Reaction 2.10 and Reaction 2.13, represent possible dissociative adsorption and the Boudouard reaction; they are included due to the excess energy in the carbon monoxide vibrational modes. These two mechanisms have been observed to occur in systems with large vibrational energy, and will be described in this section. The rate-limiting step for the oxidation of carbon monoxide is the dissociation of oxygen, rather than the adsorption of molecular oxygen. However, for our purposes, the catalysts used in these experiments will already be oxidized, to simplify the experiments; and the concentration of adsorbed oxygen will be considered to be constant. The next step in the
process is the actual chemical reaction, which takes place on the surface by the adsorbed reactants to create the products.

A rate of reaction, R, can be written if the following assumptions are made: The first is that the forward rates in Reaction 2.11, Reaction 2.12, and Reaction 2.13, the production of CO\textsubscript{2}, are large compared to the reverse reactions; thus the reverse reactions can be neglected. The next assumption is known as the Langmuir adsorption isotherm, which is that the adsorption and desorption processes of the carbon monoxide is at steady state. Thus the rate of change of [CO\textsubscript{ad}] adsorbing is approximately zero. This can be interpreted as that the number of molecules being absorbed is also being desorbed, and that this quasi steady state can be reached rapidly. The same assumption will be applied to the vibrationally excited molecules. If \( \theta \) represents the fraction of the surface taken by absorbates, then 1- \( \theta \), represents the fraction of the sites available on the surface which can be written as:

\[
[\text{CO}_{\text{ad}}] = S_0[\theta]
\]

Equation 2.16

Where \( S_0 \) is the total number of surface sites available for adsorption by CO. An expression for \( \theta \) as a function of gas pressure can be determined and is written as:

\[
\theta = \frac{K [\text{CO}]}{K [\text{CO}] + 1}, \quad \text{where} \quad K = \frac{k_{\text{ads}}}{k_{\text{des}}}
\]

Equation 2.17
An expression for the rate of the reaction can be determined generally in terms of $\theta$ and can be written as:

$$ R = \left. \frac{\partial [CO_2]}{\partial t} \right|_T = k_{f,4} S_0 \theta [O_{ad}] + k_{f,5} [CO] [O_{ad}] + k_{f,6} S_0 \theta [CO] $$

Equation 2.18

If Reaction 2.8 is excluded, and Equation 2.17 is used for $\theta$ then the rate of reaction can be written as:

$$ R = \left. \frac{\partial [CO_2]}{\partial t} \right|_T = \frac{k_{f,4} S_0 K [CO]}{1 + K [CO]} [O_{ad}] + k_{f,5} [CO] [O_{ad}] + \frac{k_{f,6} S_0 K [CO]}{1 + K [CO]} [CO] $$

Equation 2.19

Where $K$ is the ratio of $k_{ad}$ to $k_{des}$. The three terms each represent respectively the last three mechanisms producing $CO_2$, mentioned earlier, Reaction 2.11, Reaction 2.12, and Reaction 2.13. Several observations of Equation 2.19 regarding the fraction of available sites, and the concentrations of both the gas phase CO and the adsorbed oxygen should be noted. Only the first and last terms on the right hand side of Equation 2.19 depend on the fraction of available sites. The concentration of adsorbed oxygen, which could be varied, appears only in the first and second terms. The numerator in the third term in Equation 2.19 shows a second order reaction in gas phase CO. Furthermore, the rate of adsorption, $k_{ad}$, is directly proportional to the sticking probability, thus if excited vibrational energies of diatomics increases the adsorption then the constant, $K$, will increase, and hence the
more carbon monoxide molecules will be adsorbed. For convenience of discussion, the terms in Equation 2.19 may be regrouped and is:

\[
R = \frac{\partial [\text{CO}_2]}{\partial t} = k_{f,5} [\text{CO}] [\text{O}_{ad}] + \frac{k_{f,6} S_o K [\text{CO}] [\text{O}_{ad}] + k_{f,6} S_o K [\text{CO}] [\text{CO}]}{1 + K [\text{CO}]}
\]

Equation 2.20

The rewritten expression, Equation 2.20, allows for the direct comparison between the Langmuir-Hinshelwood mechanism (Reaction 2.10) and the Boudouard reaction, (Reaction 2.13), both of which depend on the surface sites for absorption, \( S_o \), and adsorption rates (or the sticking probability). The last term in Equation 2.20 represents the Boudouard mechanism, and is second order (quadratic) in CO concentration while the Langmuir-Hinshelwood mechanism, the middle term on the right hand side is only first order, or linear. Clearly with increasing CO concentrations, the Boudouard mechanism should dominate given that the other parameters are held constant. Experimentally this is difficult to test at these translational temperatures, since the Boudouard reaction, is dependent on energy portioned into the vibrational mode of the reactant. Increasing the CO concentration would decrease the energy loading per reactant. This decrease in energy loading would have the effect of lowering the fraction of molecules that would have the appropriate minimal energy, and thus less \( \text{CO}_2 \) would be produced. In this dissertation, the heterogeneous model will be examined in experiments in which vibrationally excited CO diffuses to CuO surfaces and the energy loading in the reactant is varied by the addition of helium.
References:

CHAPTER 3

GAS PHASE EXPERIMENT

3.1 EXPERIMENTAL SETUP

The experimental setup for the gas phase section consists of three main parts: The carbon monoxide laser, the experimental flow reactor and the optical setup. These components are illustrated below in Figure 3.1.

Figure 3.1: Gas Phase Experimental Setup
Infrared radiation from the carbon monoxide laser is focused, by a one-inch diameter with an eight-inch focal point, CaF$_2$ (calcium fluoride) lens into the continuous flow reactor, which contains the test gas mixture of CO (carbon monoxide), He (helium), and the diluent Ar (argon). These gases are regulated by rotameters upstream of the flow reactor, also shown in the figure. The products, from the reaction, flow out of the reactor, and pass through an absorption cell (shown in Figure 3.1), mounted in a Fourier transform spectrometer. Carbon dioxide, a product, is monitored in absorption by the spectrometer. Concurrently with the absorption measurements, emission from the fundamental and overtone of the carbon monoxide is measured by a monochromator. These emission spectra measure the populations in each vibrational level from which the VDF (vibrational distribution function) described earlier in Chapter 2 and the temperature of the gases are calculated. The VDF and the gas temperatures are correlated with the amount of the CO$_2$ (carbon dioxide) produced.

3.1.1 The Carbon Monoxide Laser

The carbon monoxide laser, used to vibrationally excite the room temperature CO in the test cell, is a liquid nitrogen cooled gas laser capable of lasing on several lines in broadband mode. Typically the gas mixtures and discharge conditions are optimized to produce as much power as possible on the $v=1 \rightarrow 0$ and $v=2 \rightarrow 1$ lines for best absorption by the room temperature carbon monoxide in the test cell. A typical output from the laser is shown below in Figure 3.2.
Figure 3.2: Laser Spectrum of Carbon Monoxide Laser (Total power ~13 Watts)

This figure shows the strongest, sixteen, lines of the carbon monoxide infrared laser radiation, ranging from 2060 cm$^{-1}$ to about 1850 cm$^{-1}$. Based on the relative peak heights of the different laser lines in Figure 3.2, approximately 0.3 milliwatts on each of the lower two lines is estimated. The laser operates typically at total powers of 13 to 14 Watts.
The carbon monoxide laser consists of three concentric glass tubes to separate three different environments. The different components are of the carbon monoxide laser are illustrated below in Figure 3.3.

![Diagram of the Carbon Monoxide Laser Tube](image)

Figure 3.3: Diagram of the Carbon Monoxide Laser Tube.

The innermost tube is the heart of the laser that contains the laser gain media, the positive column of the glow discharge also commonly referred to as the bore. This tube is approximately one inch in diameter and two meters long and has two CaF$_2$ (calcium fluoride) windows at Brewster angles at either end. A liquid nitrogen bath surrounds the bore and is contained within a second concentric tube, which is large enough to contain cooling coils wrapped around the bore. The third, most outer, concentric tube is the outside of a vacuum jacket that is used to insulate the liquid nitrogen fill. Due to the several different temperatures that the main bore experiences, there are bellows, not
shown, on either end of the tube, where the two outer tubes are joined to the bore. The main tube contains four gas inlets, two at either end of the tube, and one outlet in the center. One set of inlets, the two most outer ones, is for the purge gases, which, as shown, flow past the cathodes. The second set is for the main nozzle flow where the gases flow through a set of cooling coils that curl around the bore, and sit in the liquid nitrogen bath. All the gases flow out of one exit, at the center of the tube, past the anode, and on to the vacuum pump.

The gas mixture for the operation of the carbon monoxide laser tube contains He (helium), N\textsubscript{2} (nitrogen), CO (carbon monoxide) and air. These gases are separated into the nozzle flow and purge flow. Only helium and nitrogen are in the purge flow, which is necessary to prevent partially relaxed, gain spoiling CO from entering the ends, which sit outside the discharge and the liquid nitrogen cooled portion of the bore. The main nozzle flow contains all the gases, and flows through the cooling coils prior to injection into the main bore, bringing the gas temperature down 77 Kelvin. The cooling is necessary to keep the translation temperatures low to meet the gain criteria, as was discussed earlier in Chapter 2. The gas mixture and power conditions in the positive column of the laser tube that were used for these experiments are summarized in Table 3.1, below. The pressures were measured with a MKS Baratron pressure transducer, Model number: 122A.
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<th>Gas</th>
<th>Pressure [Torr]</th>
<th>Power Supply</th>
</tr>
</thead>
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<td>Voltage = 12.25 KV</td>
</tr>
<tr>
<td>Nitrogen Nozzle</td>
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<td>Current = 19.8 milliamps</td>
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<td>Helium Purge</td>
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<td>Laser Power = 14 Watts</td>
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<td>Nitrogen Purge</td>
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<td></td>
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<td></td>
</tr>
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<td>Trace</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Gas composition of the carbon monoxide laser for operation on the lower lines.

Figure 3.3 shows the anode at the center of the tube, where the exhaust gases exit the laser, and the two cathodes at either end of the tube. The power supply is operated in reverse polarity, because the discharge was found to be more stable in that configuration [1]. The power supplied to the positive column of the carbon monoxide laser is reported in Table 3.1.

3.1.2 Experimental Conditions

The test gas mixture passes through the flow reactor, which is a six-arm glass cell with a total volume of approximately 112 cm$^3$. Attached to the four horizontal arms of the cell are windows made of calcium fluoride (CaF$_2$); which transmits mid infrared radiation. As is illustrated above in Figure 3.1, two of the cell arms allow the passage of infrared emission from the carbon monoxide laser beam, and the other two horizontal
arms, perpendicular to the laser beam, allow for the passage of the infrared radiation from
the fundamental and overtone bands of the vibrationally excited carbon monoxide.

The test gasses used in the flow reactor are Matheson HP grade CO carbonyl free,
contained in an aluminum cylinder to prevent any reactions with the iron in steel
cylinders to form the carbonyls. The assays for these gases are given in appendix B. The
gases were used in experiments without any additional purification. There are two inlets
for the gases into the flow reactor: Most of the argon is admitted into the cell near the
window for the entrance of the carbon monoxide laser beam. The argon injection near to
the carbon monoxide laser beam inlet prevents cold CO from collecting at the entrance
window for the beam, preventing absorption of the carbon monoxide laser beam radiation
until further downstream in the cell. The reaction volume is further downstream of this
mixing region, and is positioned in front of the window passing the radiation to the
monochromator. The pressures in the test cell were measured with a MKS Baratron
pressure transducer, model number 635A. Test gas mixtures were with varying amounts
of Ar and He diluents. In general, the CO partial pressure was held constant at 12 Torr,
while the helium partial pressure was varied from 0 to 15 Torr. The argon made up the
balance, keeping the total pressure constant at approximately 130 Torr. The bulk of the
flow rate is of the argon gas at an approximately of 16.0 cm$^3$/sec. This is measured by
rotameters positioned upstream of the glass cell. The mass flow rate of the carbon
monoxide was very small only ½ % of the total flow rate, and the helium varied from 0 to
5 cm$^3$/sec. With these flow rates, the residence time in the reaction zone is quite long, ~5
seconds over the experimental flow rate range. Mixing is complete in the reaction zone.
The experimental conditions, component partial pressure and flow rates are summarized in Table 3.2 below. The first column is only the line number put in for reference. The calculated integrated absorption of the carbon dioxide produced is also included, for clarity, but will be discussed in the following section.
<table>
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Table 3.2: The experiment flow conditions for the gas phase experiments
The last line of Table 3.2 summarizes data for runs with the CO concentration reduced by 50% ($P_{CO} = 6$ Torr). Each of the rotameter readings of the different components were converted to the volumetric flow rates by using the calibrations provided by the manufacturers of the flow meters. For completeness, the parameters used in the equation for the conversion, which also includes a backpressure correction and are presented in appendix C.

All the product gases flow through one exit from the reaction. These products pass through approximately 4 feet of plastic tubing before entering the Fourier transform spectrometer. This length more than assures that the gas temperature in the absorption cell is equilibrated to room temperature. The glass absorption cell is fixed inside the spectrometer. The carbon dioxide produced in the cold optically pumped plasma is measured in this cell by an absorption method, using a 66 IFS Bruker spectrometer Fourier Transform Spectrometer (FTIR). The spectrometer is capable of resolving lines 0.25-cm$^{-1}$, however only a resolving power of 4-cm$^{-1}$ was used for the experiments, as it was not necessary to resolve the rotational lines of the carbon dioxide. The absorption cell is a seven-inch long, one-inch diameter Pyrex tube, sealed at each end by CaF$_2$ windows.

3.1.3 Instrumentation

The number density and the production rate of the CO$_2$ is determined from the cell absorption measurement and from pressure and flow rate measurements for the
reactor. Measurements for the FTIR absorption spectra of carbon dioxide produced were calibrated against absorption spectra of known number densities. The calibration measurements were performed with air, since the make up of dry air is known to contain, consistently, 3% carbon dioxide [2]. The partial pressures of the air in the flow reactor, and volume of the flow reactor was calculated. From ideal gas law, using room temperature, the number densities of the carbon dioxide could be calculated, after correcting for the humidity. Absorption spectra were taken for the different partial pressures of air in argon for a consistent total pressure of 130 Torr. Integration of the FTIR absorption spectra of the carbon dioxide asymmetric stretch was calculated and correlated with the calculated number densities. Initially calibrations were attempted with carbon dioxide from a cylinder; however, the flow could not be regulated to small enough of a partial pressure that would more accurately represent the amounts being produced in the plasma.

Absorption measurements were performed in the absorption chamber of the spectrometer, which was purged. A commercial purge by Puregas, model PCDA, was used to remove water and excess carbon dioxide from the system. However, it was found that there were still substantial amounts of carbon dioxide in the system. Since it was necessary to reduce this even further, additional purging was done. This consisted of wrapping the spectrometer with plastic, and inserting into the spectrometer a tube to carry molecular nitrogen from a cylinder. Shown in the following figure is an absorption spectrum of the carbon dioxide in the FTIR.
The absorption measurement is taken with an internal glow bar source, with an Indium Antimony detector. Figure 3.1 is a black body spectrum of the glow bar source with the absorption by the carbon dioxide. The figure shows that without the additional nitrogen purge, some carbon dioxide still resides in the spectrometer. However, just after a minute of purging it decreases rapidly, while additional purging for twenty minutes decreases the amount of carbon dioxide even more. Thus, the purge was run for twenty minutes before the experimental runs, and continued throughout the experiments.

