COMPUTATIONAL STUDIES OF VOLUME DOMINATED PLASMA PROCESSES IN THE CARBON-MONOXIDE LASER AND CALCULATION OF THE RELATIVISTIC FORM FACTOR FOR ELECTRON IMPACT IONIZATION OF ARGON.

WILLIAM LOWELL. MORGAN

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COMPUTATIONAL STUDIES OF VOLUME DOMINATED PLASMA PROCESSES IN THE CARBON MONOXIDE LASER AND CALCULATION OF THE RELATIVISTIC FORM FACTOR FOR ELECTRON IMPACT IONIZATION OF ARGON

by

William Lowell Morgan

A Dissertation submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the requirements for the Degree of Doctor of Philosophy at The University of Windsor

Windsor, Ontario, Canada

1976
ABSTRACT

COMPUTATIONAL STUDIES OF VOLUME DOMINATED PLASMA PROCESSES IN THE CARBON MONOXIDE LASER/CALCULATION OF THE RELATIVISTIC FORM FACTOR FOR ELECTRON IMPACT IONIZATION OF ARGON

by

William Lowell Morgan

PART I

The theory and methodology for the solution of the electron energy distribution function in a molecular laser discharge plasma is detailed. The steady state Boltzmann equation is solved numerically for mixtures of N₂ and CO including all the important inelastic and elastic collision processes. Predictions on the drift velocity for both N₂ and CO show good agreement with experiment. Some differences with past predictions are noted in the drift velocity of N₂/CO mixtures depending on the excitation cross sections used. In contrast to past calculations, we find that the presence of N₂ does not enhance the electron-CO excitation rate at room temperature. Results of chemical kinetics calculations on the CO-He laser with O₂ as an additive are also presented. In these calculations, the electron energy distribution function is used to compute realistic rate coefficients for electron impact processes that include the effects of collisions of the second kind. The calculations predict, in agreement with experiment, that, due to charge transfer reactions, O₂⁺ replaces C₂O₂⁺ as the dominant ion in the
plasma when \( \text{O}_2 \) is added to a CO-He discharge. In a constant current discharge this results in a lowering of the electric field in the positive column which, in turn, is responsible for more efficient coupling between the electrons and the CO vibrational levels. In addition, we find that for higher partial pressures of \( \text{O}_2 \) in the discharge, there is substantial dissociation into oxygen atoms which has a deleterious effect upon laser performance due to V-T relaxation of the CO laser levels.

PART II

Calculations in the Bethe-Born approximation of the Bethe surface and total cross section for ionization of the Argon \( \text{M}_{\text{III}} \) shell by relativistic electrons are presented. They were performed using Dirac-Hartree-Fock-Slater bound state wavefunctions and numerical continuum wavefunctions, computed from the DHFS potential. In addition, photoionization cross sections were computed in the relativistic dipole approximation. The photoionization results are in agreement with previous calculations in the single-particle central field approximation. The computed electron impact ionization cross sections are in good agreement with experiment for electron energies up to 100 keV. For higher impact energies the computed cross sections deviate greatly from the measured ones. This is shown to be due to inaccuracies in the differential cross section in the small momentum transfer (photoionization) limit which can be traced to
inadequacies in the single particle model. It is shown that these problems can be overcome by use of an approximate formulation, due to Fano, incorporating empirical photoionization data and the computed non-relativistic form factor.
To Joyce, without whose love and caring this work would not have been accomplished.
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I am greatly indebted to Dr. Edward R. Fisher and to Dr. Gordon W. F. Drake for their support and guidance during the course of this research. It is also a pleasure to acknowledge the advice and direction of Dr. Alexander J. Glass in the initial phases of this work. In addition, I would like to thank Dr. Arthur V. Phelps for his helpful comments concerning the laser modelling work discussed herein.
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PART I

COMPUTATIONAL STUDIES OF VOLUME DOMINATED PLASMA

PROCESSES IN THE CARBON MONOXIDE LASER
I. Introduction

The prediction of the operating characteristics of an electric discharge molecular gas laser requires a detailed knowledge of neutral chemistry and energy transfer processes as well as the excitation, attachment, and recombination processes occurring in the discharge plasma. Although considerable effort in the past has concentrated on developing sophisticated models for the energy transfer processes in molecular lasers\(^1,2,3\), only recently has a similar extensive effort been aimed at an understanding of the important plasma processes\(^4,5,6\). This understanding encompasses a predictive capability to model the transient electron density in CW molecular lasers but more importantly to characterize the electron energy distribution function in molecular systems where significant electron energy loss processes are present. These loss processes include excitation of vibrational, rotational and electronic levels, ionization, recombination, and dissociation and attachment processes.

The rate coefficient characterizing these various processes is calculated from
\[ K_j = \left( \frac{2e}{m} \right)^{1/2} \int_0^\infty Q_j(\epsilon) f(\epsilon) \epsilon \, d\epsilon \]  
\[ \text{cm}^3 \text{ sec}^{-1} \]  
(1)

where \( \epsilon = \) relative collision energy (eV)

\( m = \) electron mass (g)

\( Q_j = \) electron impact cross section for \( j^{\text{th}} \) state (cm\(^2\))

\( f(\epsilon) = \) distribution function (probability function) for relative collision energies \( \epsilon \):

\( e = \) electronic charge, 1.602\(^{-19}\) coul.; this is also the conversion between electron volts (eV) and joules of energy since 1 eV = 1.602\(^{-19}\) joule. The energy dependent excitation cross section comes from a wide variety of experimental and theoretical sources.

Recent calculations on the characteristics of pulsed CO/N\(_2\) molecular laser systems have assumed that the electron energy distribution function was Maxwell-Boltzmann\(^1,2\). In terms of the distribution of electron energy, this assumption means

\[ f(\epsilon) = \frac{2}{\pi^{1/2}} \left( \frac{e}{kT} \right)^{3/2} \exp\left[ -\epsilon/(kT/e) \right] \]  
(2)

where \( \epsilon = \) electron energy (eV)

and \( T = \) electron temperature (\(^{0}\)K); defined in terms of the mean electron energy, \( \bar{\epsilon} \), where \( \bar{\epsilon} = (3/2)kT \)

For preliminary calculations on molecular laser phenomenology where the total electron density is unknown, this Boltzmann assumption appears justified\(^1\); however, as more detailed and precise information on the optimum
operating characteristics of molecular laser systems is required, particularly regarding the role of additive species, considerable improvement in the above plasma description is needed. Nighan has shown, for example, that the actual electron distribution is far from Boltzmann\textsuperscript{4,5}, showing regions of underpopulation in the electron energy distribution corresponding to strong coupling to the molecular energy levels. These non-Boltzmann energy distributions are a function of $E/N$, the electric field divided by the total number density, the partial pressure of the gas species present and the state of excitation of the molecular gases (superelastic processes).

In order to incorporate realistic electron energy distribution functions into the molecular laser modeling codes, and to investigate the effects of additives on laser efficiency and power output, a program was initiated to develop a reliable and fast method for the solution to the Boltzmann equation including the coupling to the many available energy states in the gases present in the laser discharge.

A description of the calculation of the electron energy distribution function is given in sections II and III. In the later sections are discussed the applications of this calculation to the study of excitation processes in carbon monoxide lasers with particular emphasis on
the effects that additive gases have on these processes.

It is clear from several past studies on discharge sustained CO molecular lasers$^{1,2,3,34}$ that the primary energy input to the CO vibrational levels is direct electron impact excitation. This excitation occurs via the unstable negative ion, CO$^-$$^{1,23}$, and thus the excitation rates are sensitive to both the electron density (resulting from ionization and recombination processes in the plasma) and the electron energy distribution. This latter sensitivity necessitates that reliable modelling of CO laser performance accurately account for superelastic and inelastic processes which lead to non-Boltzmann electron energy distributions and subsequently alter calculated excitation rate coefficients. Once the vibrational energy is input by the electrons, rapid vibration-vibration energy exchange processes rearrange the vibrational energy until sufficient gain to lase is obtained on individual vibration-rotation-lines of the fundamental sequence in CO. The latter processes are well documented elsewhere$^{1,2,3,31-34}$. This study focuses on the plasma chemistry and plasma electron processes critical to laser operation and, in particular, the role of trace additive species.
II. Application of the Boltzmann Equation to the Electric Discharge

In order to find the distribution in electron energy (or velocity) in a laser plasma we need to start with the kinetic equation describing the dependence of the distribution function upon the electric field strength, particle density, and the various elastic and inelastic collision processes. This kinetic equation, the Boltzmann equation, can be written:

\[ \left[ \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right] f + \frac{F}{m} \cdot \mathbf{v} \cdot \nabla f = \frac{\partial f}{\partial t} \]  

(3) \text{collisions}

where the LHS is the usual hydrodynamic derivative. The form of the RHS depends upon the details of the collision processes being considered. The distribution function, \( f \), is defined such that \( f(\mathbf{r}, \mathbf{v}, t) \) represents the probability of a particle being in the differential volume element \( d^3r \) around \( \mathbf{r} \) with velocity in the range \( (\mathbf{v}, \mathbf{v} + d\mathbf{v}) \) in the time interval \( (t, t + dt) \).

We assume that the laser plasma is placed in a uniform dc-electric field (i.e., \( \mathbf{E} = e\mathbf{E} \)). If the system is in a steady state, the partial time derivative can be eliminated from equation (3). The steady state assumption implies that the time scale for the relaxation of the electron energy distribution is much shorter than the time scale characterizing the change in the populations of the various molecular states. This electron energy relaxation time is
determined by the electron-molecule collision frequency which is given by:

$$\nu = NQ\nu$$

where \(N\) = molecular density (cm\(^{-3}\))

\(Q\) = total elastic collision cross section (cm\(^2\))

and \(\nu\) = electron speed (cm/sec).

The relaxation time, \(\tau\), is defined as \(1/\nu\). The elastic collision cross sections for the major species CO and N\(_2\) lie in the range between \(10^{-15}\) cm\(^2\) and \(10^{-14}\) cm\(^2\)(7), while the molecular number densities in appropriate laser systems are between about \(10^{17}\) cm\(^{-3}\) and \(10^{20}\) cm\(^{-3}\).

Average electron energies are in the range of .5 eV to 2 eV with corresponding speeds between \(4\times10^8\) cm/sec and \(8\times10^8\) cm/sec. These values of \(N\), \(Q\), and \(\nu\) give the following approximate limits on the electron distribution relaxation time:

$$10^{-15}\ \text{sec} \leq \tau \leq 3\times10^{-11}\ \text{sec.}$$

Since the inelastic cross sections are smaller than the elastic cross sections by from one to four orders of magnitude (depending on the particular level) the characteristic time for electron impact excitation of these states will be correspondingly longer. Hence, on this longer time scale the electron distribution will always be in a quasi-steady state. Notice that in discharges possessing a large concentration of a neutral gas, such as He, the
difference between characteristic times will be further enhanced due to the increased elastic collision frequency.

If we assume further that the electron distribution is uniform in space, the spatial gradient term may be eliminated from equation (3). This is the case if the collisional mean free path (MFP) in the gas is much smaller than the characteristic dimension of the discharge tube. Since the mean free path is equal to $1/NQ$, the values of $N$ and $Q$ used above give:

$$10^{-5} \text{ cm} \leq \text{MFP} \leq 10^{-1} \text{ cm}$$

Since the discharge tube is generally much larger than 1 mm in diameter, this should also be a good assumption.

With these assumptions the Boltzmann equation is reduced to:

$$\frac{e\hat{E}}{m} \cdot \nabla_v f(v) = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} \quad (4)$$

The usual treatment$^{10}$ of the LHS involves expanding the distribution function in spherical harmonics. The first two terms would be:

$$f(\vec{v}) = f_0(v) + \frac{\vec{v}}{v} \cdot f_1(v) \quad (5)$$

The rationale behind this expansion procedure involves the assumption that the electric field, $\vec{E}$, is weak enough that the directed speed of the electrons due to the field (drift velocity) is much smaller than their random ("thermal")
speed. A spherical harmonic expansion gives us what is needed, a function having a directional part that amounts to just a perturbation on a spherically symmetric part.

For a typical glow discharge, drift speeds are on the order of $10^6 - 10^7$ cm/sec and the random speeds might be about ten to twenty times greater. For this case the first two terms in the expansion are expected to be adequate.

If the expansion (5) is substituted into the equation (4) and the resulting equation is separated into its scalar and vector parts, the following two equations result:

\[
\frac{eE}{3mv^2} \cdot \frac{d}{dv} \left[ \nabla^2 \bar{f}_1 (v) \right] = \left( \frac{\partial f_o}{\partial t} \right)_{\text{coll.}} \tag{6a}
\]

\[
-\frac{eE}{m} \frac{d f_o (v)}{dv} = \left( \frac{\partial \bar{f}_1}{\partial t} \right)_{\text{coll.}} \tag{6b}
\]

Under the above assumptions the RHS of (6b) is simple,

\[
\left[ \frac{\partial \bar{f}_1}{\partial t} \right]_{\text{coll.}} = \sum_{s} v_{ms} \bar{f}_1 \tag{7}
\]

where $v_{ms}$ is the frequency for elastic collisions between electrons and molecular species, and the sum is over the molecular species labelled by $s$.

Substitution of (7) into (6a) gives the equation for the spherically symmetric (random motion) part of the distribution function, $f_o$:
\[
\frac{1}{3} \left( \frac{eE}{m} \right)^2 \frac{1}{m} \frac{d}{dv} \left\{ v^2 \frac{\partial f_o}{\partial v} \right\} = \left( \frac{\partial f_o}{\partial t} \right)_{\text{coll.}}.
\]

In (8),

\[
\sum_{s} \delta_s Q_{ms} v
\]

where \( \delta_s \) = mole fraction of species \( s \).

\( Q_{ms} \) = elastic momentum transfer collision cross section \( (\text{cm}^2) \) for species \( s \)

and \( N = \) total number density of molecules \( (\text{cm}^{-3}) \).

Inserting \( E = \frac{1}{2}mv^2 \), and changing the variable to energy,

\( u = \frac{mv^2}{2} \), gives,

\[
\frac{1}{3} \frac{(eE)^2}{N} \frac{d}{du} \left\{ \frac{u}{\sum \delta_s Q_{ms}} \frac{\partial f_o}{\partial u} \right\} = \left( \frac{\partial f_o}{\partial t} \right)_{\text{coll.}} \cdot \sqrt{2mu}.
\]

The form of \( \left( \frac{\partial f_o}{\partial t} \right)_{\text{coll.}} \) depends upon the specific interactions that we want to consider. In the most general case it would involve integrals of \( n \)-particle correlation functions. The two assumptions usually made to simplify the collision integral are:

i) Binary collisions

ii) Molecular chaos.

The first of these assumptions is valid if the gas density is sufficiently small. An additional criterion is that the interaction forces be short range. If the interaction is long range, Coulomb forces for example, each particle then interacts with many others simultaneously. A different approach, the Fokker-Planck equation, is needed to treat
this problem.

The second assumption, molecular chaos, simply means that the velocities of two colliding particles are uncorrelated before their collision. This is valid if the gas density is low enough that the mean free path between collisions is much greater than the range of the interaction force.

With these assumptions the collision integral in the Boltzmann equation for \( f(v_1) \) becomes \(^{12}\):

\[
\left\{ \frac{\partial f(v_1)}{\partial t} \right\}_{\text{coll.}} = \int d\Omega d^3v_2 \sigma(\Omega) |\vec{v}_1 - \vec{v}_2| \left\{ f(\vec{v}_1') f(\vec{v}_2') - f(\vec{v}_1) f(\vec{v}_2') \right\}
\]

where \( \sigma(\Omega) \) is the differential collision cross section in the center-of-mass reference frame,

\( \vec{v}_1 - \vec{v}_2 \) is the relative speed of the colliding particles, and

\( \vec{v}_1, \vec{v}_2, \vec{v}_1', \vec{v}_2' \) are the velocities of the colliding particles and the product particles, respectively.

For the molecular laser plasma of interest here, the detailed form of \( \left\{ \frac{\partial f_0}{\partial t} \right\}_{\text{coll.}} \) is \(^{13}\):

\[
\sqrt{2\pi m u} \left\{ \frac{\partial f_0}{\partial t} \right\}_{\text{coll.}} = -\frac{d}{du} \left[ (N \Sigma \frac{2m}{M_s} \delta_{sQ_{ms}}) u^2 (f_0 + kT \frac{df_0}{du}) \right]
\]
\[ -N \sum_{s,j} \delta_s [(u+u_{sj})Q_{sj}(u+u_{sj})f_0(u+u_{sj}) - uQ_{sj}(u)f_0(u)] \\
- N \sum_{s,j} \delta_s [(u-u_{sj})Q_{s,j}(u-u_{sj}) - uQ_{s,j} - jf_0(u)] \]

(11)

where \( M_s \) = mass of molecular species \( s \)

\( T = \) gas temperature (K)

\( u_{sj} = \) energy of the \( j^{th} \) level of molecular species \( s \)

and \( Q_{s,j} \) = collision cross section for excitation (+j)

or de-excitation (-j) of the \( j^{th} \) level of species \( s \).

The distribution function \( f_0(u) \) is normalized such that

\[ \int_{0}^{\infty} f_0(u) u^{1/2} \, du = 1. \]

(12)

On the RHS of equation (11) the first term represents the energy lost by electrons in elastic collisions with molecules, the second term represents the energy gained by electrons in collisions with fast molecules, the third term accounts for the energy lost by electrons in inelastic (molecular excitation) collisions, and the fourth term represents the energy gained by electrons in superelastic (molecular de-excitation) collisions.