The fundamental and overtone infrared radiation from the vibrationally excited carbon monoxide was collected by an off-axis parabolic mirror and focused into a 340E Spex monochromator. This is a 0.34-meter long spectrometer with a dispersive grating
blazed at four microns. This is adequate to resolve the rotational lines of the fundamental, which were separated by approximately 10 nm, although there was interference and overlap from neighboring rotational J lines. For the case of the carbon monoxide overtone, the resolution was not capable for resolving the rotational lines, so only the vibrational lines were measured.

The monochromator is a dispersive instrument and the grating turns on its center, a Czerny-Turner mount, to bring a particular bandwidth with center at wavelength, $\lambda$, with a to focus at the exit slit. However, due to the dispersive nature of the grating, one band may be observed several times, or orders. The relationship between the order observed and the angles of the radiation is described by the grating equation:

$$m\lambda = d(\sin \alpha + \sin \beta)$$

Equation 3.1

Where $m$ is the order, $\lambda$ is the wavelength of the band center, $d$ is the size of a groove of the grating, and the angles $\alpha$ and $\beta$ are the angle of incidence and of diffraction respectively. It is important to note that due to the production of the different orders by the grating there was concern that the next order of the signal from the second overtone would interfere with the signal of the first overtone. Thus, a filter to remove any signal from the second overtone was placed in the emission path during the measurements of the overtone. The transmittance spectrum for this filter is shown below in
While this spectrum still shows some transmittance at the low wavelengths, between one and two microns, the signal from the second overtone is diminishing. So this combination should decrease the contribution from the signal from the second overtone to the first overtone, which is approximately between two and four microns.

3.2 RESULTS

The results presented here are the specific rate of the gas phase Boudouard disproportionation reaction measured as a function of the level of vibrational excitation of the CO (carbon monoxide) reactant. The experiments were constructed to monitor: 1) The CO produced in the flow reactor, 2) the vibrational energy distribution of the excited
CO reactant and 3) the temperature of the gas in the reaction zone. The section begins with the presentation of the absorption spectra used in determining the number densities of the carbon dioxide. Secondly, we show the overtone emission spectra of the CO, from which the vibrational distributions are extracted. Finally, the rotationally resolved fundamental band of the vibrationally excited CO is presented, from which the rotational and translational gas temperatures are determined. Each of these measurements was performed for different amounts of helium partial pressure, which depopulate the upper vibrational levels. The different experimental conditions, the flow rates and gas mixtures, were presented earlier in Chapter 3, the experimental section.

3.2.1 Carbon Monoxide Production Measurements

Absorption by the asymmetric stretch of CO$_2$ (carbon dioxide) at 2349.15 [cm$^{-1}$] in the infrared was measured by a Fourier Transform spectrometer, as was described earlier in Chapter 3. Each experiment was performed for a given helium partial pressure. A typical absorption spectrum is shown below in Figure 3.6.
Figure 3.6: Absorption spectrum of the asymmetric stretch of carbon dioxide produced by the gas phase Boudouard reaction.

Shown in the figure are the P and R branches of the carbon dioxide fundamental, with the R branch, $\Delta J = +1$, at higher energy, the right-most lobe. The area of the experimental spectra is calculated, as described and presented in Table 1 in Chapter 3, and is then correlated to the calculated areas of the known amounts of carbon dioxide. The resulting calculated number densities of the carbon dioxide produced in the cold optically pumped plasma are presented in the following Figure 3.7 below as a function of helium partial pressure.
Figure 3.7: Number density of the carbon dioxide produced in the thermally-cold vibrationally excited carbon monoxide with helium and argon gas mixtures.

Figure 3.7 shows the production of the carbon dioxide monotonically decreasing form approximately $14 \times 10^{14}$ cm$^{-3}$ to $2.5 \times 10^{14}$ cm$^{-3}$ as the helium partial pressure increases (solid circles). The CO partial pressure was held constant for these data at $P_{CO} \approx 12$ Torr. Also shown (open circle) is the production rate with the CO partial pressure reduced to 6.4 Torr. These data indicate that the CO$_2$ production rate is second order in the CO concentration, i.e., the Boudouard gas phase disproportion shown in Chapter 2. We infer an overall specific rate, $k_{overall}$, for this reaction from
\[ \frac{d[CO_2]}{dt} = [CO_2] \frac{(UA)}{V_{\text{reaction\ zone}}} = k_{\text{overall}} [CO][CO] \]

Equation 3.2

Where, \([CO_2]\) and \([CO]\) are, respectively, the number densities \([\text{cm}^{-3}]\) of the carbon dioxide product, in the absorption cell, and of the carbon monoxide reactant, in the reactor. The product \((UA)\) is the volumetric flow rate \([\text{cm}^3/\text{sec}]\), where \(U\) is the velocity of the flow and \(A\) is the cross sectional area, and \(V_{\text{reaction\ zone}}\) is the volume of the vibrationally pumped reactant in the reactor. This reaction volume is defined by the visible emission from the vibrationally pumped plasma. The visible radiation is almost entirely due to Swan band \(A^3\Pi_g \rightarrow X^3\Pi_u\) transition) emission from electronically excited \(C_2\). The radiative lifetime of this transition is 3.16 µsec, and the electronic excitation is supplied by transfer from the CO reactant pumped to levels \(v \geq 25\) [3]. Any electronically excited \(C_2\) that diffuses out of the reaction volume decays almost immediately, so the emission volume is essentially equal to the volume of vibrationally prepared reactant. In results reported in this chapter, the emission volume is approximately 10 cm length with a 1 mm diameter. This emission volume remained constant for the runs reported here, although diminishing in radiative intensity with the addition of He. These dimensions give a reaction volume \(V_{\text{reaction\ zone}} = 0.08\ \text{cm}^3\), which value is used to infer \(k_{\text{overall}}\) using Eq.1 above. It should also be noted that back reaction is not included in Eq.1, as the nascent C product of the Boudouard reaction is immediately removed by subsequent processes resulting in \(C_2\) and other carbon suboxide products. The specific rate, \(k_{\text{overall}}\), calculated for runs with varying amounts of helium using Equation 3.2 above is plotted
against helium partial pressure in Figure 3.8 below. The overall kinetic rate, $k_{\text{overall}}$, is in [cm$^3$/sec]. The results of these calculations as a function of helium partial pressure are presented in the following Figure 3.8:

![Overall Kinetic Rate as a Function of Helium Partial Pressure](image)

Figure 3.8: Calculated kinetic rates of the production of the carbon dioxide produced from the gas phase Boudouard reaction, as a function of helium partial pressure.

3.2.2 Carbon Monoxide Reactant Vibrational Energy Distribution

Figure 3.8 shows that the overall kinetic rate decreases monotonically with the addition of helium. The addition of helium decreases the number of highly vibrationally
excited CO molecules. These rates of Figure 3.8 can be further correlated with the available energy in the vibrational mode of the system, to be discussed later, which are determined from the overtone spectra.

Vibrational distribution functions were calculated from overtone emission spectra that were measured for three different helium partial pressures, zero, ten and sixteen Torr, and are shown below in Figure 3.9. The CO overtone, with $\Delta V = 2$, ranges approximately from 2.3 microns to 4.7 microns, which is in the mid-infrared range.

![Figure 3.9: Carbon monoxide overtone emission for three different values of helium partial pressure.](image)
The vibrationally excited CO radiates from each vibrational level for different rotational quantum number changes $\Delta J = \pm 1$, which correspond to the P and R branches. Since there are from twenty to forty vibrational states radiating, this gives a rich 1st overtone spectrum extending from near 2100 to 4400 nm. However, the overtone spectra shown in the figure are taken at a resolution not sufficient to resolve the individual vibration-rotation lines on the P and R branch structures at the resolution of Figure 3.9. What is seen is a sum total of the different emission lines, broadened by the slit of the monochromator. Each peak roughly corresponds to a single vibrational energy level, ranging from two to approximately forty. The upper vibrational levels 35-40 correspond to approximately 3.8 to 4.7 microns, which interferes with the CO fundamental, which begins about 4.65 microns. There is additional interference from the second overtone, $\Delta V = 3$, at the lower wavelengths, creating a second order radiation, and necessitating the use of a band pass filter. The transmission spectrum of this filter was shown earlier in Chapter 3. The spectra in Figure 3.9 show that all the vibrational levels from vibrational level $v = 35$ to 40 are populated. Possibly even a higher number of vibrational levels are populated, however, this is difficult to determine, due to interference by the fundamental. It is determinable, however, that even in the highest pumped ($P_{He} = 0$) case, populations above $v = 40$ are much reduced.

The populations of the vibrational states of the CO are inferred from the measured spectra by fitting a synthetic spectrum developed from modeling the dynamic processes, which are summarized in reference [4]. The results are shown in Figure 3.10. The figure shows that the resulting vibrational distribution function is highly non-Boltzmann.
Boltzmann distribution at the measured translational-rotational temperatures of the experiments, T~1000 K, would have completely negligible state populations above v = 5. That is not the case here. In this case the vibrational distribution function shows the vibrational populations decreasing more slowly than the Boltzmann relation at T=1000 K.

Vibrational Distributions of Vibrationally Excited Carbon Monoxide for Different Helium Partial Pressures

Figure 3.10: The vibrational distribution for three different helium partial pressures.

Note instead, there are substantial populations of states to at least v ≥ 20. The populations of the lower vibrational levels decrease at the same rate for each helium partial pressure, and drop rather rapidly with vibrational level v. However, vibrational energy levels from, v = 5 to v = 20, the vibrational population distributions decrease less rapidly and only by an order of magnitude; this is the region that is referred to as the
“Treanor plateau”. Of yet higher vibrational levels, the decrease in population becomes increasingly rapid with the addition of helium, although the populations at the lower and middle vibrational levels, in the plateau, remain unchanged. These vibrational energy distributions allow determining both the total energy in vibration and the energy above any selected vibrational state; these can be correlated with the measured specific reaction rate (Table 3.3 below).

3.2.3 Gas Temperature in Reaction Zone

The thermal gas kinetic temperature is determined from the rotational distribution of the fundamental vibrational emission spectrum (ν = 1 → 0). Shown in Figure 3.11 is a fundamental emission spectrum for a case where there is no helium added. This spectrum, ranging from 4300 nm to 5100 nm shows the P and R branches of the vibrational-rotational spectra, for with its band component ν = 1 → 0 its center at about 4.6 µm.
Figure 3.11: Emission spectrum from the carbon monoxide fundamental for \([\text{He}] = 0\) Torr.

The spectrum of Figure 3.11 is, again, only partially resolved. While the height of each completely resolved vibration-rotation spectral line would be directly proportional to the rotational population of a single state, at least for optically thin transitions, the peak intensities of the partially resolved spectrum are affected by overlap from more than one line. The overlapping is less severe on the left, short-wavelength side of the spectrum, which only contains the R-branch of the \(v = 1 - 0\) band component. The most valuable part of this is the less intense, shortest wavelength portion, since the test gas is optically thin here, and self-absorption is negligible. We have again used a synthetic spectrum, generated for a given rotational temperature, which includes the overlapping and self-
absorption effects, to compare with the experimental spectrum, and we infer the rotational temperature by such matching.

<table>
<thead>
<tr>
<th>Helium partial pressure [Torr]</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of carbon monoxide molecules [cm$^{-3}$]</td>
<td>3.34*10$^{17}$</td>
<td>3.42*10$^{17}$</td>
<td>3.56*10$^{17}$</td>
</tr>
<tr>
<td>Carbon dioxide produced [cm$^{-3}$]</td>
<td>6.603*10$^{14}$</td>
<td>2.231*10$^{14}$</td>
<td>2.263*10$^{14}$</td>
</tr>
<tr>
<td>Temperature [K]</td>
<td>1050</td>
<td>1220</td>
<td>1160</td>
</tr>
<tr>
<td>$k_{overall}$ [cm$^3$/sec]</td>
<td>1.04*10$^{-18}$</td>
<td>3.59*10$^{-19}$</td>
<td>3.02*10$^{-19}$</td>
</tr>
<tr>
<td>Fractional population (normalized by the population of $v = 0$) in vibrational levels $v &gt; 25$</td>
<td>6.19*10$^{-4}$</td>
<td>4.30*10$^{-4}$</td>
<td>1.069*10$^{-4}$</td>
</tr>
<tr>
<td>Total energy in all vibrational levels [ev/molecule]</td>
<td>0.260</td>
<td>0.264</td>
<td>0.254</td>
</tr>
<tr>
<td>Fractional amount of energy in vibrational levels $v &gt; 25$ ($E_{v=25} = 5.79$ ev) [ev/molecule]</td>
<td>3.95*10$^{-3}$</td>
<td>2.67*10$^{-3}$</td>
<td>6.51*10$^{-4}$</td>
</tr>
</tbody>
</table>

Table 3.3: Experimental conditions and the corresponding calculations for the carbon dioxide and overall kinetic rate for three different helium partial pressures.

3.2.4 Experiments at Reduced Reactant Concentration

Additional experiments were performed with half the amount of CO, to study the effect on the overall kinetic rate. The measurements, the same that were discussed earlier, were performed which includes measuring the amount of carbon dioxide produced, as well as the vibrationally excited CO overtone and fundamental spectrum. For these experiments, only a partial pressure of 6.4 Torr of CO was present, and the
partial pressure of argon was 112.8 Torr. There was no helium present for these experiments. The calculated results are shown in Table 3.4:

<table>
<thead>
<tr>
<th>Helium partial pressure [Torr]</th>
<th>He = 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of carbon monoxide molecules [cm⁻³]</td>
<td>1.7666*10¹⁷</td>
</tr>
<tr>
<td>Carbon dioxide produced [cm⁻³]</td>
<td>4.018*10¹⁴</td>
</tr>
<tr>
<td>Temperature [K]</td>
<td>920</td>
</tr>
<tr>
<td>$k_{\text{overall}}$ [cm³/sec]</td>
<td>2.62*10⁻¹⁸</td>
</tr>
<tr>
<td>Fractional population (normalized by the population of $v = 0$) in vibrational levels $v &gt; 25$</td>
<td>6.956*10⁻⁴</td>
</tr>
<tr>
<td>Total energy in all vibrational levels [ev/molecule]</td>
<td>0.268</td>
</tr>
<tr>
<td>Fractional amount of energy in vibrational levels $v &gt; 25$ ($E_{v=25} = 5.79$ ev) [ev/molecule]</td>
<td>4.505*10⁻³</td>
</tr>
</tbody>
</table>

Table 3.4: Experimental conditions and the corresponding calculations for the carbon dioxide and overall kinetic rate for 6.4 Torr of carbon monoxide.

Table 3.4 contains the results of the numerical calculations for the amount of carbon dioxide produced, in column four, the temperature of the reaction zone, in column 5 and the corresponding kinetic rate in the final column.

Figure 3.12 shows the emission from the CO overtone for this case. The resulting spectrum at the lower pressure of 6.4 Torr is shown along side the spectra of the higher concentration at 12.4 Torr.
The spectrum shows that for both concentrations, the higher vibrational levels of CO are populated. A vibrational distribution can be inferred from the data and is shown in the following graph.

Figure 3.12: Carbon monoxide overtone spectra for two different concentrations of carbon monoxide
Figure 3.13: Vibrational distribution function of vibrationally excited carbon monoxide for two different partial pressures of carbon monoxide, 6.4 Torr and 12.4 Torr.

Figure 3.13 shows that the vibrational distribution functions for both cases, the lower and higher concentrations do not vary from each other by much. However, from this figure, it is apparent that the higher vibrational levels are a bit more populated for the case of the lower CO concentration.

Emission from the CO fundamental was also measured. The R-branch data of the fundamental is shown in the following figure, against the case of the higher CO partial pressure.
Figure 3.14: Carbon monoxide fundamental the R-branch data for two different carbon monoxide concentrations.

Figure 3.14 shows that the intensity has decreased, for the case of the lower CO pressure. It is difficult to speculate from the graph if the temperature has also decreased, but a synthetic spectrum matched to the data shows that it has. This inferred temperature is reported in Table 3.4, to be 920 Kelvin, which is lower than the temperature for the higher concentration of CO, inferred to be 1050 Kelvin.

3.3 ERROR ANALYSIS

The gas phase experiments are quantitative in nature and are subjected to measurement errors, which can influence the results. The overall kinetic rate depends on
several quantities that were described earlier and are: The CO concentration, the total volumetric flow rate, the volume of the reaction zone, and the amount of CO₂ (carbon dioxide) produced.

The CO₂ calibrations were performed with measurements of known amounts of CO₂ that are in the atmosphere. Originally, pure CO₂ from a cylinder was used for the calibrations. However, the flow rates could not be easily regulated to a flow rates sufficiently low, to be comparable to the amount of CO₂ produced in experiments. For this reason, atmospheric air was passed through the absorption cell at low flow rates, and the CO₂ in these samples was used for calibration. The amount of CO₂ in the atmosphere was taken to be a constant .03% mole fraction in dry air [2]. Corrections for humidity were included in the calculations. However, there are local fluctuations in the mole percent, which are not accounted for. However, it was assumed that fluctuations would not be more than 10% of the CO₂ in the air, thus it was assumed that the measured CO₂ to within 0.0003 ± 0.00003 fractional amounts of the measured pressures. This error would be seen in the calculation of the areas of the absorption spectra. Shown in the following figure are the measured carbon dioxide FTIR (Fourier transform infrared spectrometer) absorption spectra:
Figure 3.15: Absorption Spectrum of room air carbon dioxide for three different partial pressures.

Figure 3.15 shows absorption spectra of CO\textsubscript{2} for three different cases of room air partial pressures. The spectra show the both the P and R branches at low resolution of 4 cm\textsuperscript{-1}. The Bruker FTIR software has different methods of determining the base line to be used in the integration of the areas. Specifically the base line representation was a line interpolated between four points, two on either side of the lobes. The areas under the absorption spectra were calculated to the interpolated baseline. The spectra in Figure 3.15 show a good strong signal at 8 millitorr of CO\textsubscript{2} in the air, which is in the range of the partial pressures of the CO\textsubscript{2} from the experiment, which were on the order of one to twenty millitorr. The spectra still show reasonable signal-to-noise levels at the lowest
partial pressures of the experimental range. Many gas phase experimental CO\textsubscript{2} measurements were made with higher a number of scans, which were then averaged to improve the signal. It is very important to note that the moving mirror velocity in the FTIR was never changed, as that directly influences the signal; a faster mirror velocity decreases the signal and increases the noise.

The measurement of the volume of the reaction zone is also a source of both systematic and random error. The volume was visually estimated with a linear scale, measuring the volume of the emission of the blue glow from the C\textsubscript{2} Swan system. The systematic error is due to the assumption that the C\textsubscript{2} blue glow approximates the reaction zone to a reasonable degree; this visible volume is very close to the focal volume fo the pump laser volume. The C\textsubscript{2} blue glow is assumed to be present only where vibrationally excited CO exists. The radiative lifetime of the C\textsubscript{2} Swan is 3.16 \mu sec, so any electronically excited C\textsubscript{2} diffusing out of the vibrationally excited volume would almost immediately be quenched. However, there may be some residual CO, with lower levels of vibrational excitation, which would have diffused out of the visible volume. Thus, the region containing vibrationally excited CO could be somewhat larger than what is seen, so the volume is considered to be underestimated. In addition, due to the focusing the carbon monoxide laser beam, the reaction zone was not shaped as a uniform cylinder. However, due to the very long focal length, 8 inches, and the short length of the reaction zone, it was assumed that the pumped volume was constant. In fact, visual inspection of the blue glow region shows a uniform cylinder shaped blue glow. If anything, again, the volume was underestimated, and the reaction rate would be lower. One of the factors
contributing to the random errors is the reaction volume changing with the argon purge. As described earlier, the argon purge was used to keep CO from diffusing to the window where the carbon monoxide laser beam enters the cell. This had the effect of pushing the vibrationally excited zone downstream, and while the argon remained constant for an experimental run, it would change with the addition of helium. As the helium partial pressure was increased, the argon pressure was decreased to maintain a constant pressure. This would cause the reaction zone to be longer than what was assumed and calculated at zero Torr of helium. Again, the volume was under estimated. It is assumed that this factor is not a large source of error, the change in length was not perceptible, and the estimate is that it may have changed by a tenth of a millimeter, which represents a tenth of a percent of a change in the volume.

The correlation of the CO overtone spectra with the amount of CO$_2$ produced is another source of error, due to problems in keeping the helium concentration constant. The helium was observed to drop during experimental runs by approximately a little over a Torr an hour. This pressure drop was assumed to not have influenced measurements of the CO$_2$ produced because only the data from the first ten minutes of the experimental runs were used in the CO$_2$ calculations. During this time-period, the helium pressure would be relatively constant, and close to the measured and reported pressure. However, the decrease in helium partial pressure during relatively longer run times necessary to measure a complete 1$^{\text{st}}$ overtone spectrum (a few hours) did have some influence on the CO overtone and fundamental spectra. Specifically, the inference of higher vibrational state population (the long wavelength part of the 1$^{\text{st}}$ overtone emission spectrum) may be
overestimated, particularly at lower He partial pressures. The effect of this error is further addressed in the discussion of Chapter 6.

The helium pressure drop is assumed to have a small influence, however, on the fundamental spectra, from which the translational temperature is derived. Temperatures measured for the different helium partial pressure show that the temperatures are comparable to the each other and do not change by much. Thus it would appear that the small variation in helium partial pressure does not have a significant influence on the translational temperature. Rather, the data suggest that it is the partial pressure of CO that is the major determinant of the temperature. For example, the temperature measurement of the lower CO concentration, 6 Torr, was the lowest, at 920K when compared to the higher amounts of CO. At higher CO concentrations, more of the pump laser power was absorbed, and the heating of the translational mode of the gas components, by V-V and V-T processes, increased. The largest source of error in the temperature measurements would be due to errors in fitting the synthetic spectrum to the fundamental data. In the fundamental band spectrum, overlapping lines from adjacent transitions would result in an over estimation of the population. However, this would be countered by an underestimation of the populations due to self-absorption by the cold CO in the gas mixture. These errors are minimized by using the temperature inferred by matching the synthetic spectrum to high rotational lines (high J values) of the $v = 1 \rightarrow 0$ R-branch fundamental transitions only. These are the least affected by either the line overlapping or the self-absorption errors.
Additional errors are found in the measurement of the pressure by the Baritron pressure gauge, the volumetric flow rate, and the temperature readings. MKS, makers of the Baritron pressure gauge, reports an error of 0.25% of the reading. Fisher and Porter, makers of the variable flow meters, report an error of 2% of full scale. Following the methods of estimating the percent error [5] the error is the square root of the sum of the squares of the percent relative uncertainties. Another source of error that was systematically overestimated was the temperature measurements that were taken to be approximately 300K (~80 °F), which would give a relative error of 4%. Using the estimates of the previously discussed errors, the CO₂ produced is to within 10%, and the estimation of the volume would be to within 1%, then the overall relative percent error in the kinetic rate would be: %error = \sqrt{10^2 + 1^2 + 2^2 + 2*2.5^2 + 2*4^2} = 11.71\%. The scatter seen in Figure 3.8 for zero Torr of helium is approximately 50% of the reading. This is much higher than the predicted percent error of 11.71%. We conclude that there is another major source of error. This error is one that affects the vibrational energy loading per reactant CO molecule which we proceed to discuss.

The most important source of error is due to the variable power of the carbon monoxide laser infrared radiation that is absorbed by the reactants. During operation of the laser, the lines may hop from transition to transition. This happens very quickly with respect to characteristic time scales of the flow and the measurement of the CO₂ produced. Nevertheless, within one multi-hour run, the laser power can vary by as much as a Watt, and the distribution of lasing spectral lines is not constant. Due to both this wavelength and amplitude variation of the laser, the power absorbed per CO molecule
varies. Further, the run-to-run variation of total laser power was somewhat larger, with a maximum variation of two watts, which is ~20% of the total power. Finally, the (much smaller) variations in the CO flow rate also directly affect the power loading. The largest deviation due to the power loading variation is shown in Figure 3.7. It can be seen that the data for pure CO show the highest variation. The two of the highest [CO₂] produced points represent experiments in which the carbon monoxide laser power was at the highest amplitude deviation closer to 14 Watts rather than the typical 12½ Watts. With a higher power loading per reactant, more [CO₂] was produced, as a consequence of the higher vibrational energy content per CO molecule.
References:

HETEROGENEOUS PHASE EXPERIMENTS

Experiments with the CO (carbon monoxide) Boudouard reaction on solid surfaces, using vibrationally excited room temperature reactant, are presented in this chapter. These experiments were undertaken to determine if the non-equilibrium reaction rate on such surfaces was enhanced over the purely gas phase rate. Results from these surface reaction studies are presented in this chapter.

Heterogeneous phase experiments were divided into two tasks. The first task was surface reaction experiments conducted with CO reactant in thermal-equilibrium. The second task repeated the surface reaction experiments, but using vibrationally excited non-equilibrium CO reactant prepared by the optical excitation method presented in previous chapters. The thermal-equilibrium task was performed as a test of catalytic activity of the surfaces used, and as a control basis for comparison with the non-equilibrium experiments. For both tasks, the experimental conditions were duplicated as much as possible. In particular, identical surface materials were used. The surface materials used were of CuO (copper oxide) that was coated onto a monolith. The monoliths were blank (no impregnated active metals) automobile catalyst, which is a
ceramic honeycomb material, having long narrow and parallel rectangular cross section channels of approximately one square millimeter. The typical dimensions of the monoliths are shown in the following figure.

![Diagram of the Automobile monolith](image)

**Dimensions of the Automobile monolith used in the catalytic experiments**

- **Top View**
  - Length ~ 1-1+1/4 in
  - Width ~ 1/4-1/2 in

- **Side View**
  - Height ~ 1/2-1/4 in
  - d=1 mm

Figure 4.1: Diagram and dimensions of the sections used in the surface experiments of a non-impregnated active metal automobile catalyst.

Additional experiments were conducted with blank automobile catalysts, no CuO coating, to serve as an added control.

4.1 EXPERIMENTAL SETUP

The experimental setups for the two tasks differ because of the methods used to put energy into the reactants. For the thermal-equilibrium-based experiments energy from a heater is absorbed by all energy modes in the system, raising the reactants to a
selected reaction temperature, and maintaining a Boltzmann equilibrium energy
distribution among all reactant modes. In the non-thermal-equilibrium experiments,
energy is directed specifically into the vibrational modes of the reactants, and the
translational and rotational energy modes are maintained at a low temperature.

4.1.1 Thermal Equilibrium Experiments

The thermal equilibrium experiments were conducted to determine the catalytic
activity of the surfaces used, i.e. a measurement of thermal energy (temperature)
necessary for the reaction to occur. Thermal program desorption (TPD) experiments
were performed to ascertain and possible quantify this energy. The TPD equipment used
and the experiments performed were with Dr. Umit Ozkan at The Ohio State University
Chemical Engineering Laboratories. The basic components of the TPD experimental set
up are shown below in Figure 1, for more information please see Ozkan et al. [1,2].
Figure 4.2: Thermal program desorption experimental setup.

The figure shows the flow reactor, which is a ¼ inch Pyrex U-tube inserted into a thermal heater. Gas mixtures containing the reactants, CO in He (helium), are delivered to the thermal reactor via mass flow controllers upstream. The flow rates for CO and He respectively are 6.21 SCCM and 55.96 SCCM. The CO and He mixture was delivered in pulses each for in duration of approximately less half a minute, while the a He feed delivery was continuous at 51.43 SCCM. A sample of a pulse of CO, for the flow configuration where the reactor is by-passed, is shown in the following figure:
Figure 4.3: A mass spectrometer measurement of pulsed carbon monoxide

Figure 4.3 shows two pulses of CO in time, each pulse is from a volume of 0.1 cc. The duration between pulses is controlled by the operator, and this length of time was chosen to observe the time dependence of the system, and to experimentally determine the rate of decay of the CO pulse. The catalysts were coarsely ground to fit into the quartz tube, and held in place by quartz wool placed on both sides of the ground catalyst. The gas flow mixture enters the reactor by-pass valve, where reactants can be diverted into the mass spectrometer before entering the furnace. The reactants flow through the quartz U-tube and over the catalyst; a fraction is diverted into a mass spectrometer, downstream of the reactor for analysis, while the bulk of the flow is expelled through a vent.
The gas mixture and catalyst was brought up to a prescribed temperature by a thermal heater, which was controlled by a Hewlett Packard computer. It took approximately an hour for the system to reach steady state. This also drove off any excess \( \text{H}_2\text{O} \) and \( \text{CO}_2 \). There was no preheating of the gases before entering the furnace; however, the gases traveled through approximately \( \frac{3}{4} \) of a foot before reaching the catalyst's position in the middle of the U-tube. This length at the prescribed flow rate yields a residence time of 72 seconds, or just over a minute in the furnace before reaching the catalyst. This is adequate to insure thermal equilibration. Experiments were performed at two different temperatures, one at 200 Celsius, and one at 400 Celsius.

4.1.2 Non-Equilibrium Experiments

The basic design of the non-equilibrium heterogeneous phase experimental setup consists of three major components: The carbon monoxide gas laser, the flow reactor, which contains the gas mixtures and the catalyst, and the optical diagnostics. These are illustrated in the following figure.
Figure 4.4: Experimental Setup for heterogeneous phase. Carbon monoxide laser beam is not focused.