The superelastic cross sections are related to the inelastic cross sections by a detailed balance relation giving: \(^{14}\)
uQ_s,\ j(u) = \frac{N_s j}{N_s o} (u+u_{s j}) Q_{s, j} (u+u_{s j}) \quad (13)

where $N_{s o}$ and $N_{s j}$ are the populations of the ground and $j$th states, respectively, of species $s$. Applying detailed balance and combining (11) and (9) gives:

$$
\frac{1}{3} \left( \frac{eE}{N} \right)^2 \frac{d}{du} \left[ \frac{u}{\sum_s \delta_s Q_{s m s}} \frac{df}{du} \right] + \frac{d}{du} \left[ \frac{1}{\sum_s \frac{u}{M_s} \delta_s Q_{s m s}} \right] 
$$

$$
+ \sum_s \delta_s \left[ \frac{Q_{s j} (u+u_{s j}) f(u+u_{s j})}{u^2 (f(u) + kT \frac{df}{du})} \right. 
$$

$$
- uQ_{s j} (u) f(u) 
$$

$$
- \sum_s \frac{N_s j}{N_s o} \left[ \frac{Q_{s j} (u+u_{s j}) f(u)}{u^2 (f(u) + kT \frac{df}{du})} \right. 
$$

$$
- uQ_{s j} (u) f(u-u_{s j}) \right] = 0 \quad (14)
$$

Note that integrating this once over energy gives the equivalent integro-differential equation:

$$
\frac{1}{3} \left( \frac{eE}{N} \right)^2 \frac{u}{\sum_s \delta_s Q_{s m s}} \frac{df}{du} \left( \sum_s \frac{2m}{M_s} \delta_s Q_{s m s} \right) u^2 
$$

$$
+ \sum_s \delta_s \frac{u+u_{s j}}{u} \int du' u' Q_{s j} (u') 
$$

$$
\left[ f(u') - \frac{N_s j}{N_s o} f(u'-u_{s j}) \right] = 0 \quad (15)
$$

In these equations we have dropped the subscript from $f_o$. From here, unless noted otherwise, $f_o(u)$ will be called
the distribution function and will be denoted simply by $f(u)$. Boundary
conditions on these equations are that $f(u)$ be finite at $u = 0$ and $f(u) \to 0$ as $u \to \infty$. The population factor, $\frac{N_{s_j}}{N_{s_0}}$, is related to the vibration temperature, $T_{s_j}$, defined with respect to the ground state by the relation:

$$\frac{N_{s_j}}{N_{s_0}} = e^{-u_{s_j}/kT_{s_j}}$$

Hence, when $T_{s_j} = T_s$ for all levels, we have the Boltzmann population distribution that would exist if the molecules of species $s$ were in thermal equilibrium at temperature $T_s$. This vibrational temperature is a commonly used method of describing the relative populations of vibrational levels.

Frost and Phelps\textsuperscript{15}, Carleton and Megill\textsuperscript{16}, Gibson\textsuperscript{17}, Rockwood, Brau, Proctor, and Canavan\textsuperscript{3}; and Lowke, Phelps and Irwin\textsuperscript{19} solved equation (14) in their respective works. Nighan\textsuperscript{5} used equation (15) in his calculations. Both approaches have been used in the CO\textsubscript{2} calculations of Elliot, Judd, Lockett, and Rockwood\textsuperscript{18}.

If they are important, terms for rotational excitation\textsuperscript{15,16,17}, and long range interactions\textsuperscript{20} can be included in $\left(\frac{\delta f}{\delta t}\right)_{\text{coll}}$. In order to neglect electron-electron (Coulomb) collisions, we assume that the plasma is weakly ionized. Rotational excitation can be neglected if the electron mean energy is much greater than the energy as-
associated with rotational excitation.

As they stand, these equations are independent of electron density. As long as the fractional ionization is small, allowing us to neglect electron-electron interactions this will be valid. For highly ionized gases the electrons will interact with each other, tending to push the distribution function, now electron density dependent, toward the Maxwell-Boltzmann distribution. The effects of electron-electron collisions on the distribution function have been investigated by Rockwood. He found that the effects were negligible for fractional ionization less than about 4×10⁻⁴ in calculations on Hg discharges. Lasers typically have fractional ionizations of less than 10⁻⁵. Hence electron-electron collisions can probably be safely neglected.

Equations (14) and (15) relate the energy gained by electrons from the electric field and the energy gained by de-excitation of higher molecular states to the energy lost by elastic collisions with molecules and by inelastic collisions which excite molecules. This can be more easily seen if equation (14) is integrated over the energy range (0,∞). The result is:

\[
\frac{1}{3} \left(\frac{eE}{N}\right) \int_0^\infty \frac{u}{\delta S_{Qms}} \frac{df}{du} \, du
\]

\[
= \int_0^\infty \left(\frac{2m}{\delta S_{Qms}}\right) \left(\frac{df}{du}\right) \left(f(u) + kT \frac{df}{du}\right) \, du
\]
Recalling that here \( f(u) = f_0(u) \) and noting the relation between \( f_1(u) \) and \( \frac{df}{du} \) expressed by equations (6b) and (7) we see that the LHS of (16) is proportional to the mean particle velocity for the distribution \( f_1 \). This is, of course, the drift velocity. More precisely,

\[
\frac{1}{3} \left( \frac{eE}{N} \right)^2 \int_0^\infty \delta_s Q_{ms} \frac{df_0}{du} \, du = \left[ e \frac{eE}{N} \left( \frac{m}{2e} \right) \right]^{1/2} v_D \quad (17)
\]

Now, looking at the second term on the RHS of (16) we note the similarity between it and equation (1) which defines the rate constants. Simplification of this term, using (1), gives:

\[
\left( \frac{m}{2e} \right)^{1/2} \sum_{s,j} \delta_s u_{sj} \left[ k_{sj} - \frac{N_{sj}}{N_{so}} k_{s-j} \right] \quad (18)
\]

Combining (16), (17), and (18), we get an energy balance equation relating all of the various processes:

\[
\left( \frac{eE}{N} \right) v_D = \int_0^\infty \left[ \frac{2m}{M_s} \delta_s Q_{ms} \right] u^2 \left( f(u) + kT \frac{df}{du} \right) \, du
\]

\[
+ e \left( \frac{m}{2e} \right)^{1/2} \int_0^\infty \delta_s \sum_{j} u_{sj} \left[ k_{sj} - \frac{N_{sj}}{N_{so}} k_{s-j} \right] \quad (19)
\]
III. The Numerical Solution of the Boltzmann Equation

Examination of equation (14) will show that in order to compute \( f(u) \) at some energy \( u \), the values of \( f \) at higher energies, \( u + u_{sj} \), must be known. This characteristic makes the computation of \( f(u) \) difficult. Note, however, that if superelastic collisions can be neglected (i.e., the excited molecular levels are not highly populated) \( f(u) \) only depends upon terms of the form \( f(u + u_{sj}) \); Sherman\(^{22} \) showed that there exists a unique solution to equation (14), in the absence of superelastic processes, subject to the following conditions:

i) \( f(u) \geq 0 \)

ii) \( \int_{0}^{\infty} f(u) u^{1/2} \, du = 1 \) (normalization)

iii) \( \int_{0}^{\infty} f(u) u \, du < \infty \).

Since \( \lim_{u \to \infty} f(u) = 0 \) as \( u \to \infty \), it is possible to start at some high energy, \( u_0 \), where the value of the distribution function \( f(u) \) is small, and integrate equation (14) in toward zero energy, a process which Sherman\(^{22} \) calls "backward prolongation". Another alternative involves the standard finite difference technique of superposing an \( N \) point grid on the interval \((0, u_0)\) and solving the resulting \( N \) simultaneous equations.

When the population of excited molecules is small (i.e., low vibrational temperature) we solve equation (14)
by backward prolongation. This is done by separating
equation (14), which is a second order differential equa-
tion, into two coupled first order equations:

\[
\frac{1}{3} \left[ \left( \frac{eE}{N} \right)^2 \frac{u}{s} \delta s Q_{ms} + \left( \sum \frac{2m}{s} \delta_s Q_{ms} \right) u^2 kT \right] \frac{df}{du} \quad (20)
\]

\[
= \left[ \sum \frac{2m}{M_s} \delta_s Q_{ms} \right] u^2 f(u) - g(u)
\]

\[
\frac{dg}{du} = \sum_{s,j} \delta_s \left[ (u+u_{sj}) Q_{sj} (u+u_{sj}) f(u+u_{sj}) \right.
\]

\[
- u Q_{sj}(u) f(u) \left. - \sum_{s,j} N_{sj} \delta_s N_{so} \right]
\]

\[
\left[ (u+u_{sj}) Q_{sj} (u+u_{sj}) f(u) - u Q_{sj}(u) f(u-u_{sj}) \right]
\]

These equations are solved numerically using a modified
fourth order Hamming Predictor-corrector scheme\textsuperscript{23}.

The initial values \( f(u_0) \) and \( g(u_0) \) are obtained using
an approximate solution to the Boltzmann equation given
by Holstein\textsuperscript{10}.

When the superelastic terms cannot be neglected, the
integration is performed as before until the energy range of
non-zero vibrational cross sections is reached (generally
1-3 eV) where a simple polynomial extrapolation technique
is then used for the terms containing \( f(u-u_{sj}) \). When these
superelastic terms are large (high vibrational tempera-
tures) the polynomial extrapolation causes the numerical
integration to become unstable. If the extrapolated value
is too low the calculated distribution function is too
high, and if it is too high, the computed distribution is too low. In both cases the instability rapidly grows. When instability sets in, the integration is stopped and the standard finite difference technique is used over the remainder of the energy range.

Our solution is an iterative one in that the distribution function calculated on the first run through the above procedure is used for the extrapolation on the next iteration. On higher iterations, if they are needed, a logarithmic average of the previous two distribution functions is used in the extrapolation procedure.