This figure shows the infrared radiation from the carbon monoxide gas laser being directed, via flat mirrors into a glass experimental cell. The gas-phase reactants were fed into the glass cell, top view shown in the figure, which also contains the catalyst (not shown). The products, after desorbing from the catalyst, flow out from the reactor then through a FTIR (Fourier transform infrared) spectrometer for analysis.

Many of the components for the heterogeneous phase experiments are similar to the gas phase experiments and are not re-described in this chapter. These would be the carbon monoxide gas laser used in these experiments, the absorption cell, the FTIR
spectrometer, and the monochromator. The details of the laser were given in the previous chapter. The functions of the different components are the same. The infrared radiation from the carbon monoxide laser is absorbed by the CO reactant, which is vibrationally excited via up-pumping kinetics already described. The CO overtone emission is measured by the monochromator, while the CO$_2$ product is measured by the FTIR concurrently. The absorption cell is also the same one used in the gas phase experiments. While the flow reactor is the same one used in the gas phase experiments, there is additional functionality used in the heterogeneous experiments that needs to be described.

The flow reactor is a six-arm glass cell with an internal volume of 582 cm$^3$. Four of the arms are shown in the previous Figure 4.4, and are for passing the infrared radiation of the carbon monoxide laser and for passing spontaneous emission and are sealed with CaF$_2$ (calcium fluoride) windows. The following Figure 4.5 shows the third (vertical) axis through which the catalyst and thermocouple are positioned.
Figure 4.5: The glass flow reactor that allows for the insertion of a surface.

Figure 4.5 shows the side view of the flow reactor, which shows the position of the catalyst with respect to the carbon monoxide laser beam. Glass caps, in the vertical axis, seal the flow reactor by a compression O-ring fitting. One of the caps contains a ¼ inch hole admitting a glass tube, also sealed by a compression seal. This arrangement allows the tube to slide through the O-ring seal, and thereby adjusting the position of the catalytic surface mounted at the tube end. The glass cell has six gas-ports: Four are for the flow of the reactants and products, and are fitted with valves so that the direction of the gas flow can be directed along appropriate paths. The remaining two ports are for dedicated functions: One is for the pressure gauge, an MKS Baratron (Model A623), and the second port is for an Ar (argon) purge. This port is near the CaF$_2$ window where the carbon monoxide laser beam enters the cell. The Ar purge is necessary to prevent the CO
(carbon monoxide) gas from back diffusing to the window; CO near the window would simply absorb all the carbon monoxide infrared laser radiation far from the reaction zone near the surface.

The gas mixtures used for these experiments are CO/He in Ar, the same used for the gas phase experiments. The amount of CO (approximately 12 Torr) used was experimentally determined by balancing the highest concentration of CO with maintaining the highest vibrational-energy-loading into the CO reactant. This was done by visually examining the characteristic blue glow from C₂, the Swan system. It is assumed, as was discussed in more detail earlier in chapter 2, that this blue glow region could approximate the vibrationally excited zone. Carbon monoxide was added to the system, until the blue glow from the Swan system began to fade. Argon was added to make the pressure total 130 Torr.

Catalysts, attached to the tube shown in Figure 4.5, could be positioned a fixed distance away from the carbon monoxide laser beam inside the flow reactor. The catalyst could also be positioned into several different orientations with respect to the carbon monoxide laser beam axis. The one criterion that had to be met was that vibrationally excited CO had to reach the surface. Different orientations were tested, in an effort to expose the surface to as much vibrationally-excited CO as possible. Finally, detailed experiments were performed with the catalyst in two different orientations. One configuration, which is shown in Figure 4.5 has the surface positioned away from the carbon monoxide laser beam, and monolith’s channels are perpendicular to the direction of the propagation of the carbon monoxide laser beam. The flow path taken by the gases
was such that it went through the channels of the monolith, through the tube, then to the absorption cell in the FTIR. There was no measurable increase in pressure, so the channels in the monolith did not apparently choke the flow. The second configuration is the placement of the surface into the laser beam, such that the channels are parallel to the propagation of the carbon monoxide laser beam. In this configuration the catalyst was inserted into the path of the carbon monoxide laser beam, which passed through the channels. The second configuration was done to create a higher surface area available for the reaction. In both cases, the reaction relies on the diffusion of the vibrationally excited CO to the surface.

A thermocouple attached to the catalytic surfaces was used to measure the surface temperature. The thermocouple hot junction, approximately ¼ of a cm in diameter, was fitted into the monolith, flush with the surface. This was accomplished by carving (by hand) a small hole into which the thermocouple is placed, and Delcon 2-Ton Epoxy glue was used to hold it in place. The iron-constantan thermocouple used was connected to a multimeter, which measured the voltage. Correlation tables were used to convert the voltage into the temperature at the junction.

4.2 RESULTS

For both experiments, the key results were the measurement of the CO$_2$ produced in the surface reaction, and corresponding temperature measurements. Additional experimental results for the non-equilibrium experiments were the CO overtone emission spectra that measure the amount of energy in the vibrational modes of the CO reactant.
4.2.1 Thermal Equilibrium Results

The thermal equilibrium experiments were performed at 200 and 400 Celsius, for both the blank and the CuO (copper oxide) surfaces. Carbon dioxide produced in this thermal control experiment was measured with both the blank and the CuO-covered surface. No CO$_2$ production was observed for the experiments performed at 200 °C. The results for the 400 Celsius case are shown, in Figure 4.6 for the blank surface and Figure 4.7 for the CuO surface:

Figure 4.6: CO$_2$ produced in a reactor at 400 °C versus time with the blank surface. Average area under peak = 17,692.83.
Figure 4.7: CO$_2$ produced in a reactor at 400 °C versus time with the CuO surface. Average area under peak = 195,412.6.

The figures show a mass spectrum of CO$_2$ produced as a function of time. Each of the spikes in the mass spectra corresponds to a pulse of CO introduced into the reactor, and shows the production of CO$_2$ to decay back to the base line, before the introduction of the next pulse. Calculation of the area under the peaks by an integration performed by the mass spectrometers software is proportional to the amount of CO$_2$ produced in the reaction. The calculations gave 17,692.83 for the blank surface, and 195,412.6 for the copper oxide surface. The ratio of the amount of CO$_2$ produced with the blank to the amount produced with the copper oxide surface is: 1/11.
4.2.2 Non-Equilibrium Results

The surface Boudouard reaction was studied in a variety of non-thermal-equilibrium conditions for characterization. The product, CO\textsubscript{2} (carbon dioxide) was measured downstream of the surface reaction for different vibrational-energy-loading conditions. Emission spectra taken concurrently were used as a measurement of the amount of energy in the vibrational modes of the reactant, CO.

Different amounts of helium were added ranging from 1.4\% to 4.0\% of the total gas make up, to decrease the upper vibrational level’s populations. Emission from the vibrationally excited CO was measured by a monochromator for the three different helium concentrations and is shown in the following figure.
Figure 4.8: Emission spectrum of the overtone, of the vibrationally excited carbon monoxide, for the three different partial pressures of helium.

The spectra are of the emission from the CO overtone, $\Delta v = 2$, ranging from 2400 nm to 4200 nm which corresponds to the first 40 vibrational levels. Each spectrum in the figure corresponds to different helium pressures of 0, 0.7 and 3 Torr. For the case of no helium, all 40 vibrational levels are populated and there is signal at the higher vibrational levels, although for the top few levels, the population is small. As the helium partial pressure is increased, the populations of the higher vibrational levels decrease, which is shown in the graphs by the decrease in emission at the higher wavelengths.

Absorption spectra of the gas phase products were taken to monitor the carbon dioxide concentrations during the reaction. Spectrum backgrounds were taken in which
the spectrum was scanned for the absorption cell and the gases from the cylinders, without vibrational excitation. Additional backgrounds were taken to measure the CO$_2$ produced in the gas phase due to the vibrational excitation by the carbon monoxide laser.

A typical absorption spectrum is shown in Figure 4.9:

![Absorption Spectrum](image)

Figure 4.9: Carbon dioxide production: --- gas phase production, ——copper oxide production, no helium.

The area under the peaks is proportional to the quantity of CO$_2$ present. These areas can than be compared against calibrations to determine the concentration of the CO$_2$ that was produced.

The CO$_2$ partial pressures were calculated from the absorption spectra and correlated with the calibrations for different partial pressures of helium. These
calculations were performed for both the gas phase and the surface CO₂ production and the results are shown in the following figure.

Figure 4.10: Carbon dioxide production as a function of helium partial pressure for the copper oxide surface, gas phase Boudouard reaction.

Figure 4.10 shows the amount of CO₂ produced in the flow reactor, for different helium partial pressures, for both the gas phase and the surface. These are surface results with the monolith in the second configuration, in the carbon monoxide beam path. The graph shows that for the case of no helium, there is almost twice as much CO₂ produced with the copper oxide surface than in the gas phase. The graph also shows that with increasing helium, decreasing vibrational-energy-loading, there is still CO₂ being produced.
Carbon dioxide production was only observed for the geometry in which the surface was placed into the CO laser beam path. The other geometry, where the surface was brought near the laser beam, but not placed into it, was tested but no additional amount of CO$_2$ was observed.

Temperature measurements, using the thermocouple imbedded into the surface, as described earlier, were taken during the experiments. It is assumed that the thermocouple adequately represents the temperature of the portion of the surface that is impinged by the carbon monoxide laser beam. For the data to be presented the thermocouple was approximately 1/2 cm away from the CO laser beam, and the temperatures ranged from 100 °C to 120 °C, which is still below the temperatures used in the thermal desorption studies. The maximum temperature measured in these experiments corresponded to the thermocouple being in the CO laser beam, near the edge, and was measured to be approximately 200 °C, which is still well below the temperatures from the thermal equilibrium control studies. There was no noticeable change in temperature with the addition of helium to the gas mixture. Gas phase temperatures, of the excited region, can be determined by the rotational population distribution, which is assumed to be in equilibrium with the translational modes. This is accomplished by resolving the rotational lines of the CO overtone. Previous experiments by Plonjes et. al. [3] have measured the temperatures in these environments to be 100 – 200 °C. However, in current gas phase experiments, using weak focusing of the laser beam, rotational distribution of the CO fundamental for the same gas mixtures have shown temperatures to be much higher, nearer 1000 K. However, the carbon monoxide laser beam was not
focused for these present heterogeneous experiments, thus, the temperatures for the heterogeneous experiments are considered to be much lower. Since no rotationally resolved CO fundamental measurement was taken, the temperature must be estimated; and is estimated to be below 200 °C.

As was to be expected, a time dependence of the surface temperature and of CO$_2$ production was observed. The results for the different helium partial pressures are shown in the following three figures showing surface temperature and CO$_2$ production as a function of time after the placement of the surface in the carbon monoxide laser beam path:

Figure 4.11: Carbon dioxide partial pressures and temperature measurements as a function of time, He = 0 Torr.
Figure 4.12: Carbon dioxide partial pressure and temperature measurements as a function of time, He = 0.7 Torr.
Figure 4.13: Carbon dioxide partial pressures and temperature measurements as a function of time, He = 3 Torr.

These graphs represent the partial pressures of the production of CO$_2$ and are given in Torr, and are in the range of 2 millitorr to over 5.5 millitorr. Production of CO$_2$ reached steady state in a period of ten minutes, after the surface is positioned to begin the reaction. The data points of Figure 4.10 use these steady state values. An inverse function ($1/x$) is fitted to the data on the plots. All three show an increase in the CO$_2$ production as temperature increases. In addition, for experiments with helium added, the production of CO$_2$ decreases.
References:


CHAPTER 5

CYROGENIC LIQUID PHASE EXPERIMENTS

5.1 EXPERIMENTAL SETUP

This section presents the experimental setup for the cryogenic experiments and consists of three main topic areas: The carbon monoxide laser, the experimental cryogenic liquid constituents in batch reactor, and the optical setup. The following Figure 5.1 illustrates these main components.

Figure 5.1: The liquid phase experimental setup.
Infrared radiation from a carbon monoxide laser gas enters the batch reactor, which contains mixtures of carbon monoxide, nitrogen, and argon. Emission from the carbon monoxide overtone is collected from the side port of the batch reactor and focused into a monochromator. There are similarities to the gas phase experiments; refer to chapter 3 for more details on the gas phase experiments. However, for the liquid experiments the molecular constituents are in liquid phase and experiments are conducted in a non-flowing batch reactor.

The batch reactor is a small brass cell with a volume of approximately 1 cm$^3$, that is in thermal contact with a cryogenic reservoir as is shown in the following, Figure 5.2, The cell was developed for optical pumping experiments in liquid CO by Dr. G. Ewing at University of Indiana. It is the device described in references [1,2]

Figure 5.2: Diagram of the liquid phase batch reactor connected to the mixing system [1,2]
The cryogenic reservoir is a container that is open to the atmosphere through a ¼ hole. This reservoir holds liquid argon at 87 Kelvin. The reservoir and the attached cell are enclosed by a vacuum jacket to provide insulation for the liquid argon. The vacuum jacket enclosure also prevents condensation on the cell windows. The windows are sapphire, which are transparent in the infrared region, and are sealed to the cell with indium wire. The outside of the vacuum chamber was fitted with calcium fluoride windows, which were coaxial with the windows on the brass cell. The cryogenic brass cell batch reactor is connected to a large mixing chamber with a volume of approximately 2866 cm$^3$, shown in Figure 5.2.

The gases are slowly metered into the mixing chamber, which is in thermal contact with the room air, to a prescribed pressure. Two different pressure gauges were used to accommodate the wide pressure range, from a hundredth of an atmosphere to 3 atmospheres. For the lower range, on the order of one Torr, a MKS Baratron, model 622A, was used. For the higher range, two to three atmospheres, an Edwards Pirani gauge was used. To condense the gases, the valve to the cryogenic batch reactor is opened to admit the gas mixture.

The specific components used for the liquid experiments are heavier isotopes of normal carbon monoxide, a heavier and a normal isotope of nitrogen, and argon diluent. The carbon monoxide was a mixture of two isotopes in fixed proportions: 88% $^{13}\text{C}^{16}\text{O}$ and 12% $^{13}\text{C}^{18}\text{O}$, provided by Isotec, Inc.; the nitrogen used in these experiments were the normal and heavy isotopes: $^{14}\text{N}_2$ and $^{15}\text{N}_2$. The normal isotope was from Matheson Co.
while the isotope, $^{15}\text{N}_2$ was from Isotec. The argon used as the diluent was ultra high purity from Matheson, while the argon used for the cryogenic reservoir was “4.8 O$_2$ free grade” from Praxair. The assays for the gases used are presented in appendix B. For the experiments the concentrations of carbon monoxide and nitrogen were varied, ranging from a few millitorr to several Torr of CO; and from a few Torr to several hundred Torr of N$_2$. The total pressure was kept constant with the addition of argon to make up the balance to approximately 30 psig, which is approximately 2280 Torr. Three different types of batch experiments were performed: One batch, A, the carbon monoxide concentration was kept constant at one Torr while the nitrogen was varied from fifty to a thousand Torr. A second batch, B, is a variation of the first set, A, but using the heavier nitrogen isotope, which was at two hundred Torr, while the carbon monoxide remains constant at one Torr. The third batch, C, contains only a mixture of two diatomics, carbon monoxide and nitrogen. The carbon monoxide constituent was varied ranging from one, two and five Torr, while the nitrogen, the normal isotope, made the balance to approximately 30 psig. These gas mixtures are respectively summarized in the following three tables.
Table 5.1: Gas mixtures for experiments performed with varying nitrogen concentrations while the carbon monoxide is held constant.