Some Additions to the Formalism

The solution of equation (14) is difficult due to the high vibrational temperatures that we normally deal with in modeling molecular lasers. Because we must treat systems characterized by large excited state populations, it is desirable to include in the calculations transitions between all molecular vibrational levels rather than just between the ground level and the other levels. The cross sections $Q_{sj}(u)$ in the equations represent transitions between the ground level ($j=0$) and the $j$th vibrational level or electronic level. With the exception of theoretical calculations on $N_2^{(24)}$, the cross sections $Q_{j \rightarrow j + \Delta j}$ are generally unavailable. In order to do the calculations
allowing for transitions between arbitrary vibrational levels we assume that:

\[ Q_{j \rightarrow j+\Delta j} = Q_{0 \rightarrow \Delta j} \]

This approximation appears reasonable from the calculations on \( N_2 \) (25) and is also applied to CO which couples to electrons by a similar mechanism.

With this assumption equation (20b) becomes:

\[
\frac{dg}{du} = \sum_{s,j} \delta_s \left( \sum_{i=1}^{j_{\text{max}}-j} \frac{N_{si}}{N_{so}} \right) \left[ (u+u_{sj})Q_{sj}(u+u_{sj})f(u+u_{sj}) - uQ_{sj}(u)f(u) \right] - \sum_{s,j} \delta_s \left( \frac{N_{si}}{N_{so}} + \sum_{i=j+1}^{j_{\text{max}}} \frac{N_{si}}{N_{so}} \right) \left[ (u+u_{sj})Q_{sj}(u+u_{sj})f(u) - uQ_{sj}(u)f(u+u_{sj}) \right]
\]

In equation (21), \( j_{\text{max}} \) is the number of vibrational levels used in the calculation. In calculations involving CO or \( N_2 \), we generally use eight vibrational levels. The vibrational states higher than \( v=8 \) have very small cross sections which have only recently been measured (26).

Ionization processes are included in the calculations using the formulation given by Holstein (10). Let \( Q_{iu}(u,u') \) be the cross section for an electron of energy \( u \) producing an electron in the energy range \( (u',u'+du') \) in an ionizing collision with a molecule of species \( a \) having an ioniza-
tion potential \( u_s^i \). Then as an additional term in equations (14), (20b), and (21) we have:

\[
\left. \frac{dg}{du} \right|_{\text{ion}} = \Sigma_s \left[ \int_{u+u_s^i}^{\infty} du' u Q_s^i(u', u) f(u') \right] - uf(u) \frac{u-u_s^i}{2} \int_0^{u+u_s^i} Q_s^i(u, u') du'
\]

(22)

The first term on the RHS of (22) represents the addition of electrons to the energy range \((u, u+du)\) due to ionizing collisions. The second term represents the loss of electrons from the range \((u, u+du)\).

We generally have no information on ionization cross sections with regard to how the energy remaining after ionization is divided between the resulting electrons.

Since we are dealing with low energies we assume that one of the electrons has zero energy after an ionizing collision. This is a good assumption when the primary electron energy is relatively low, when ionizing collisions are infrequent compared to the other elastic and inelastic collisions, and when there is an electric field to drive the secondary electrons from zero energy so that they relax into the distribution in a short time consistent with the steady state assumption. All of these assumptions are expected to be valid for most molecular gas discharge lasers of interest. In this case, equation (22) becomes:
\[
\frac{dg}{du}\bigg|_{\text{ion}} = \int_{s} (u+u_{s}^{i}) \left[ Q_{s}^{i} (u+u_{s}^{i}) - uQ_{s}^{i} (u)f(u) \right]
\]

where \( Q_{s}^{i}(u) \) = the total cross section for ionization of molecular species \( s \) by an electron of incident energy \( u \).

If the calculation were to be dependent upon electron density we would need to include the electrons produced by ionization in a balance of electron number density, as is done by Rockwood\(^{20}\). Since our calculation is steady state, we treat the electron density as a parameter and assume that the new electrons (the ones produced at zero energy) relax into the distribution on a time scale that is short compared to the time scale of interest to us. This assumption is consistent with our previous arguments concerning the steady state approximation.

**Calculated Distribution Functions for Electrons in Carbon Monoxide**

In Figure III-1 are shown some computed energy distribution functions for electrons in CO. These calculations, which contain no superelastic contributions, illustrate the dependence of the distribution function on \( E/N \). A discussion of the cross sections used will appear in Section IV. The dip in the distribution in the 1-4 eV range is due to strong vibrational coupling of the CO.
Figure III-1: Electron Energy Distribution Functions in CO vs. Energy for Various E/N Using the Cross Sections of Ehrhardt, et al.
with the electrons. At high E/N the distribution function is controlled by the electric field and this structure is washed out. At high E/N the distribution function approaches, as a limiting form, the Dryvesteyn distribution \(8,10\) which has an \(\exp(-\text{const.} \cdot u^2)\) energy dependence. The effects due to superelastic processes are shown in Figure III-2 for a CO vibrational temperature of 4000K. Here electrons in the 1-4 eV energy range gain quanta of energy from the vibration levels, ranging from .27 eV for \(V = 1\) to 2.03 eV for \(V = 8\), increasing the mean energy of the distribution.

The quantity \(\bar{u}\) shown along with these calculations is a "reduced" average energy \(5\) for the distribution which is related to the effective "electron temperature", \(T_e\), and mean energy, \(E_m\), of the distribution by

\[
\bar{u} = kT_e = \frac{2}{3} E_m
\]

where

\[
E_m = \frac{\int_0^\infty f(u)u^{3/2}du}{\int_0^\infty f(u)u^{1/2}du}
\]

In Figure III-3 is shown the fractional energy balance, that is the fraction of the electron energy which is transferred to the internal states of CO, for two values of E/N. As E/N is increased the fraction of energy going into electronic excitation increases at the expense of vibrational excitation, leading to decreased inversion efficiency.
Figure III-2: Effect of Superelastic Collisions on the Electron Energy Distribution Function in CO vs. Energy for an E/N = 4x10^-16 V-cm^2 Using the Hake and Phelps Cross Sections.
Figure III-3: Fractional Energy Balance in CO for Two Values of $E/N$ Using the Cross Sections of Hake and Phelps.
This suggests that CO laser operation at low E/N is desirable except that this means low ionization rates and low electron densities unless appropriate additives or external ionization sources are used. The use of low ionization potential additives to overcome this problem will be discussed later.
IV. Vibrational Excitation Processes in CO/N₂ Mixtures

This electron energy distribution analysis has been applied to the study of CO/N₂ discharges. N₂ is used in carbon monoxide lasers to increase the pumping efficiency of the CO. N₂ is vibrationally excited by electrons just as is CO but cannot radiate the energy away because it lacks a dipole moment. Since the vibrational spacing of N₂ is slightly larger than that of CO it exchanges vibrational energy with the CO and thereby assists in pumping the laser. Nitrogen also affects the electron energy distribution function and, consequently, has an effect upon vibrational excitation rate coefficients, electron temperature, and the partition of electron energy into the various states of excitation. These effects will be discussed in this section.

Vibrational Excitation Cross Sections Used in CO/N₂ Calculations

As will be evident from the results discussed in this study, even the qualitative characteristics of CO laser systems are affected by the set of input cross sections used in the calculation. This is particularly true in CO where the vibrational excitation cross sections are large and, consequently, the power output or gain is sensitive to the shape of the vibrational distribution curve.

Table IV-1 lists the cross section data used in the current calculations to solve equation (20) for the electron energy distribution f(u). All data from these references has
\begin{tabular}{ll}
momentum transfer (elastic) & Hake & Phelps\textsuperscript{27} (1967) & Engelhardt, Phelps,\textsuperscript{28} & Risk (1964) \\
& & & & \\
vibrational excitation & Hake & Phelps (1967) & & \\
& or & & & \\
electronic excitation & Hake & Phelps\textsuperscript{+} (1967) & & \\
\textsuperscript{+}see section V & & & & \\
\end{tabular}

Table IV-1: References to cross sections used in the calculations.
been taken from the recent compilation of Kieffer. Two sets of data appear in the literature for the vibrational excitation cross sections of CO by electrons. Although the shapes of the excitation cross sections from these sources are similar as shown in Figure IV-1, the quantitative differences are important in assessing the role of N₂ in CO laser plasmas (vide infra). The CO and N₂ excitation cross sections for levels v=9 and v=10 for N₂ and CO are also available but were not included in the calculations which follow because they are very small and have a negligible effect on the computed distribution function.

**Calculation of the Distribution for CO/N₂ Mixtures**

Figure IV-2 shows the effect on the electron energy distribution calculated without superelastic contributions by the addition of N₂ to a CO discharge. The presence of N₂ appears to increase the number of electrons in the energy region 1-3 eV which results in both increased mean electron energy as well as enhanced CO excitation rate coefficients. This result suggests, as found previously by Rockwood, that the presence of N₂ in the laser plasma might enhance the power output from the CO laser independently of the N₂-CO pumping process via vibrational-vibrational energy exchange known to occur in this mixture. However, actual calculations performed on the CO/N₂ system are found to be strongly dependent on the CO vibrational cross section set used and generally do not show this enhanced CO pumping as will be discussed later.
Figure IV-1: CO Vibrational Excitation Cross Sections
Taken from the Compilation of Kieffer (7).
Figure IV-2: Effect of N₂ on the Electron Energy Distribution Function in CO/N₂ Mixtures Using the Cross Sections of Hake and Phelps.
The addition of \( N_2 \) to the discharge will have an additional effect that may lead to greater efficiency in vibrational excitation. Because its cross sections for vibrational excitation are smaller, the addition of \( N_2 \) at constant value of \( E/N \) increases the mean electron energy as shown in Figure IV-2. This raises the high energy "tail" of the distribution function causing an increase in the rate coefficient for ionization which, in turn, results in increased electron density in the plasma. The addition of \( N_2 \) will, then, via this sequence of events, cause an increase in the vibrational excitation rates and thereby increase the efficiency of a CO laser.

**Plasma Drift Velocities**

One measure of the successful operation of a molecular plasma code is agreement between predicted and measured transport properties. In this context, drift velocity measurements in \( N_2 \) and CO are available and are herein presented in comparison with predicted values from the laser plasma code. Figure IV-3 shows the drift velocity versus \( E/N \) for both CO and \( N_2 \) in comparison to literature values. Note that the two sets of cross section data for CO shown in Table IV-2 are used and are so labeled in the figure.

The \( N_2 \) drift velocities and the CO drift velocities using the Hake and Phelps cross sections agree well with the measured values from Massey and Burhop\(^{30}\). Both sets of cross sections give results that are substantially different from the experimental results at low \( E/N \). Both
Figure IV-3: Calculated Drift Velocities vs. E/N for CO and N$_2$ Compared to Data from Massey and Burhop (30).
sets of CO cross sections give good agreement at high E/N 
(i.e. above about 2x10^-16 V-cm^2).

The predictions for the CO/N\textsubscript{2} mixture drift velocities 
versus mole fraction of CO for various E/N are shown in 
Figure IV-4 in comparison to the earlier predictions of 
Rockwood\textsuperscript{29}. The velocities predicted using the cross sections 
of Hake and Phelps are in substantial agreement with the 
Rockwood predictions while the Ehrhardt cross sections give 
rise to a somewhat different mixture dependence. These 
differences become more dramatic when we look at electron 
excitation rates in CO/N\textsubscript{2} mixtures which are given in the next 
section.

The Effect of CO/N\textsubscript{2} Mixtures on Electron Excitation Rates

Of major interest in laser plasma predictions is the 
total rate at which energy flows into the vibrational modes of 
CO due to hot electrons. In Figure IV-2 we noted that the 
presence of N\textsubscript{2} causes a favorable shift in the electron energy 
distribution function, increasing the mean electron energy at 
fixed E/N and reducing the dip in the electron energy distribu-
tion associated with coupling to the CO vibrational modes. 
To investigate the direct effect on the CO excitation rates as 
a function mixture ratio, we calculated the total excitation 
rate for CO, \( \dot{f}_{\text{CO}} \),

\[
\dot{f}_{\text{CO}} = \delta_{\text{CO}} \sum_j \left( k_j - k_{-j} \exp(-u_j/kT_j) \right)
\]
Figure IV-4: Calculated CO/N₂ Mixture Drift Velocities for Several E/N Compared to the Calculations of Rockwood (Solid Lines).
where \( \delta_{CO} \) = fraction of CO

\( u_j \) = energy of \( j^{th} \) level

\( k_j \) = inelastic rate constant

\( k_{-j} \) = superelastic rate constant

and \( T_j \) = vibrational temperature of \( j^{th} \) level.

Figure IV-5 shows the results for the total CO excitation rate versus fraction of \( N_2 \) for various \( E/N \) in comparison with the previous calculations of Rockwood\(^{29}\). Three effects are particularly important to note. When the Hake and Phelps cross sections are used we find rather good agreement with Rockwood's predictions for high \( E/N \) but poor agreement at low \( E/N \). The inclusion of a superelastic contribution, however, (arbitrarily chosen as \( T_v = 4000 \) °K for illustrative purposes) leads to a disagreement even at high \( E/N \).

The conclusions reached by Rockwood that an optimum \( N_2/CO \) mixture ratio exists as shown by Rockwood's curves in Figure IV-5 appears questionable when another cross section set is used as well as when superelastic processes are included. These calculations, though, do not take into account other processes due to the addition of \( N_2 \) that may affect these results. One effect, an increase in electron density, has been discussed above. In addition, there will be other molecular species, atomic species, and negative ions produced in the discharge that, although in small concentrations will not alter the distribution function appreciably, may affect the vibrational excitation via a variety of energy transfer processes. In order to assess the
Figure IV-5: Total Electron Energy Flow into Vibrational Modes of CO as a Function of \( \text{N}_2/\text{CO} \) Mole Fraction for Several \( E/N \). (—— calculations of Rockwood)
importance of these processes a study of the plasma chemistry of the discharge is needed. Because the CO-N₂ system would be an extremely difficult one for which to model the chemistry, since it would involve neutral and ionic reactions of molecules composed of C, O, and N atoms, the simpler CO-O₂ laser was chosen for study. This system is important because it is known that O₂ as an additive enhances the power output of a CO laser. The plasma chemistry of the CO-O₂ laser is discussed in the next section.
V. The Plasma Chemistry of the CO-O₂-He Discharge

A number of experimenters\textsuperscript{35-39} have found that a small amount of O₂ added to a CW CO laser plasma has a pronounced effect upon the operation of the laser. Bhaumik, et al.\textsuperscript{36} have found that small amounts of O₂ (approximately 5\% of the CO partial pressure) enhanced the power output by a factor of 10\%-20\% and reduced carbon deposits on the walls of the laser tube. They suggested that the O₂ affected the dissociation reaction CO⁺C+O by driving it to the left. Greater amounts of O₂ had a deleterious effect on laser operation, possibly due to the large electron attachment cross section of O₂ or to the formation of CO₂, in their opinion. Hartwick and Walder\textsuperscript{37} found that total laser output increased and that the laser became more stable with the addition of O₂ to a CO-He discharge. The optimum mixture was found to be 28 torr He, 2 torr CO, and 0.1 torr O₂. In addition, they measured the gas temperature in the plasma using a thermocouple and correlated it to laser output finding that the minimum in temperature, approximately 295 °K, corresponded to the maximum in power output as the O₂ flow rate was varied for a liquid nitrogen cooled laser. At slow oxygen flow rates the measured kinetic temperature was approximately 320 °K.

Extensive work involving the effects of O₂ upon CO lasers has been done by Keren, Avivi, and Dothan\textsuperscript{38,39}. They found that the addition of O₂ increased the power output and decreased the operating E/N of a water cooled CO flow laser.
At a constant current of 17 mA, the laser output power reached a maximum of 4 watts with the addition of 50 m-torr of O₂ to a mixture of 1.4 torr CO in 18 torr He and the axial field strength in the discharge dropped from 136 V/cm to 88 V/cm. Power output then decreased with the addition of larger concentrations of O₂ and lasing was completely quenched at an O₂ partial pressure of 100 m-torr. They also pointed out that the discharge was very unstable and that laser action could not be obtained in the absence of the O₂ additive. On the basis of the measured decrease in E/N and a calculation of the fraction of electron energy flowing into CO vibrational and electronic states as a function of E/N (similar to that presented in Figure III-3 here) they concluded that the enhanced power output was due to more efficient vibrational pumping because of the lower E/N.

Keren, et al. also analyzed the composition of the ions leaving the discharge using a mass spectrograph and found that with the addition of 20 m-torr O₂ to the laser plasma (1.4% of the CO partial pressure), O₂⁺ became the dominant positive ion in the discharge. With no oxygen present the dominant ion is the C₂O₂⁺ cluster as has been observed in the past. They suggest that the dominance of O₂⁺ is due to ionization via a three step process:

\[ \text{e}^- + \text{CO} \rightarrow \text{CO}^*(a^3\Pi) + \text{e}^- \]
\[ \text{CO}^* + \text{O}_2 \rightarrow \text{CO} + \text{O}_2^*(\text{metastable}) \]
\[ \text{O}_2^* + \text{e}^- \rightarrow \text{O}_2^+ + 2\text{e}^- \]

claiming that the probability of producing O₂⁺ by direct
ionization is at least a factor of twenty lower than the probability of this process. They discount the charge transfer reaction,

$$\text{CO}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}$$

as a means of forming the $\text{O}_2^+$ because, in their opinion, it cannot explain the decrease in $E/N$ that occurs with the addition of molecular oxygen. Using this three-step model they compute that about 0.5% of the $\text{O}_2$ molecules are excited to $\text{O}_2^*$ for a total $\text{O}_2$ partial pressure of 25 m-torr.

Because very small amounts of molecular oxygen added to a CO laser have significant effects upon laser performance, it appears clear that the plasma properties of the discharge are affected but, at present, it is not known how. The calculations that follow are directed toward providing some systematic explanation of the observed properties of additive $\text{O}_2$ in a CO discharge. This is accomplished by studying the electron impact excitation processes in the discharge using the electron energy distribution calculation described above and by studying the chemical kinetics of the system by numerically integrating the rate differential equations for the formation and removal of each chemical species.

**Electron Impact Processes**

The cross sections for electron impact excitation of the vibrational modes of CO have been discussed in section IV above. For the electronic excitation of CO by electron impact
there is little data available. What most workers have used in the past has been a single composite cross section, due to Hake and Phelps, with a threshold of 6 eV and a peak value of $5 \times 10^{-16}$ cm$^2$ at 10 eV. This corresponds to the CO(a$^3\Pi$) state. This cross section, however, is not a measured or computed cross section but, rather, just a value that was included in their calculations to "prevent electrons which penetrate the vibrational barrier from reaching unrealistically large energies." They point out that "the magnitude chosen for this cross section is probably much larger than the true excitation cross section for this state." This became apparent when, in the course of this work, computed ionization rate coefficients were several orders of magnitude smaller than their values realistically should have been. For example, in a 7% CO and 93% He mixture with $E/N = 3 \times 10^{-16}$ V-cm$^2$ the Hake and Phelps electronic cross section gives an ionization rate coefficient of $1.3 \times 10^{-13}$ cm$^3$/sec while the cross sections discussed below give a coefficient of $2.3 \times 10^{-10}$ cm$^3$/sec. This comes about because the ionization rate coefficient, which is the integral over energy of the ionization cross section times the distribution function (equation 1 of section I), is very sensitive to the magnitude and shape of the high energy tail of the distribution function. As the electronic cross section is increased, the tail of the distribution function drops and thus the ionization rate coefficient decreases.