<table>
<thead>
<tr>
<th>Experiment A</th>
<th>Carbon monoxide, 88% $^{13}\text{C}^{16}\text{O}$ and 12% $^{13}\text{C}^{18}\text{O}$, pressure [Torr]</th>
<th>Nitrogen, $^{14}\text{N}_2$, pressure [Torr]</th>
<th>Argon pressure [Torr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>50</td>
<td>2285</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>100</td>
<td>2135</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>200</td>
<td>2035</td>
</tr>
<tr>
<td>4</td>
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<td>1</td>
<td>700</td>
<td>1635</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>1000</td>
<td>1335</td>
</tr>
</tbody>
</table>

Table 5.2: Gas mixture for the isotopically substituted nitrogen.

<table>
<thead>
<tr>
<th>Experiment B</th>
<th>Carbon monoxide, 88% $^{13}\text{C}^{16}\text{O}$ and 12% $^{13}\text{C}^{18}\text{O}$, pressure [Torr]</th>
<th>Nitrogen, $^{12}\text{N}_2$, pressure [Torr]</th>
<th>Argon pressure [Torr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line number</td>
<td>Carbon monoxide, 88% $^{13}\text{C}^{16}\text{O}$ and 12% $^{13}\text{C}^{18}\text{O}$, pressure [Torr]</td>
<td>Nitrogen, $^{12}\text{N}_2$, pressure [Torr]</td>
<td>Argon pressure [Torr]</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>200</td>
<td>2110</td>
</tr>
</tbody>
</table>

Table 5.3: Gas mixtures for the experiments of diatomics only, with carbon monoxide varying and the nitrogen remaining constant.

<table>
<thead>
<tr>
<th>Experiment C</th>
<th>Carbon monoxide, 88% $^{13}\text{C}^{16}\text{O}$ and 12% $^{13}\text{C}^{18}\text{O}$, pressure [Torr]</th>
<th>Nitrogen, $^{14}\text{N}_2$, pressure [Torr]</th>
<th>Argon pressure [Torr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1023</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1023</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1023</td>
<td>0</td>
</tr>
</tbody>
</table>
Details of the carbon monoxide laser can be found in Chapter 3, the experimental setup for the gas phase experiments, and do not change for the liquid phase experiments. However, it is important to note that even though the carbon monoxide used in the laser is the normal isotope, the heavier isotope $^{13}\text{C}^{16}\text{O}$ is used in the liquid phase. This is deliberate. At the 87 K temperature of the liquefied CO in the cell population of all the excited vibrational states, $v \geq 1$, is completely negligible. However, at liquid densities, the $v=0 \rightarrow 1$ absorption bands of $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ are very broadened, and overlap the $v=1 \rightarrow 0$, $2 \rightarrow 1$, and $3 \rightarrow 2$ laser lines. The infrared radiation from the laser is still absorbed. This is illustrated in Figure 5.3 [2]:

![Figure 5.3: An FTIR absorption spectrum of $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ with the vibrational carbon monoxide laser lines shown as vertical lines, labeled $1 \rightarrow 0$, $2 \rightarrow 1$, etc [2].](image)

Figure 5.3 shows the absorption of the isotopomers $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ of the normal isotope, $^{12}\text{C}^{16}\text{O}$. The larger peak is the absorption due to the 88% $^{13}\text{C}^{16}\text{O}$, while the
smaller peak sitting at lower energy is due to the $12\%^{13}\text{C}^{18}\text{O}$. Figure 5.3 also shows the carbon monoxide lines superimposed on the absorption band, which lie within the carbon monoxide band. The high densities also cause the fundamental bands of the diatomic constituents to be slightly red shifted [2,3].

The emission from the vibrationally excited carbon monoxide and from the nitrogen fundamental is measured by a 340E Spex monochromator. Details of the monochromator can be found in the experimental setup in Chapter 3. An off-axis parabolic mirror collects the overtone emission as is shown in Figure 5.1, and with mirrors, the radiation is directed into the monochromator. One difference from the gas phase experiments is the position of the chopper, which is used in the signal averaging. In the gas phase experiments, the chopper is positioned near the silt entrance to the monochromator. For the liquid phase experiments, it is positioned at the entrance of the carbon monoxide laser beam into the batch reactor. This was necessary due to a background signal superimposed on the carbon monoxide overtone emission from the chopper. The relatively high background was due to the contrast of temperatures between the very cold cryogenic cell (87 K) and the chopper wheel (293 K).

5.2 RESULTS

Energy transfer between dissimilar diatomics is studied by monitoring the emission spectra from these vibrationally excited molecules. Specifically to be presented are overtone emission spectra of vibrationally excited CO (carbon monoxide) and structure found in the emission spectra, which has been concluded to be the emission
from the fundamental of N\textsubscript{2} (nitrogen). These energy exchanges were studied for a variety of concentrations of CO, N\textsubscript{2} in liquid Ar (argon) as was outlined in chapter 5. Summarizing these experiments: A) Nitrogen concentrations were varied for a fixed amount of CO, B) Nitrogen was replaced with the heavier isotope, \textsuperscript{15}N\textsubscript{2}, and C) Liquid mixtures of CO and N\textsubscript{2} at liquid nitrogen temperatures 77 Kelvin, with CO being varied. In addition, corresponding vibrational distribution functions for some chosen experimental results have been calculated and are presented.

Initially, the overtone of the vibrationally excited CO in liquid argon was measured, as a test of the experimental setup and to verify vibrational excitation of the cold CO reactant. These overtone spectra illustrate energy transfer between vibrational modes of two isotopomers of carbon monoxide, \textsuperscript{13}C\textsuperscript{16}O and \textsuperscript{13}C\textsuperscript{18}O, dissolved in liquid argon. The gas mixtures used for these experiments are 1 Torr of CO in 2310 Torr of argon, and were liquefied to a total pressure of 2100 Torr. A typical experimental overtone, \(\Delta v = 2\), spectrum of vibrationally excited carbon monoxide is shown in Figure 5.4, against a synthetic spectrum.
Figure 5.4: Emission spectra of the overtone of carbon monoxide, experimental (red or dotted) versus kinetic modeling (black or solid).

The red (or dotted) spectrum is the experimental data, while the black (or solid) spectrum shown in Figure 5.4 is the result of the theoretical kinetic modeling, based on gas phase data. It should be noted that each peak shown occurs at the band center of a particular 1st overtone component, $v \rightarrow v-2$. These are the Q-branch ($\Delta J=0$) transitions. There are no P ($\Delta J=+1$) or R($\Delta J=-1$) branches, due to the hindered rotation in the liquid. The presence of the Q-branch structure only is a guarantee that we are looking at liquid phase emission. The spectrum, shown in Figure 5.4, illustrate that the higher vibrational levels are strongly populated creating a marked “Treanor plateau” in the vibrational distribution.
function. Figure 5.5 shows the vibrational distribution function inferred from the spectra, for both the $^{13}_{}C^{16}_{}O$ and $^{13}_{}C^{18}_{}O$ plotted as a function of vibrational quantum number [4].

![Figure 5.5: The vibrational distribution as a function of vibrational quantum number for the isotopomers $^{13}_{}C^{16}_{}O$ and $^{13}_{}C^{18}_{}O$.](image)

From the vibrational distribution functions of the two isotopomers of CO, in Figure 5.5, is it evident that the vibrational populations of the heavier isotope, $^{13}_{}C^{18}_{}O$, are larger for all vibrational levels than the populations of the lighter isotope, $^{13}_{}C^{16}_{}O$. In addition, the vibrational levels of the heavier isotope are populated to higher levels, $V=40, 41$, if not
higher. In contrast, the population of the lighter isotope decreases rapidly with vibrational quantum number, and Figure 5.5 shows that the vibrational levels of the lighter isotope is populated only up to \( v = 18 \) or 19.

5.2.1 Experiment A: Varying nitrogen and fixed carbon monoxide concentration

Emission from the radiating molecules was measured from approximately 2000 nm to 4700 nm. Spectra were taken for several different concentrations of \( \text{N}_2 \), while \( \text{CO} \) remained at one Torr. One of these spectra, 700 Torr of \( \text{N}_2 \), 1 Torr of \( \text{CO} \) and 1610 Torr of \( \text{Ar} \), is shown in the following Figure 5.6,

![Graph](image)

**Figure 5.6:** Emission spectra of the overtone of \( \text{CO} \) and of the fundamental of \( \text{N}_2 \), experimental versus kinetic modeling.
Specifically shown in Figure 5.6 is the experimental, red (or dotted), and kinetic modeling, black (or solid), spectra of the emission from the radiating molecules. The experimental emission is the overtone of the vibrationally excited CO. The modeling spectrum shows in addition to the CO emission, a weak fundamental band emission from the N$_2$ vibration at 4291.9 nm. Unlike the gas phase, a weak emission spectrum from the N$_2$ fundamental can be expected for the liquid phase. This is due to electric multipole moments, which are induced by collisions at the very high densities of the liquid phase. The experimental spectrum shows also shows this N$_2$ emission. In contrast to the spectra of Figure 5.4 of CO/Ar mixtures, Figure 5.6 shows that only the first 35 vibrational levels of CO are vibrationally excited, with the population beginning to decrease around 3600 nm. Between 4000 nm to 4500 nm Figure 5.6 shows structure that we believe to be from the v=1$\rightarrow$0 vibrational fundamental band of nitrogen. The corresponding vibrational distributions were calculated and for each of the radiating molecules and are shown in Figure 5.7 [4].
Figure 5.7: Vibrational distribution as a function of vibrational quantum number for the isotopomers $^{13}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ and $\text{N}_2$.

Figure 5.7 shows the vibrational distribution function for both isotopes of CO and $\text{N}_2$. It is again observed that the heavier isotope has larger populations in the higher vibrational levels, confirming results presented earlier; and that the vibrational population levels of the molecular nitrogen are very small.

To further understanding of the kinetics the concentration $\text{N}_2$ of the was varied to observe the overall effect on the extent of the vibrational up-pumping of both the CO and $\text{N}_2$. Nitrogen concentrations were varied from 50 to 1000 Torr, while the CO was kept constant at one Torr. Argon was added to have a total pressure of 2310 Torr, liquefied to
2100 Torr. The emission spectra of the overtone of CO and the fundamental of N\textsubscript{2} are shown in Figure 5.8, for each of the different N\textsubscript{2} concentrations.

**Carbon Monoxide Overtone Emission Spectrum**  
in Liquid Argon  
for Different Nitrogen Concentrations

![Emission spectra of CO overtone and N\textsubscript{2} fundamental](image)

Figure 5.8: Emission spectra of the overtone of CO and the fundamental of N\textsubscript{2}, for varying amounts of N\textsubscript{2}, and for 1 Torr of CO.

The CO overtone emission spectra in Figure 5.8 show that the overall population decreases monotonically for all vibrational levels with increasing N\textsubscript{2} concentrations. However, it is interesting to note that the first 30 to 35 vibrational energy levels are still populated for each of the different N\textsubscript{2} concentrations. Due to differences in scales, the
emission from the \( \text{N}_2 \) is difficult to view in Figure 5.8, and a blown up view of the fundamental of the \( \text{N}_2 \) is renormalized and is shown in the following Figure 5.9.

![Molecular Nitrogen Fundamental in Liquid Argon as a Function of Nitrogen Concentration](image)

Figure 5.9: An expanded view of the \( \text{N}_2 \) fundamental, for the different concentrations of \( \text{N}_2 \). The “eaten out” portion is due to the carbon dioxide in the system.

Figure 5.9 shows a closer view of the emission of the fundamental of molecular nitrogen between 4000 nm and 4600 nm. Figure 5.9 also shows the location of the \( \text{CO}_2 \) v3 gas phase band center at 4257.13 nm and the \( \text{N}_2 \) fundamental gas phase band center at 4291.9nm. The \( \text{N}_2 \) band centers for \( v=v \rightarrow v-1 \) for the first 5 vibrational levels are also
shown in Figure 5.9 as dot, which can be seen under the N\textsubscript{2} fundamental spectrum. The nitrogen emission spectrum has a portion that appears to be have been removed and is due to absorption by carbon dioxide in the optical path of the emission. As the nitrogen concentration increases, in contrast to the CO, the populations of the N\textsubscript{2} fundamental appear to increase to an optimum value and then to decrease.

5.2.2 Experiment B: Carbon monoxide and the heavier nitrogen isotope experiments

Experiments were conducted to confirm that the structure observed in the spectra shown in Figure 5.8 and Figure 5.9 between 4000 nm to 4600 nm is indeed molecular nitrogen. The isotope \textsuperscript{15}N\textsubscript{2} was substituted into the mixture for the regular isotope to observe a corresponding isotopic shift in the structure. The \(v=1 \rightarrow 0\) band center for the gas phase \textsuperscript{14}N\textsubscript{2} is 4291.92 nm; the corresponding band center for \(v=1 \rightarrow 0\) \textsuperscript{15}N\textsubscript{2} is 4442.49 nm, a red shift by 150.57 nm. The results are shown in the following, Figure 5.10, where CO ~ 1 Torr and \textsuperscript{15}N\textsubscript{2} ~ 265 Torr, the conditions for which previous experiments gave the strongest nitrogen emission.
Figure 5.10: Emission of the overtone of carbon monoxide and the fundamental of nitrogen. The first two (---) with the normal isotope of nitrogen and the third (-----) with the heavier isotope of nitrogen. Also shown (•) are the band centers for the normal and heavier isotopes.

Figure 5.10 compares the CO overtone emission from 1Torr of CO in two different mixtures: one is with 200 Torr of $^{14}\text{N}_2$ and the second is with 265 Torr of $^{15}\text{N}_2$. Comparing the two spectra, one sees that emission from the CO vibrational levels with the heavy isotope are not evident, except for absorption of the laser energy by the first two or three vibrational energy levels by the lighter isotope. However, there is evidence of a strongly pumped isotopically shifted $\text{N}_2$ fundamental in the mixture with the heavier
isotope, which implies that energy being absorbed by the CO is transferred to and stored in the nitrogen. Due to the isotopic shift, the energy levels are now much closer to the $^{13}\text{C}^{16}\text{O}$, the lighter isotope, and thus there is now a direct energy conversion to the nitrogen.