The information available on CO electronic cross sections
is summarized as follows. Lassettre and Silverman\textsuperscript{41} and Trajmar, Williams, and Cartwright\textsuperscript{42} have published experimental differential cross sections for the excitation of a number of CO electronic states. Their data is of little use in this work because it is taken at energies substantially higher than the energy range of importance in gas discharges—400 to 600 eV in reference (41) and 20 eV in reference (42). We need total cross sections from threshold to about 25 eV. For this we have the work of Mumma, Stone, and Zipf\textsuperscript{43} on the excitation of CO($a^3\Pi$) and CO($A^1\Pi$), and the theoretical work of Chung and Lin\textsuperscript{45} on the excitation of eleven CO electronic states.

In these calculations we have included the two CO electronic states with the largest cross sections: the $a^3\Pi$ state at 6.04 eV and the $A^1\Pi$ state at 8.07 eV. The cross sections used are composites of those given in references 43-54. They are in substantial agreement with a similar set of cross sections due to Sawada, et al.\textsuperscript{46}. It should be pointed out that revisions such as this in the electronic excitation cross sections used in solving the Boltzmann equation have a negligible effect on the results of the calculations presented thus far. They will affect energy flow calculations such as those shown in Figure III-3 but that particular figure is meant just to be an illustration of how vibrational pumping efficiency can vary with $E/N$.

The references to all of the cross section data used
in these calculations are given in Table V-1. Some comments are in order for several of the excitation processes shown. With reference to excitation of the \( A^3\Sigma_u^+ \) and \( B^3\Sigma_u^- \) states of \( O_2 \), it is known that these excited states predissociate. The \( O_2(A^3\Sigma_u^+) \) state\(^{49}\) predissociates into \( O(^3P) + O(^3P) \)\(^{48}\) and \( O_2(B^3\Sigma_u^-) \) predissociates into \( O(^3P) + O(^1D) \)\(^{48,49}\). Although there are several ways for the \( O_2(B) \) state to predissociate into \( O(^3P) + O(^3P) \) via curve crossings\(^{49}\) the probabilities of this occurring are unknown. It has been assumed in this work that all of the excitation follows the \( ^3P + ^1D \) predissociative path. The cross section for ionization of the \( O_2^* \) metastable is unknown and has been taken to be the same as that for ionization of \( O_2(X) \). This is about the least arbitrary method of obtaining an estimate of the cross section for this process in the absence of experimental or theoretical data. There is some support for this assumption from the work of Burrow\(^{50}\) on dissociative attachment from \( O_2^* \). He measured the ratio of the ionization cross section of the \( ^1\Delta_g \) state to that of the \( x^3\Sigma_g^- \) state at approximately 0.5 eV above each respective threshold and found it to be 0.8 \( \pm \) 0.3.

Chemistry of the CO-O\(_2\)-He system

In order to assess the importance of some of the processes that can occur in the discharge, the computer code for calculating the electron energy distribution function
<table>
<thead>
<tr>
<th>Electron Impact Processes</th>
<th>Energy Loss (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>e(^-) + CO:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. CO(^+(8\ \text{levels}))</td>
<td>0.266-2.034</td>
<td>26</td>
</tr>
<tr>
<td>2. CO(a(^3\Pi))</td>
<td>6.04</td>
<td>see text</td>
</tr>
<tr>
<td>3. CO(A(^1\Pi))</td>
<td>8.07</td>
<td>see text</td>
</tr>
<tr>
<td>4. C + O(^-)</td>
<td>9.00</td>
<td>75</td>
</tr>
<tr>
<td>5. C(^+) + O(^-)</td>
<td>12.55</td>
<td>75</td>
</tr>
<tr>
<td>6. CO(^+)</td>
<td>14.013</td>
<td>7</td>
</tr>
<tr>
<td>e(^-) + O(_2):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. O(_2)(8\ \text{levels})</td>
<td>0.193-1.46</td>
<td>7</td>
</tr>
<tr>
<td>8. O(_2)(a(^1\Delta))</td>
<td>0.98</td>
<td>76</td>
</tr>
<tr>
<td>9. O(_2)(b(^1\Sigma))</td>
<td>1.64</td>
<td>76</td>
</tr>
<tr>
<td>10. O(_2)(A(^3\Pi))</td>
<td>4.5</td>
<td>27,77</td>
</tr>
<tr>
<td>11. O(_2)(B(^3\Pi))</td>
<td>8.4</td>
<td>27,77</td>
</tr>
<tr>
<td>12. 9.7 eV allowed(^51)</td>
<td>9.7</td>
<td>77</td>
</tr>
<tr>
<td>13. O + O(^-)</td>
<td>3.62</td>
<td>75</td>
</tr>
<tr>
<td>14. O(_2)^{\pm}</td>
<td>12.063</td>
<td>7</td>
</tr>
<tr>
<td>15. O(^+) + O</td>
<td>19.54</td>
<td>75</td>
</tr>
<tr>
<td>e(^-) + O:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16. O(^{1}\ \text{D})</td>
<td>1.96</td>
<td>78</td>
</tr>
<tr>
<td>17. O(^{1}\ \text{S})</td>
<td>4.17</td>
<td>78</td>
</tr>
<tr>
<td>18. O(^+)</td>
<td>13.6</td>
<td>7</td>
</tr>
<tr>
<td>e(^-) + O(_2)^*:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19. O(_2)^{\pm}</td>
<td>11.0</td>
<td>see text</td>
</tr>
</tbody>
</table>

Table V-1: Electron impact processes in the CO-O\(_2\) system.
was combined with a chemical kinetics code. This allows the concentrations of chemical species to be computed as a function of time. Since we are studying a CW laser, this computation is carried out in time until the species concentrations are approximately in steady state. We integrate the differential rate equations rather than directly solving the steady state equations because the coupled non-linear algebraic equations that arise out of a steady state analysis are exceedingly difficult to solve in a systematic way. In addition, there are some species in a fast flow laser (such as CO₂ in a CO laser) that do not reach steady state. The chemistry code that was used in this work is based on the Runge-Kutta-Merson algorithm for the integration of stiff differential equations used by Keneshea in his studies of ionospheric chemistry. In this scheme initial CO, O₂, and He densities and an initial electron density close to their expected steady state values are specified. A value for E/N and an initial vibrational temperature are also specified as inputs to the calculation of the electron energy distribution. As time progresses and the CO vibrational temperature changes the electron distribution function is recomputed and new rate coefficients calculated to reflect these changes.