5.2.3 Experiment C: Liquid phase mixture of diatomics carbon monoxide and nitrogen

Additional experiments with mixtures consisting only of diatomics, CO and the normal isotope $^{14}\text{N}_2$, were also performed. The gas mixtures used in these experiments were of $\text{N}_2$ held at a constant pressure of 1030 Torr, while the CO partial pressures were varied from 1, 2 and 5 Torr and no argon was added. The final liquefied total pressure was approximately 2 psig or 864 Torr. The results of these experiments are shown in Figure 5.11, which clearly shows that CO is still vibrationally excited, although the populations are not as high at the upper vibrational levels as they were for the CO/N$_2$/Ar mixtures.
Figure 5.11: Emission spectra of the overtone of carbon monoxide and the fundamental of nitrogen with nitrogen pressure at 1030 Torr and CO pressures at 1, 2, and 5 Torr.

From the figure, it is clear that there is a sudden change in the vibrational population distribution at about 3200 nm, or approximately vibrational level 20. The spectra show that the populations of the higher vibrational levels suddenly decrease, which is usually an indication of energy transfer at that vibrational level. This particular change in the population distribution occurs at the same vibrational level, for the three different CO concentrations. In addition, this is accompanied with a corresponding overall decrease in
the populations with increasing CO concentrations. No evidence of this change is shown in the CO/N\textsubscript{2} in liquid Ar mixtures. The spectra also show that there is a collisionally induced emission spectrum from nitrogen, although not as strong as for the CO/N\textsubscript{2} in liquid Ar.
References:

This research has been an investigation into energy transfer and chemical reactions of vibration-vibration pumped CO (carbon monoxide). The carbon monoxide, in an optical absorption cell, maintained at a low temperature, was vibrationally excited by resonance absorption of radiation from a continuous wave carbon monoxide laser. This method created an extreme thermal non-equilibrium system, and studies of these processes have been conducted in gas phase CO, in CO reacting on solid surfaces, and in liquid phase CO. Specific results from this research are:

1. The gas phase and surface Boudouard disproportionation reaction of CO can be enhanced by vibrationally exciting the gas phase reactant, CO.

2. The specific rate of the gas phase Boudouard reaction has been measured as a function of the level vibrational excitation in the CO reaction. These results determine an effective activation energy for the reaction, and provide insight into high temperature shock tube experiments that reported CO thermal “dissociation” rates.

3. Carbon monoxide overtone spectra from liquid diatomic mixtures indicate energy transfer, among particular vibrational levels, which has not been previously observed. Also V-V energy transfer from CO to N₂ (nitrogen) has been shown and emission from
the \( v=1 \to 0 \) fundamental band of the isotopes of \( \text{N}_2 \) has been observed. In addition, the liquid phase work indicates a possibility of reactions taking place, which suggests paths for further study of this unique non-equilibrium system.

6.1 GAS PHASE EXPERIMENTS

The key result of the gas phase experiments is the measurement of the specific rate for the gas phase Boudouard disproportionation reaction of CO, as a function of the degree of vibrational excitation of the reactant. These rate data are summarized in Table 3.3 and Table 3.4, which are also in the plot shown in Figure 3.8. In Figure 3.8, data for the overall kinetic rate, in \([\text{cm}^3/\text{sec}]\), of the reaction, Equation 3.2, are plotted as a function of He (helium) partial pressure in Torr. As the Ar (argon) diluent is replaced by He, an increasing number of higher vibrational levels of the CO reactant are depopulated by V-T quenching. As He concentration increases and fewer CO molecules have sufficient energy to react, the rate rapidly decreases. Figure 3.8 shows this dramatically, the specific rate decreasing from a mean value of \(2 \times 10^{-18} \, [\text{cm}^3/\text{sec}]\) in CO/Ar mixtures to \(3 \times 10^{-19}\) with 17 Torr of helium, which is lower by almost an order of magnitude. The influence of He addition on the CO vibrational state population distribution function, (the”VDF”) in these optically pumped reaction cells has been well established. Figure 2.4 shows the result of the most detailed of such VDF measurements. As noted in Chapter 2, the VDF follows the Treanor distribution prediction, Equation 2.9 to the “Treanor minimum”. Beyond this point, the VDF is in a gently-falling “plateau”, with a dependence on vibrational quantum number of \( N_v \sim v^{-1} \). It will be observed that the
effect of the He is to cause a fall-off from this plateau, the location of the fall-off point
going to lower quantum numbers as He partial pressure increases.

The specific rate of the gas phase Boudouard reaction can be correlated with this
dependence of the level of vibrational excitation on He concentration. This was done
using a slightly modified form of the statistical rate prediction presented in Chapter 2,
Equation 2.14, for the reaction of two vibrationally excited CO molecules reacting in the
Boudouard disproportionation reaction. Equation 2.14 is essentially a transition state
theory, and its derivation estimates the probability of accumulation of energy in one C-O
bond exceeding the activation energy, \( E_a \). As written Equation 2.14 assumes that the
energy levels of the CO vibrational states can be represented by the standard SHO
(simple harmonic oscillator) expression that is linear in the vibrational quantum number.
Given the extreme level of vibrational excitation in the present experiments, the energy
levels are more properly represented by the AHO (an-harmonic oscillator) expression of
Equation 2.3. With this change, the statistical rate expression for the reaction of two
molecules, one in level \( v \) and the other in level \( w \), is:

\[
k_{v,w}\text{statistical} = Z(T) \frac{\hbar \left( \omega_{c,CO} (v + 1/2) - \omega_{c,CO} \omega_{e,CO} (v + 1/2)^2 + \omega_{c,CO} (w + 1/2) - \omega_{c,CO} \omega_{e,CO} (w + 1/2)^2 \right) - E_a}{\hbar \left( \omega_{c,CO} (v + 1/2) - \omega_{c,CO} \omega_{e,CO} (v + 1/2)^2 + \omega_{c,CO} (w + 1/2) - \omega_{c,CO} \omega_{e,CO} (w + 1/2)^2 \right)} \left( \frac{\omega_{CO}^2}{\omega_{CO}^2} \right) \theta
\]

Equation 6.1

where the \( \omega \)'s are the main frequencies of the specified molecule, \( \omega_{CO} \) is the CO
fundamental vibrational frequency, \( \omega_{CO2} \) is the \( CO_2 \) asymmetric stretch frequency, and \( \theta \)
is a step function, which equals one for \( E_a > 6 \text{ ev} \), and zero for \( E_a \leq 6 \text{ ev} \). The term, \( E_a \), is the activation energy for the process, \( h \) is Planck’s constant, \( c \) is the speed of light, and \( v \) and \( w \) are the vibrational energy levels of the two colliding carbon monoxides. The factor, \( Z(T) \), is the gas kinetic collision frequency as a function of temperature, \( T \), and is expressed as:

\[
Z(T) = 3 \times 10^{-10} \left( \frac{T}{300} \right)^{1/2} \quad [\text{cm}^3/\text{sec}]
\]

Equation 6.2

Using this modified rate expression, the total disproportionation rate for the reaction of two CO molecules is obtained by summing over all the reacting vibrational quantum states.

\[
\sum_v \sum_w k_{\text{statistical}}^{v,w} n_v n_w
\]

Equation 6.3

where, \( k_{\text{statistical}}^{v,w} \) is the theoretical transition state kinetic rate for two vibrationally excited molecules colliding, given in chapter 2. It is dependent on \( v \) and \( w \), and is constrained by the total energy \( E_T = E(v) + E(w) \geq E_a \). Calculations of the theory, Equation 6.3 above, using the measured vibrational distributions from overtone spectra as given in Figure 3.10, and an activation energy of \( E_a = 6.0 \text{ ev} \), yield three data points for the three separate cases of helium partial pressures. These results were normalized to the measured kinetic
rate at zero Torr of helium, and are presented along-side the measured rates in the following graph.

![Graph showing the comparison of the measured kinetic rate with the $k_{\text{statistical}}$ using experimental vibrational distribution functions.](image)

Figure 6.1: Comparison of the measured kinetic rate with the $k_{\text{statistical}}$ using experimental vibrational distribution functions.

There are three points (the square points) that were calculated from transition state theory using the experimentally measured VDF’s (vibrational distribution function) of Figure 3.10. The calculations for the pure CO, and for large amounts of helium (the points for zero Torr of helium, and the third data point, at 16 Torr of helium), are in close agreement with the experimental data points and with the exponential curve fit. The calculated point for the intermediate pressure of 10 Torr of helium shows considerable deviation from experiment. We believe the reason for this deviation is due to the error in
the measurement of the VDF at this helium concentration. As discussed in the error
analysis of Chapter 3, in section 3.3, there is significant variation in helium flow rate
during the measurement time necessary to obtain the VDF. The VDF obtained at 10Torr
is very probably more representative of somewhat lower helium partial pressures; the He
flow rate was slightly falling during the measurement period for this VDF. We note that,
because of this, the helium partial pressures decreased by approximately the same amount
for both, the 10 Torr and the 16 Torr of helium cases. This error is considerable larger for
the lower He pressure. The deviation in the inferred rate at $P_{He} = 10$ Torr is largely a
consequence of this effect.

To provide a more precise prediction of the effect of the level of vibrational
excitation on the specific rate, the more accurate and extensive VDF measurements of
Figure 2.4 were used in the statistical rate expression of Equation 6.1 above, in lieu of the
VDF’s of Figure 3.10. The VDF measurements of Figure 2.4 were performed in a CO
laser-pumped reaction cell similar to that of the present rate measurements. Ar and He
partial pressures included the range of the rate measurements, but extend to much higher
He concentrations, as well. These VDF measurements were made with 0.34 meter
monochromator. Note, however, that the two measurements show agreement on the
extent of the V-V pumped plateau, indicating a fall-off at higher He concentrations at
approximately the same vibrational quantum numbers for similar He partial pressures.
Figure 6.2 below shows the specific rate dependence on quantum number, calculated with
these more precise VDF’s, using the theoretical expression of Equation 6.1; the
experimental data are also displayed.
Figure 6.2: Measured kinetic rate as a function of helium partial pressure (●), compared with the calculated transition state theory (▲), $k_{\text{statistical}}$ using VDF of Figure 2.4, measured over an extended He range.

Note that with these VDF distributions were measured with helium partial pressures out to 98 Torr, as is shown on the graph. From the graph it is clear that the measured and theoretical kinetic rates follow a similar trend, with the rate decreasing as the energy storage in the vibrational modes decreases. Both graphs show a decrease in the rate of the reaction with increasing helium concentration. The increase in helium concentration corresponds to the degree of vibrational energy loading. This can be quantified by the calculating the fractional amount of energy in the vibrational modes of CO. The basic equation for this fraction is

$$\sum_v \sum_w n_v n_w$$
Equation 6.4

Including the transition state kinetic rate, Equation 6.4 becomes, as we have shown above,

\[ \sum_{v} \sum_{w} k_{v,w} n_v n_w. \]

Equation 6.5

The following table, Table 6.1, shows the fraction of molecules such that the combined energy of two vibrationally excited CO reactants contain energy above \( E_T = E(v) + E(w) \geq 6\text{eV}. \) The first two top lines describe the gas mixtures used for the experiments that have corresponding measured VDFs.
Table 6.1: Fractional amount of energy in the vibrational modes, such that the total energy between two vibrationally excited carbon monoxide reactants is six ev or higher.

Table 6.1 shows the double sums with the transition state kinetic rate-weighting factor in the double sum, line 4. The original theory is based on a harmonic molecule, so the theoretical equation was adjusted to account for the anharmonicity, as was discussed earlier, and the double sums decreased by a little more than a factor of a third, which is shown in line 5. The calculation of kinetic rate with the gas kinetic rate, to yield and overall rate for the different cases of helium partial pressure, is shown on line 6, and is approximately four orders of magnitude above the measured rates. The theory, however, includes no steric effect, considering only that all collisions with the activation energy $E_a = 6.0 \text{ ev}$ in the vibrational modes will react. In the plot of Figure 6.2, the theoretical calculation was normalized to the rate for pure CO, yielding a steric factor of $1.9 \times 10^{-4}$. It
is important to note that this data analysis does indicate an activation energy somewhat higher than 6 ev, as plotted in the following figure:

![Calculated (Statistical) Kinetic Rates](image)

Figure 6.3: Calculated statistical kinetic rates for three different activation energies, $E_a = 5$, 6 and 7 ev.

Figure 6.3 shows the calculated rates using Equation 6.1 for $E_a = 5$, 6 and 7 ev. The comparisons shown in this figure indicate that a value of 7 ev is more consistent with the measured rate dependence. Additional calculations show that much higher values near the, CO dissociation energy of 11.09 ev, are not in agreement.

The activation energy, $E_a \approx 6$ ev, obtained is suggestive of a two-step process for this disproportionation reaction. In Chapter 2, measurements of CO disproportionation by direct excitation of cold ground state CO into the electronically excited $a^3\Pi$ state, with vibrational level, $v = 0$, at 6 ev were reviewed. As noted there,
this reaction proceeds with an apparent steric factor of about $10^{-2}$, of gas kinetic $10^{-10}$ [cm$^3$/sec]. It does not appear coincidental that the activation energy of the reaction studied here is very close to the energy of the CO($a^3\Pi$); the reaction may proceed by production of the CO($a^3\Pi$) in the collision of two vibrationally excited CO molecules, followed by the disproportionation step. Further support for this idea is provided by the thermal “dissociation” experiments in CO at high temperatures, reviewed in Chapter 2, section 2.3. As noted there, the data for these experiments, shown in Figure 2.8, suggest a multistep mechanism and kinetic rate data fits suggest activation energies below the dissociation energy of 11.09 ev. This can be demonstrated by plotting the simple Arrhenius rate expression:

$$k_{\text{kinetic theory}} = \left(\frac{8kT}{\pi \mu}\right)^{1/2} \exp\left(-\frac{E_a}{kT}\right)$$

Equation 6.6

Where $k$ is Boltzmann’s constant, $T$ is the gas temperature, $\mu$ is the reduced mass, and $E_a$ is the activation energy. For the relevant reduced mass, $\mu$, with $E_a = 6.0$ ev, we plot Equation 6.6 on the dissociation data of Figure 2.8. This is shown in the following figure:
Figure 6.4: Comparison of thermal data [1], Chackerian [2], Hanson [3], Presley [4], Davies [5], Appleton [6], Jurgen Mick [7] with the calculated gas kinetic rate of Equation 6.6.

It can be seen that the slope of this Arrhenius plot is in good agreement with the considerable database, over the large temperature range from 5,000 to 15,000 K. As noted before, the absolute specific rate values reported here vary enormously, and involve varying collision partner ratios i.e., varying CO/Ar ratios. To agree with the bulk of the measurements for pure CO, a steric factor of $\sim 10^{-2}$ would be required in Equation 6.6 above. This gives a rate in good agreement with the direct CO($^3\Pi$) disproportionation measurements reviewed in Chapter 2. The data of Mick et. al. [7], are for the most dilute concentrations of CO in Ar, and fall considerable below this. It could be suspected that even these data are heavily influenced by the CO-CO disproportionation process, and possibly there is little effect of ladder-climbing to near CO dissociation at 11.09 ev by
CO-Ar collisions. A closer examination of the mechanisms controlling the CO($a^3\Pi$) state could yield information about the overall kinetic rates of the Boudouard reaction thought to occur through the CO($a^3\Pi$) state.

The kinetic rates describing the processes into and out of the CO($a^3\Pi$) state were reviewed in chapter 2. Expressions for the rate of production of the CO($a^3\Pi$) state may be written, by considering that the population of the CO($a^3\Pi$) state is in steady state, and thus all the processes must balance out, In = Out. The particular processes that will be considered are, the forward reaction, the population of the CO($a^3\Pi$) state by two vibrationally excited CO:

$$\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}(a^3\Pi) + \text{CO}(v'),$$

with kinetic rate $k_{\text{forward}}$

Reaction 6.1

The reverse reaction would be:

$$\text{CO}(a^3\Pi) + \text{CO} \rightarrow \text{CO}(v) + \text{CO}(w),$$

with kinetic rate $k_{\text{backward}}$

Reaction 6.2

While there are other process, emission to the ground state, or energy transfer to other states, they are considered to be small and are neglected. The final important reaction to be considered here would be the formation of CO$_2$. The CO$_2$ produced is assumed to not back react because the free carbon created in the reaction reacts very quickly to form C$_2$ and carbon suboxides. In addition, it is assumed that the activation energy of the reverse is so high, that the mechanism can be neglected. This reaction is written as:
CO(a³Π) + CO(v') \rightarrow CO_2 + C, with kinetic rate \( k_{CO2} \)

Reaction 6.3

The rate of change with time of the CO(a³Π) state is written as:

\[
\frac{d[CO(a³Π)]}{dt} = k_{\text{forward}}[CO(v)][CO(w)] - k_{\text{backward}}[CO(a³Π)][CO] - k_{CO2}[CO(a³Π)][CO]
\]

Equation 6.7

Where the [CO] in the last two terms represent CO in any vibrational energy level. The steady state assumption allows Equation 6.7 to be set to zero, and an expression for [CO(a³Π)][CO] may be written as:

\[
[CO(a³Π)][CO] = \frac{k_{\text{forward}}[CO(v)][CO(w)]}{k_{\text{backward}} + k_{CO2}}
\]

Equation 6.8

To develop the expression of the rate of production of CO\(_2\) from the [CO(a³Π)] state, consider Reaction 6.3 and the expression is written as:

\[
\frac{d[CO_2]}{dt} = k_{CO2}[CO(a³Π)][CO]
\]

Equation 6.9

Substitution of Equation 6.8 into the right hand of Equation 6.9 side gives the expression:

\[
\frac{d[CO_2]}{dt} = k_{CO2}\frac{k_{\text{forward}}[CO(v)][CO(w)]}{k_{\text{backward}} + k_{CO2}}
\]

Equation 6.10
Equation 6.10 is an expression for the rate of production of CO$_2$ with time that is based on reactions of CO with the CO($a^3\Pi$) state. The kinetic rates can be grouped to give an overall kinetic rate:

$$k_{\text{overall}} = k_{\text{CO}_2} \frac{k_{\text{forward}}}{(k_{\text{backward}} + k_{\text{CO}_2})}.$$ 

Equation 6.11

Moreover, Equation 6.10 can now be written, in the more familiar form, of Equation 3.2:

$$\frac{d[\text{CO}_2]}{dt} = k_{\text{overall}} [\text{CO}(v)][\text{CO}(w)].$$

Equation 6.12

This equation, using the expression developed in Equation 6.11, can be useful in comparing the measured kinetic rates with reported kinetic rates. Using the rates reported earlier in chapter 2, ($k_{\text{forward}} \sim 10^{-13}$ [cm$^3$/sec], $k_{\text{backward}} \sim 10^{-10}$ [cm$^3$/sec], and $k_{\text{CO}_2} \sim 10^{-12}$ [cm$^3$/sec]), an overall kinetic rate would be approximately $10^{-12} \times 10^{-13} / (10^{-10} + 10^{-12}) \sim 10^{-15}$ [cm$^3$/sec]. This overall rate is three orders of magnitude faster than the kinetic rates that were measured. However, it is important to note that the kinetic rate forward was inferred by fitting kinetic expressions to the experimental data, and has not been measured. Thus, if this particular rate is considered to be an unknown, and using the newly measured overall kinetic rate, then a new forward kinetic rate into the CO($a^3\Pi$) state can be calculated, which is: $k_{\text{forward}} \sim k_{\text{measured}} \times (k_{\text{backward}} + k_{\text{CO}_2})/k_{\text{CO}_2} \sim 10^{-18} \times (10^{-10} + 10^{-12})/ 10^{-12} \sim 10^{-16}$ [cm$^3$/sec]. This forward rate is three orders of magnitude below the proposed value. These calculations could suggest that the measured CO$_2$, and hence the
measured kinetic rate, would be a combination of both mechanisms: Two vibrationally excited CO reactants, and by CO and the CO(\(a^3\Pi\)) state.

6.2 HETEROGENEOUS PHASE EXPERIMENTS

Obtaining kinetic rates for the heterogeneous phase experiments is very difficult due to the several different processes that take place during the reaction. More specifically the experiments rely on several steps: The absorption of the CO onto the surface, the reaction with oxygen and finally the desorption of CO\(_2\) at low temperatures, about 200 °C. The specific processes were outlined in chapter 2, in the final section 2.3. In addition, the reaction rate depends on the number of free surface sites, and oxygen concentration, which were constantly decreasing as the experiments were conducted. However, it was sufficient to show the production of CO\(_2\) above the gas phase, and above the thermal experiments.

The sources of errors in the heterogeneous phase experiments are very similar to experiments in the gas phase, as similar experimental setups were used. Surface phase experiments used similar measurement techniques as the gas phase, and were subjected to similar errors. For example, there are the errors in the correlation of the CO\(_2\) produced with the measurement of the overtone spectra for different helium partial pressures. However, in these experiments the resolution of the CO overtone spectra were not was not sufficient for inferring the VDFs, as the signal was much weaker. In addition, even though the helium partial pressure would fall during experimental runs, the measurements were conducted as faster times then in the gas phase, and thus the decreases had smaller impact on the measurements.
Other errors are in the temperature measurements, and the distance between the thermocouple and the CO laser beam. Temperatures were measured by a thermocouple positioned in the monolith but set away from the carbon monoxide laser, as described earlier in chapter 4. The main source of error was from the assumption that the monolith was capable of conduction faster than the response of the thermocouple itself, and that the temperature was constant throughout the monolith. The conditions for lumped parameter, no spatial heat gradients are present, are for Biot numbers less than 0.1. The Biot number is the ratio of the convection, of the heat from the gas to the surface, to the thermal conductivity, of the surface. The calculated Biot number was \(4.62 \times 10^{-4}\), for a convection value of, \(h_{\text{gas}} = 2.376 \, [\text{kg} \, \text{s}^{-3} \, \text{K}^{-1}]\), which was calculated from known correlations for laminar flow through rectangular channels. The length of the surface, considered for the presence of convection was taken as \(l = 7 \times 10^{-3} \, \text{m}\), and the thermal conductivity of the catalyst was based on the material polycrystalline aluminum oxide (Al\(_2\)O\(_3\)) and is:

\[
k_{\text{cat}} := 36 \left[ \frac{\text{kg} \, \text{m}^2}{\text{sec}^3 \cdot \text{m} \cdot \text{K}} \right]
\]

Additional information on automobile catalysts report thermal conductivity with ranges from 150 W/m-K to 10 W/m-K depending on the material used. The only factor that was left out was influence on the thermocouple by the infrared radiation from the carbon monoxide laser beam. However, this would cause the temperature to be larger than that of the surface. The final influence on the temperature measurements was the contact between the thermocouple and the surface. It was very difficult to determine if the
contact was reasonable. One method was to look for responses in the voltages measuring the temperature, when the carbon monoxide laser beam was positioned. At distances where the thermocouple is ½ an inch away from the carbon monoxide laser beam, the time response was approximately a degree Celsius for every ten seconds. It was considered that this was fast enough for the time ranges for which data was gathered.

Another particular problem was that the same catalyst would be used for the different cases of helium. Thus, the oxygen and free adsorption sites would change, and influence the data. The approach to handle this problem was to work backwards, that is to do the runs with the most amount of helium first, then reduced the amount of helium, so that the last run, which would correspond to the lowest amount of oxygen, would be for the case of no helium. This way, for the sake of comparison, the runs, sequentially in time would underestimate the amount of CO$_2$ produced.

The final largest source of error is that the carbon monoxide laser beam is traveling through the channels, and some of the radiation is impinging on the edge of the monolith. Thus, there is some heat transferred to the surface, causing the temperature of the surface to rise, and possible increase the reaction rate. (In addition, if the surface were at an angle, the carbon monoxide laser beam would be intercepted by the surface, it was insured that this did not occur). However, the orientation of the surface was controllable, and could be placed so that it would not glow red. However, there was always the concern that there was a substantial contribution to the temperature of the surface, aiding the thermal channel of the reaction. It also could have enabled the CO$_2$ that was produced to have desorbed from the surface. The complexity of these reactions
and experiments prevents any quantitative summary of the reaction. However, it is clear
that additional CO$_2$ was being produced by the vibrationally excited CO.

6.3 LIQUID PHASE EXPERIMENTS

Experiments in the liquid phase focused on qualitatively examining energy exchanges, by measuring the vibrational distribution of the CO. Other emission spectra, specifically that of the nitrogen fundamental, were observed in the measured spectra.

Spectra representing the vibrationally excited CO in the liquid phase are compared to spectra taken in the gas phase for the comparison of the vibrational distributions. One such emission is shown below in the figure.
Figure 6.5: Carbon monoxide overtone spectra comparing both the liquid and the gas phase vibrational populations.

Figure 6.5 shows the CO overtone for two different experimental conditions, one is in the gas phase, and the second in the liquid phase, for which the translational temperatures are much lower (87 K). From this figure, it is clear that the liquid phase populations are much higher in the vibrational levels $v = 10$ to $v = 30$. At about vibrational energy level thirty, both distributions begin to fall quickly. Whether there is transfer into the CO($a^3\Pi$) state in the liquid phase is difficult to determine. However, since it has been proposed that the energy transfer requires the presences of free electrons, then due to the high densities of the liquid phase, there is a possibility that there is no transfer into the CO($a^3\Pi$) state.
Energy transfer from the CO to the N\textsubscript{2} was also examined, and shown that it would occur, even at the high densities. The most interesting observation of the CO overtone spectra with nitrogen is the feature at 4.3 \(\mu\text{m}\). It is believed to be the fundamental emission from the nitrogen, however, as was shown in Figure 3 of Chapter 5, the structure was difficult to replicate. The instrument and emission path was not purged, and there was CO\textsubscript{2} present, affecting the structure. The N\textsubscript{2} \(v=1\rightarrow0\) structure lies very close to the carbon dioxide \(v3\) band. (N\textsubscript{2} band at 4291.92 nm and the CO\textsubscript{2} \(v3\) band at 4257.13 nm). Figures 5.8 and 5.9 also show that there is a correlation between the concentrations of CO and N\textsubscript{2} and the structure. Essentially, as the nitrogen concentration increases, the observed amplitude of the structure increases, to a maximum, after which the structure decreases with increasing nitrogen. It is difficult to perform any modeling without fully understanding the structure, and thus the beam path needs to be purged.

To verify that the 4300 nm feature is the N\textsubscript{2} fundamental emission, other experiments with the isotopomer of nitrogen, \(^{15}\text{N}\textsubscript{2}\), were performed. In this case, the heavier nitrogen would have a fundamental band spectrum further to lower energies. Unfortunately, this spectrum is closer to the fundamental of the CO, which adds to the difficulty of fully resolving the structure. There is also a closer resonance between the CO and the heavy N\textsubscript{2}. Thus the vibrational energy in the CO could be transferred into the heavier isotope of nitrogen more efficiently. The spectra shown in figure 7 indicates that this is the case, and the structure sitting on the edge of the CO fundamental is concluded to be the nitrogen fundamental.
The transfer of energy was further studied by examining the CO overtone in liquid nitrogen for different concentrations of CO, which is shown in figure 8 of chapter 5. In this case, it is more difficult to observe any nitrogen fundamental, and the overtone spectra show a very interesting feature in that the populations begin to decrease suddenly at about vibrational energy level $v = 22$. This is the case for all three concentrations of CO. The reason for this sudden decrease is not understood. In addition this vibrational level is too low to be iso-energetic with the CO($a^3\Sigma^+$) state, which occurs at about vibrational energy level $v = 26$. Considering a possibility of energy transfer to another molecule, the best candidates would be $C_2$ and NO. The band centers for the fundamentals for these two molecules are approximately 1828 cm$^{-1}$ for $C_2$ and 1875.84 cm$^{-1}$ for NO, and are their fourth or fifth vibrational level is iso-energetic with the CO($v\sim20, 21$) and further investigation is warranted.
References:

APPENDIX A

RATE EQUATIONS

A.1 MASTER EQUATION

The rate of change of the total number of molecules in vibrational energy level $v$ is represented by the master equation and is written as $[1,2,3]$:}

$$\frac{dn_v^i}{dt} = VV_v^i + VT_v^i + VE_v^i + SRD_v^i + CHEM_v^i$$

Equation A.1

Where $n_v^i$ is the number density of the $v^{th}$ vibrational level for diatomic species $i$. The first three terms on the right hand side are the energy exchange terms due to collisions for the $v^{th}$ vibrational level, for species $i$. The different energy exchange processes are: VV (vibration-to-vibration), V-T/R (vibration-to-translation and vibration-to-rotation), and VE (vibration-to-electronic). The next, fourth, term SRD represents any possible
spontaneous radiative decay from the molecule, from vibrational energy level v, for the i\textsuperscript{th} diatomic species. Finally, the last term, CHEM, represents the change in population in the v\textsuperscript{th} vibrational level due to chemistry. The first two terms, and the spontaneous radiative decay term are known, and will be presented in the following sections. The VE transfer and chemical reactions are known to occur, and an expression for this transfer will be presented. The final term, CHEM, is the rate equation presented in this thesis.