A list of the seventy-nine chemical reactions included in this calculation is presented in Table V-2. Only a relative few, however, are really important and will be discussed here. The rate coefficients for the reactions and
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coeff.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CO + E-</td>
<td>CO' + E-</td>
<td>9.4E-09</td>
</tr>
<tr>
<td>2. CO' + E-</td>
<td>CO + E-</td>
<td>2.2E-08</td>
</tr>
<tr>
<td>3. CO + E-</td>
<td>CO* + E-</td>
<td>6.8E-11</td>
</tr>
<tr>
<td>4. CO* + E-</td>
<td>CO + E-</td>
<td>1.6E-08</td>
</tr>
<tr>
<td>5. CO + E-</td>
<td>CO+ + E- + E-</td>
<td>2.4E-14</td>
</tr>
<tr>
<td>6. CO + E-</td>
<td>C + O-</td>
<td>2.8E-14</td>
</tr>
<tr>
<td>7. CO + E-</td>
<td>C+ + O- + E-</td>
<td>9.3E-17</td>
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<td>8. CO' + E-</td>
<td>CO+ + E- + E-</td>
<td>2.4E-14</td>
</tr>
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<td>9. O2 + E-</td>
<td>O2' + E-</td>
<td>2.3E-10</td>
</tr>
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<td>10. O2' + E-</td>
<td>O2 + E-</td>
<td>4.2E-10</td>
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<td>11. O2 + E-</td>
<td>O2* + E-</td>
<td>1.9E-10</td>
</tr>
<tr>
<td>12. O2* + E-</td>
<td>O2 + E-</td>
<td>5.4E-10</td>
</tr>
<tr>
<td>13. O2 + E-</td>
<td>O2+ + E- + E-</td>
<td>6.6E-14</td>
</tr>
<tr>
<td>14. O2 + E-</td>
<td>O + O-</td>
<td>5.1E-11</td>
</tr>
<tr>
<td>15. O2 + E-</td>
<td>O + O-</td>
<td>5.5E-12</td>
</tr>
<tr>
<td>16. O2 + E-</td>
<td>O+ + O- + E-</td>
<td>6.1E-18</td>
</tr>
<tr>
<td>17. O2 + E-</td>
<td>O + O* + E-</td>
<td>2.6E-11</td>
</tr>
<tr>
<td>18. O + E-</td>
<td>O* + E-</td>
<td>6.1E-10</td>
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<tr>
<td>19. O + E-</td>
<td>O+ + E- + E-</td>
<td>4.9E-14</td>
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<td>20. O2* + E-</td>
<td>O2+ + E- + E-</td>
<td>1.6E-13</td>
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<tr>
<td>21. O- + CO</td>
<td>CO2 + E-</td>
<td>7.3E-10</td>
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<tr>
<td>22. CO* + CO</td>
<td>CO' + CO'</td>
<td>9.9E-11</td>
</tr>
<tr>
<td>23. CO* + CO</td>
<td>C + CO2</td>
<td>1.1E-11</td>
</tr>
<tr>
<td>24. CO+ + CO + CO</td>
<td>C2O2++ CO</td>
<td>1.4E-28</td>
</tr>
<tr>
<td>25. C2O2++ CO</td>
<td>CO+ + CO + CO</td>
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</tr>
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<td>26. C2O2++ E-</td>
<td>CO + CO</td>
<td>7.4E-08</td>
</tr>
<tr>
<td>27. O2+ + E-</td>
<td>O + O-</td>
<td>1.0E-08</td>
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<tr>
<td>28. O2+ + E-</td>
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</tr>
<tr>
<td>29. O* + O2</td>
<td>O + O2</td>
<td>7.5E-11</td>
</tr>
<tr>
<td>30. O2 + O + M</td>
<td>O3 + M</td>
<td>6.4E-34</td>
</tr>
<tr>
<td>31. O* + O3</td>
<td>O2 + O2</td>
<td>3.8E-12</td>
</tr>
<tr>
<td>32. O + O3</td>
<td>O2 + O2</td>
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<tr>
<td>33. O2 + O3</td>
<td>O2 + O2 + O</td>
<td>1.5E-13</td>
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<tr>
<td>34. O+ + O2</td>
<td>O2+ + O</td>
<td>4.0E-11</td>
</tr>
<tr>
<td>35. O2+ + E- + M</td>
<td>O2 + M</td>
<td>8.0E-29</td>
</tr>
<tr>
<td>36. O- + O2+</td>
<td>O + O2</td>
<td>1.0E-07</td>
</tr>
<tr>
<td>37. O- + O</td>
<td>O2 + E-</td>
<td>2.0E-10</td>
</tr>
<tr>
<td>38. O- + O2</td>
<td>O3 + E-</td>
<td>5.0E-15</td>
</tr>
<tr>
<td>39. O3 + E-</td>
<td>O- + O2</td>
<td>1.0E-11</td>
</tr>
<tr>
<td>40. O- + O2*</td>
<td>O3 + E-</td>
<td>3.0E-10</td>
</tr>
<tr>
<td>41. O- + O2+ + M</td>
<td>O3 + M</td>
<td>1.9E-27</td>
</tr>
<tr>
<td>42. O2 + E- + M</td>
<td>O2- + M</td>
<td>1.0E-33</td>
</tr>
<tr>
<td>43. O + E- + M</td>
<td>O- + M</td>
<td>1.0E-31</td>
</tr>
<tr>
<td>44. C + O2</td>
<td>CO' + O*</td>
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<tr>
<td>45. C + CO2</td>
<td>CO + CO</td>
<td>7.0E-19</td>
</tr>
<tr>
<td>46. C + O2+</td>
<td>CO+ + O</td>
<td>2.3E-10</td>
</tr>
<tr>
<td>47. C+ + CO2</td>
<td>CO+ + CO</td>
<td>1.8E-09</td>
</tr>
<tr>
<td>48. C+ + O2</td>
<td>CO+ + O</td>
<td>1.1E-09</td>
</tr>
<tr>
<td>49. CO+ + E-</td>
<td>C + O</td>
<td>9.2E-08</td>
</tr>
<tr>
<td>50. CO+ + E- + M</td>
<td>CO + M</td>
<td>8.5E-27</td>
</tr>
</tbody>
</table>

Table V-2: Reactions used in the plasma chemistry calculation.
### Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coeff.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>51. C + O + M = CO + M</td>
<td>1.0E-32</td>
<td>65</td>
</tr>
<tr>
<td>52. CO+ + O2 = CO + O2+</td>
<td>2.0E-10</td>
<td>62</td>
</tr>
<tr>
<td>53. CO+ + O = CO + O+</td>
<td>1.4E-10</td>
<td>63</td>
</tr>
<tr>
<td>54. C2O2++ + O2 = CO + CO + O2+</td>
<td>2.0E-10</td>
<td>†</td>
</tr>
<tr>
<td>55. O+ + CO2 = O2+ + CO</td>
<td>1.1E-09</td>
<td>63</td>
</tr>
<tr>
<td>56. CO* + O2 = CO + O2*</td>
<td>2.0E-10</td>
<td>54</td>
</tr>
<tr>
<td>57. O* + CO = O + CO'</td>
<td>1.7E-11</td>
<td>66</td>
</tr>
<tr>
<td>58. O* + CO = O + CO</td>
<td>5.6E-11</td>
<td>66</td>
</tr>
<tr>
<td>59. 0 + CO' = 0 + CO</td>
<td>5.9E-15</td>
<td>67</td>
</tr>
<tr>
<td>60. O2- + O = O3 + E-</td>
<td>5.0E-10</td>
<td>62</td>
</tr>
<tr>
<td>61. O2- + O = O2 + O-</td>
<td>3.3E-10</td>
<td>63</td>
</tr>
<tr>
<td>62. O2- + O2+ = O2 + O2</td>
<td>4.2E-07</td>
<td>63</td>
</tr>
<tr>
<td>63. O2- + O2 = O2 + O2 + E-</td>
<td>2.0E-18</td>
<td>63</td>
</tr>
<tr>
<td>64. O2- + O3 = O2 + O3-</td>
<td>4.0E-10</td>
<td>63</td>
</tr>
<tr>
<td>65. O2- + O2* = O2 + O2 + E-</td>
<td>2.0E-10</td>
<td>63</td>
</tr>
<tr>
<td>66. O- + O3 = O + O3-</td>
<td>1.0E-09</td>
<td>63</td>
</tr>
<tr>
<td>67. O2+ + O3- = O3 + O + O</td>
<td>1.0E-07</td>
<td>68</td>
</tr>
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<td>68. O2+ + O3- = O3 + O2</td>
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<td>68</td>
</tr>
<tr>
<td>69. O3- + O = O2- + O2</td>
<td>1.0E-10</td>
<td>68</td>
</tr>
<tr>
<td>70. O3- + O = O2 + O2 + E-</td>
<td>1.0E-13</td>
<td>68</td>
</tr>
<tr>
<td>71. O2+ + O2 + O2 = O4+ + O2</td>
<td>2.8E-30</td>
<td>63</td>
</tr>
<tr>
<td>72. O2+ + O2 + M = O4+ + M</td>
<td>1.0E-31</td>
<td>63</td>
</tr>
<tr>
<td>73. O4+ + O2 = O2+ + O2 + O2</td>
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<td>63</td>
</tr>
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<td>74. O4+ + O = O2+ + O3</td>
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<td>63</td>
</tr>
<tr>
<td>75. CO' + HE = CO + HE</td>
<td>1.7E-17</td>
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</tr>
<tr>
<td>76. CO' + = CO</td>
<td>3.4E+01</td>
<td>1</td>
</tr>
<tr>
<td>77. O2' + HE = O2 + HE</td>
<td>1.6E-15</td>
<td>70</td>
</tr>
<tr>
<td>78. O4+ + E- = O2 + O2</td>
<td>1.8E-07</td>
<td>59</td>
</tr>
<tr>
<td>79. O+ + E- + M = 0 + M</td>
<td>2.0E-27</td>
<td>63</td>
</tr>
</tbody>
</table>

† This rate coefficient has been taken to be equal to that of reaction (52).
references to them are also given in Table V-2. The rate coefficients for the first twenty reactions, except number (8), are computed using the electron energy distribution code and the cross sections discussed above. The rate coefficient used for ionization of vibrationally excited CO (reaction 8) is taken to be the same as that for ionization of ground state CO (reaction 5). The rate coefficients shown in Table V-2 for reactions (1) through (20) were computed using an $E/N = 1 \times 10^{-16}$ V-cm$^2$, and a CO vibrational temperature of 3000° K for a gas mixture corresponding to 1.4 torr CO, 50 m-torr O$_2$, and 18 torr He. These values are shown for illustrative purposes as they are typical for the conditions being discussed in this work. The electron temperature under these conditions is 1.0 eV. The gas temperature has been taken to be 300°K. The rate coefficients in reactions (21) through (79), where they are dependent upon electron or gas temperature, have been computed using these values.