A.2 VIBRATION-TO-VIBRATION ENERGY EXCHANGES

Vibrational-to-vibration energy exchanges were described earlier in chapter 2, and the mathematical expressions for the rates are given in this section. The rate of change in population of the v\textsuperscript{th} vibrational energy level is given by:

\[ \text{VV}_i^v = \sum_w \left[ Q_{i,v,w-1} \left( n_{i,v+1} n_{i,w} - e^{-(\epsilon_{v+1} - \epsilon_v - \epsilon_{w+1})/kT} n_{i,v} n_{i,w+1} \right) \right] - \left[ Q_{i,v,w+1} \left( n_{i,v} n_{i,w} - e^{-(\epsilon_v - \epsilon_{v+1} - \epsilon_{w-1})/kT} n_{i,v+1} n_{i,w-1} \right) \right] \]

Equation A.2

Where the Q’s are the probability of energy exchanges between two species i diatomics, molecules A and B. The indices of the terms in the above equation are for molecule A initially in level v and moving down or up a level, while simultaneously molecule B initially in state w increases its energy level by one or decreases the level by one. The expression for the Q’s are given by:
\[ Q_{i,j,w,w+1}^{v,v-1} = Z_{i,j} \left[ S_{i,j,w,w+1}^{v,v-1} + L_{i,j,w,w+1}^{v,v-1} \right] e^{-\Delta E/2kT} \]

Equation A.3

Where, \( Z_{i,j} = 4\sigma_{i,j}^2 \sqrt{\frac{\pi kT}{2\mu_{i,j}}} \)

Equation A.4

is the gas kinetic collisional factor \([\text{cm}^3/\text{sec}]\), \( T \) is temperature, \( k \) is Boltzmann’s constant, \( \mu_{ij} \) and \( \sigma_{ij} \) are the reduced mass \([\text{kg}]\) and hard sphere collision cross section \([\text{m}^2]\). The \( S \) and \( L \) are the short and long range interactions between the diatomics and are given by:

\[ S_{i,j,w,w+1}^{v,v-1} = S_{i,j}^{\alpha} \frac{v}{1 - \chi_{e,i}v} \frac{w}{1 - \chi_{e,i}w} F_{i,j,w,w+1}^{v,v-1} \left( \lambda_{i,j,w,w+1}^{v,v-1} \right) \]

Equation A.5

Where \( \chi_{e,i} \) is the anharmonic factor for diatomic \( i \), and \( S_{i,j}^{\alpha} \) is an experimental parameter given for CO (carbon monoxide) in Table A.1 at the end of this appendix, and

\[ \lambda_{i,j,w,w+1}^{v,v-1} = 2^{\gamma_{i,j}} \left[ \frac{\Theta_{i,j}}{T \Theta_i^2} \right]^{1/3} \frac{\Delta E}{k} \]

Equation A.6

where \( \Delta E \) is the change in energy between reactants and products and is given by:

\[ \Delta E = E(v) + E(w) - E(v-1) - E(w+1), \]

Equation A.7

and the energy expression used for Equation A.7 is the anharmonic expression as a function of vibrational energy level, \( v \):

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\[ E(v) = \omega (v + \frac{1}{2}) - \omega \chi_e (v + \frac{1}{2})^2 \]

Equation A.8

The and finally the term

\[ F_{i,w,w+1}^{v,v-1} = \frac{1}{2} \left[ 3 - e^{-\frac{2}{\lambda_1} \chi_e} \right] e^{-\frac{2}{\lambda_1} \chi_e} \]

Equation A.9

The long-range dipole-dipole interaction is given by

\[ L_{i,j,w,w+1}^{v,v-1} = \frac{L^0_{i,j}}{T} \left( \frac{g_i^{v,v-1}}{g_i^{1,0}} \right)^2 \left( \frac{g_i^{w,w+1}}{g_i^{1,0}} \right)^2 \exp \left( \frac{-\Delta E^2}{b_{i,j} T} \right) \]

Equation A.10

where

\[ \left( \frac{g_i^{v,v-1}}{g_i^{1,0}} \right)^2 = \left[ \frac{a_i + 1}{a_i + 3 - 2v} \right]^2 \frac{v(a_i + 2 - 2v)(a_i + 4 - 2v)}{a_i(a_i + 3 - v)} \]

Equation A.11

with \( a_i = \frac{1}{\chi_e} \)

Equation A.12

The factor \( L^0_{i,j} \) is also given in the table at the end of this appendix.

A.3 VIBRATION-TO-TRANSLATION ENERGY EXCHANGES
The VT energy exchange between a diatomic and a monatomic, usually a diluent such as argon or helium, results in the vibrational energy either increasing or decreasing while the translational energy of the collision partner respectively decreases or increases.

This complex equation is given as:

\[
\text{VT}_i = \left\{ P_{i,V,v-1} \left[ n_{k,v_i} n_i - e^{-(\varepsilon_i - \varepsilon_{v,v-1})/kT} n_{v,v-1} n_i \right] - P_{i,V,v+1} \left[ n_{k,v_i} n_i - e^{-(\varepsilon_i - \varepsilon_{v,v+1})/kT} n_{v,v+1} n_i \right] \right\}
\]

Equation A.13

The factor, \( P_{i,V,v-1} \) in \([\text{cm}^3/\text{sec}]\), is the probability of the exchange occurring and is given by

\[
P_{i,V,v-1} = P_{i}^0(T) \frac{\nu}{1 - \chi_{v,v-1}} F_{i,v,v-1}\left(\chi_{v,v-1}\right)
\]

Equation A.14

with the similar quantities given above:

\[
\chi_{v,v-1} = 2^{-\frac{3}{2}} \sqrt{\frac{T\Theta_{v,v-1}}{\Theta_i^2 k_B}} \left| \frac{\Delta E}{k_B} \right|
\]

Equation A.15

and, \( F_{i,v,v-1} = \frac{1}{2} \left[ 3 - e^{-\frac{3}{2}\chi_{v,v-1}} \right] e^{-\frac{3}{2}\chi_{v,v-1}} \)

Equation A.16

and

\[
P_{i}^0(T) = \frac{(1 - \chi_{v,v-1})kT}{\left\{ \left[ \tau_i \right]^{\frac{1}{0}} F_{i,v,v-1} \left[ 1 - \exp\left( -\frac{\Theta_i}{kT} \right) \right] \right\}}
\]

Equation A.17
\[ \ln(\tau \rho P) = A_{ij} + B_{ij} T^{-1/3} + C_{ij} T^{-2/3} \]

Equation A.18
The constants for these terms are given in the table at the end of this appendix.

A.4 VIBRATION-TO-ELECTRONIC ENERGY EXCHANGTES

The energy exchange resulting in a transition into an electronic state is given by the simpler expression for diatomic i:

\[ \text{VE}_i = n_T \left( S_{i,v}^{w} [n_{i,v} - n_{i,v} e^{-(e_{v} - e_{w}) / kT}] \right) \]

Equation A.19
where,

\[ S_{i,v}^{w} = S_{\text{VE}}^0 \exp \left[ -\frac{\Delta E}{C_{\text{VE},\sigma_t}} \right] \exp \left[ -\frac{\Delta E}{2kT} \right] \]

Equation A.20
where the constant \( S_{\text{VE}}^0 \) is given at the end of the appendix for two electronic transitions of CO, CO(\( \chi^1 \Sigma^+) \rightarrow \text{CO}(a^3 \Pi) \) and CO(\( \chi^1 \Sigma^+) \rightarrow \text{CO}(A^1 \Pi) \).

A.5 SPONTANEOUS RADIATIVE DECAY

The spontaneous radiative decay term for molecule i, is given by the expression for each vibrational level, v.

\[ \text{SRD}_i^v = \sum_u \left\{ A_{i,v,v}^{v+u,v} n_{k+u} - A_{i,v,v}^{v,v-u} n_{k,v+u} \right\} \]

Equation A.21
where \(v+u\) or \(v-u\) is the final vibrational energy level. The spontaneous radiative decay for vibrational energy level, \(v\) is given by:

\[ A_{i}^{v,v-1} = A_{i}^{10}(v+1) \]

Equation A.22
where \(A_{i}^{10} = 30.3 \text{ [1/sec]}\)

A.6 PARAMETERS

<table>
<thead>
<tr>
<th>Parameters / Species</th>
<th>CO-CO</th>
<th>CO-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_{jk}) [K]</td>
<td>-15.23</td>
<td>10.38</td>
</tr>
<tr>
<td>(B_{jk} [K^{1/2}])</td>
<td>280.5</td>
<td>0</td>
</tr>
<tr>
<td>(C_{jk} [K^{2/3}])</td>
<td>-549.6</td>
<td>0</td>
</tr>
<tr>
<td>(\Theta_{jk}/\Theta_{j}^2 [K^{-1}])</td>
<td>45.6*10^{-2}</td>
<td>1.335*10^{-3}</td>
</tr>
<tr>
<td>(S_{0j}^0 [K^{-1}])</td>
<td>1.64*10^{-6}</td>
<td>-</td>
</tr>
<tr>
<td>(L_{0j}^0 [K])</td>
<td>1.614</td>
<td>-</td>
</tr>
<tr>
<td>(b_{jk} [K])</td>
<td>7.78*10^{-11}</td>
<td>-</td>
</tr>
<tr>
<td>(S_{CO}^0 [\text{cm}^3/\text{sec}])</td>
<td>13.58*10^{-2}</td>
<td>5.49*10^{-2}</td>
</tr>
<tr>
<td>(S_{CO,VE}^0 [-])</td>
<td>5.0*10^{-13}</td>
<td>9.94*10^{-13}</td>
</tr>
</tbody>
</table>

Table A.1: Numerical values for the parameters used in the above equations.
References:

For the majority of the experiments, the gases used were the same, however, in the following assays, the quantities are repeated. These assays were obtained from the published assays by the company, which is reported. Also reported are the grades (current) for the different gases. The information is divided into the sections corresponding to the different experiments. Information regarding the carbon monoxide laser is given last.

**B.1 GAS PHSE EXPERIMENTS**

**Carbon monoxide**

Company: Matheson  
Grade: Ultra High Purity 99.9% min  
Assay: Sum of N₂, CO₂, CH₄, and H₂O < 1000 ppm
Argon

Company: Praxair
Grade: 4.8 O₂ Free 99.995%
Assay: O₂ < 0.5 ppm

Helium

Company: Praxair
Grade: 4.5 grade 99.995%
Assay: O₂, < 5 ppm, and H₂O < 5 ppm

B.2 HETEROGENEOUS EXPERIMENTS

Carbon monoxide

Company: Matheson
Grade: Ultra High Purity 99.9% min
Assay: Sum of N₂, CO₂, CH₄, and H₂O < 1000 ppm

Argon

Company: Praxair
Grade: 4.8 O₂ Free 99.995%
Assay: O₂ < 0.5 ppm

Helium

Company: Praxair
Grade: 4.5 grade 99.995%
Assay: O₂, < 5 ppm, and H₂O < 5 ppm
B.3 LIQUID PHASE EXPERIMENTS

**Carbon monoxide isotope** 88% $^{13}$C$^{16}$O and 12% $^{13}$C$^{18}$O

- **Company:** Isotec Inc., Matheson  
  **CAS Number:** 1641-69-6
- **Grade:** $^{13}$C 99 %
- **Assay:** ~12% $^{18}$O

**Argon**

- **Company:** Spectra Gases, Inc.
- **Grade:** Research Grade 99.9995%
- **Assay:** CO$_2$<0.5 ppm, CO, <0.5ppm, H$_2$<1ppm, N$_2$<1ppm, O$_2$<0.5ppm, Total hydrocarbons<0.5ppm and H$_2$O<0.5ppm

**Nitrogen**

- **Company:** Praxair
- **Grade:** 5.0 Semiconductor Process Gas 99.999%
- **Assay:** O$_2$ < 1ppm, H$_2$O < 3ppm, CO$_2$ < 1ppm, CO < 2ppm, THC < 1ppm, H$_2$ < 2 ppm.

**Nitrogen isotope** $^{15}$N$_2$

- **Company:** Isotec Inc., Matheson  
  **CAS Number:** 29817-79-6
- **Grade:** $^{15}$N 98 %

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B.4 CARBON MONOXIDE LASER

**Carbon monoxide**

Company: Matheson  
Grade: Ultra High Purity 99.9% min  
Assay: Sum of N₂, CO₂, CH₄, and H₂O < 1000 ppm

**Nitrogen**

Company: Praxair  
Grade: 5.0 Semiconductor Process Gas 99.999%  
Assay: O₂ < 1ppm, H₂O < 3ppm, CO₂ < 1ppm, CO < 2ppm, THC < 1ppm, H₂ < 2 ppm.

**Helium**

Company: Praxair  
Grade: 4.5 grade 99.995%  
Assay: O₂, < 5 ppm, and H₂O < 5 ppm
APPENDIX C

CONVERSION OF GAS ROTAMETER SETTINGS TO FLOW RATES

This appendix contains the information necessary to convert the rotameter settings to volumetric flow rates. Information regarding the tube used and the corresponding flow rates provided by the manufacturer is the following, Table C.1.

<table>
<thead>
<tr>
<th>Gas:</th>
<th>Carbon monoxide</th>
<th>Helium</th>
<th>Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of tube</td>
<td>Cole Palmer N112-02</td>
<td>Matheson E600</td>
<td>Cole Palmer NO62-01</td>
</tr>
<tr>
<td>Bottom Rotameter Setting, Rb</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Corresponding flow rate [cm$^3$/min], Frb</td>
<td>21</td>
<td>6</td>
<td>58</td>
</tr>
<tr>
<td>Top Rotameter Setting, Rt</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Corresponding flow rate [cm$^3$/min], Frt</td>
<td>374</td>
<td>150</td>
<td>454</td>
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<tr>
<td>Pressure correction ratio of delivery pressure to atmosphere [-], Pc</td>
<td>44.7atm/14.7 atm</td>
<td>44.7atm/14.7 atm</td>
<td>44.7atm/14.7 atm</td>
</tr>
<tr>
<td>Gas correction term [-], Gc</td>
<td>0.98</td>
<td>0.37</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table C.1: Parameters used in the equations for the calculations of the volumetric flow rates
In this table, the first column contains the definitions for the variables that are used in the following Table C.1 to calculate the volumetric flow rate. The general equation used to calculate the volumetric flow rates for each of these gases is given by:

$$\hat{\nu} = \frac{(F_{rt} - F_{rb}) \cdot R \cdot P_c \cdot \frac{1\text{min}}{G_c} \cdot \frac{60\text{sec}}{1\text{min}}}{(R_{t} - R_{b})}$$

Equation C.1

Where $\hat{\nu}$ is the volumetric flow rate for the corresponding gas, and $R$ is the experimental rotameter setting, which are reported in the following Table C.2:
<table>
<thead>
<tr>
<th>Exp. run</th>
<th>CO Partial Pressure [Torr]</th>
<th>He Partial Pressure [Torr]</th>
<th>Ar Partial Pressure [Torr]</th>
<th>CO Rotameter (R) [-]</th>
<th>He Rotameter (R) [-]</th>
<th>Ar Rotameter (R) [-]</th>
<th>Integration of CO$_2$ Produced [-]</th>
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<tr>
<td>1</td>
<td>14.2</td>
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<td>105</td>
<td>2</td>
<td>0</td>
<td>139</td>
<td>0.1527</td>
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<tr>
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<td>14.2</td>
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<td>103.2</td>
<td>2</td>
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<td>102.4</td>
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<td>134</td>
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<td>5.0</td>
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<td>8</td>
<td>132</td>
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<td>0</td>
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<td>1.5</td>
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<td>2.1</td>
<td>112.7</td>
<td>1</td>
<td>2.5</td>
<td>139</td>
<td>0.0653</td>
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<td>8.9</td>
<td>135</td>
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<td>8.7</td>
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<td>139</td>
<td>0.0361</td>
</tr>
</tbody>
</table>

Table C.2: Rotometer settings for the different experimental conditions for the gas phase experiments.
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20. Farrenq, R., Rossetti, C., Guelachvili, G., and Urban, W., “Experimental rovibrational populations of CO up to v=40 from doppler-limited Fourier spectra
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