To illustrate how the parameters critical to the calculations being presented here vary with $E/N$ and vibrational temperature we have in Figures V-1 through V-3 plots of the ionization rate coefficient of CO, mean electron energy, and CO$^+$, C$_2$O$_2^+$, and O$_2^+$ recombination rate coefficients. These were computed for mixtures of 1.4 torr CO, 50 m-torr O$_2$, and 18 torr He corresponding to the experimental conditions of Keren, et al.$^{39,39}$ The sensitivity
Figure V-1: CO ionization rate coefficients for a 7% CO-93% He mixture.
Figure V-2: Electron Mean Energy as a Function of E/N and CO Vibrational Temperature for a Mixture of 7% CO and 93% He.
Figure V-3: Recombination Rate Coefficients as Functions of E/N and Vibrational Temperature.

\[ k_{\text{co}^+} = 1.33 \times 10^{-5} T_e^{-.53} \]
\[ k_{\text{c}_2\text{o}_2^+} = .243 T_e^{-1.6} \]
\[ k_{\text{o}_2^+} = 3.88 \times 10^{-6} T_e^{-5.6} \]
of the ionization rate coefficient to E/N (Fig. V-1) is striking and graphically explains why, for the sake of stability, these discharges are operated in a current regulated mode.\textsuperscript{36}

The results of the calculation of the time evolution of chemical species in a CO-O\textsubscript{2}-He discharge are displayed in Figures V-4 through V-7. In these calculations, the electron density was taken to be $5 \times 10^{-9}$ cm\textsuperscript{-3} initially with a gas mixture of 1.4 torr CO, 50\textmu{} torr O\textsubscript{2}, and 18 torr He and E/N equal to $1.05^{-16}$ V-cm\textsuperscript{2}. The initial CO vibrational temperature was chosen to be 1000\textdegree{}K and as it increased the electron impact rate coefficients were recomputed as $T_{\text{vib}} = 1500^0, 2000^0, 2200^0, 2400^0$, etc. The species CO, O\textsubscript{2}, O, O\textsubscript{2}\textsuperscript{+}, and He were included in the calculation of the electron energy distribution function, but, as can be seen in Figure V-8 for a CO-O\textsubscript{2}-He mixture, the presence of oxygen in small concentrations has little effect upon the shape of the distribution function.

These calculations show that O\textsubscript{2}\textsuperscript{+} becomes the dominant ion in CO lasers containing O\textsubscript{2} due to charge transfer reactions and that, as a consequence of recombination kinetics, it is responsible for the lowering of the E/N in a current regulated discharge. This is in direct opposition to the explanation advanced by Keren, et al.\textsuperscript{38,39} This lowering of E/N allows for more efficient pumping of the CO vibrational levels leading to increased power output. The calculations also demonstrate that O atoms, formed by
Figure V-5: CO-O₂ Kinetics
Figure V-6  CO-O_2 Kinetics
Figure V-7: CO−O₂ Kinetics
Figure V-8: Electron Energy Distribution Function for CO-O₂-He Mixture.
electron impact dissociation of $O_2$, have an adverse effect upon laser performance when $O_2$ is added in large enough concentrations. This is due to relaxation of the CO laser levels by vibrational translational energy exchange in CO-O collisions. The details of these findings, and others, are presented in the following sections.

**Ion kinetics of the CO-O$_2$-He discharge**

It was pointed out above that $O_2^+$ is found$^{39}$ to be the dominant positive ion in CO discharges containing oxygen, even when the $O_2$ is present in partial fractions less than 1%. The results of the calculation (Figure V-6) are in agreement with this observation. The dominance of $O_2^+$ is due to $O_2$ having the lowest ionization potential of the major species in the discharge and is formed almost entirely through charge transfer reactions. $C_2O_2^+$, which is the dominant ion in CO discharges without oxygen, and $CO^+$ both readily charge transfer with $O_2$ (reactions 52 and 54). Even though there is a large amount of atomic oxygen formed in the discharge, as will be discussed later, the $O^+$ ion does not appear in large concentrations because it too has a large rate coefficient for charge transfer with $O_2$ (reaction 34). The same is true of CO although it has not been included in these calculations.

Ionization from the $O_2$ metastable, which appears in large concentrations due to reactions (11) and (56), $O_2^+e^- \rightarrow O_2^*+e^-$ (11); $CO^*O_2 \rightarrow CO + O_2^*$ (56), has been included in
these calculations but is unimportant as a source of $O_2^+$ in comparison to the charge transfer processes. This observation is in disagreement with Keren et al. 38, 39 who postulated that ionization via metastable $O_2$ is the dominant process for $O_2^+$ production.

This replacement of $CO^+$ and $C_2O_2^+$ by $O_2^+$ as the major ionic species has an important effect upon the voltage-current characteristics of the discharge. As can be seen in Figure V-3 the rate coefficient for recombination of $O_2^+$ is substantially smaller than that of either $CO^+$ or $C_2O_2^+$. This results in an increased electron density so that, under constant current operation, the electric field must be reduced. As has been repeatedly pointed out in this work, a lower electric field increases the efficiency of electron impact excitation of the CO vibrational states eventually resulting in increased power output.

As a test of this hypothesis a simple calculation was performed in which, given a recombination rate coefficient (as a function of electron temperature), $E/N$ and CO vibrational temperatures were varied and ionization rate coefficients calculated in order to achieve a chosen current density. Current density, $j$ (amp/cm$^2$) is related to electron drift velocity $v_d$ (cm/sec) and number density $N_e$ (cm$^{-3}$) by

$$j = ev_dN_e \text{ where } e = 1.6\times10^{-19} \text{ Coul.}$$

The usual assumption is that the radial distribution of electron density in a cylinder of radius $R$ is proportional
to the zeroth Bessel function of \( r/R \):

\[
\frac{N_e(r)}{N_e(0)} = J_0 \left( 2.4 \frac{r}{R} \right)
\]

so that \( N_e(r=R) = 0 \). The total current, \( i \), is then the integral of the current density over the discharge area,

\[
i = 4\pi v_d N_e(0) \int_0^R J_0 \left( 2.4 \frac{r}{R} \right) r \, dr
\]

\[
= 2.72 \, R^2 j \, (A)
\]

Hence, the experiments of Keren, et al.\(^{38}\) on a 0.5 cm radius discharge at a current of 17 mA involve a current density of about 25 mA/cm\(^2\). The drift velocity \( v_d \) can be computed from the electron energy distribution function. If one assumes that the only formation and removal processes for electrons are ionization and recombination, respectively, a steady state electron density can be computed from

\[
\frac{d[e^-]}{dt} = k_{ion} [e^-][CO] - k_{recomb} [e^-][+ \text{ion}]
\]

If the ion and electron densities are assumed to be equal (i.e., one ion dominates), at steady state:

\[
\frac{d[e^-]}{dt} = 0 \Rightarrow [e^-]_{ss} = \frac{k_{ion}}{k_{recomb}} [CO]
\]

Now if the same procedure is carried out for excitation of CO (\( v=1 \)) by electrons and deexcitation by superelastic collisions with electrons, which is predicted (see below) to be the major loss process for low vibrational levels, we find at steady state
\[
\frac{[\text{CO} (v=1)]}{[\text{CO} (v=0)]} = \frac{k_{0+1}}{k_{1+0}}
\]

Using these two expressions and the equation for current density we can choose an \( E/N \) and \( \text{CO} \) vibrational temperature, solve the Boltzmann equation obtaining rate coefficients, temperature, and drift velocity, and calculate a current density and new vibrational temperature. This process can be repeated until the assumed and computed vibrational temperatures are equal and the desired current density has been obtained. This approach is, admittedly, crude, but contains the essence of the processes involved in establishing the electron density in the plasma. The greatest inaccuracy lies in the assumption concerning vibrational excitation and deexcitation of \( \text{CO}(v=1) \) since there are other important processes, such as excitation and deexcitation to and from \( \text{CO}(v=2, 3, ...) \), that affect the population of the \( v=1 \) level.

Despite its defects, this calculation gives results reasonable enough to illustrate the point concerning the relationship between recombination rate, \( E/N \), and efficiency of vibrational excitation. The results are presented in Table V-3. To achieve similar current densities and vibrational temperatures using the \( \text{O}_2^+ \) recombination coefficient required a 10% decrease in \( E/N \) from the value needed using \( k_{\text{recomb}} (\text{CO}^+) \). The lowering of \( E/N \) resulted in a 34% decrease in the fraction of energy flowing into \( \text{CO} \) electronic states and a 9% increase in the fraction being
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<th>Using $k_{\text{O}_2^+}$</th>
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<td>$[e^-]$ (cm$^{-3}$)</td>
<td>$4.93 \times 10^{10}$</td>
<td>$4.99 \times 10^{10}$</td>
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<td>$j$ (amp/cm$^2$)</td>
<td>$23.4 \times 10^{-3}$</td>
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<td>$\overline{\varepsilon}$ (eV)</td>
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<td>$v_{\text{drift}}$ (cm/sec)</td>
<td>$2.97 \times 10^6$</td>
<td>$2.78 \times 10^6$</td>
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<td>$f(\text{CO}^*)$</td>
<td>$21.3%$</td>
<td>$14.0%$</td>
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<td>$f(\text{CO}_{V=1})$</td>
<td>$18.1%$</td>
<td>$19.8%$</td>
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Table V-3: Results of the simplified calculation of ionization-recombination processes.
channeled into v=1 alone. Thus, in contrast to Keren et al., we have shown that O$_2^+$ directly affects both the E/N of the plasma and the excitation of CO vibrational energy in agreement with the experimental observations.

**Negative ions in a CO discharge**

The time development of the negative ion densities is shown in Figure V-7. Although O$^-$ is rapidly formed by dissociative attachment of CO and O$_2$, CO + e$^- + C + O^-$ (6), O$_2$ + e$^- + O + O^-$ (15), it is rapidly removed by detachment collisions with CO: CO + O$^-$ $\rightarrow$ CO$_2$ + e$^-$ (21). This is in contrast to the chemistry of CO$_2$ lasers as discussed by Nighan and Wiegand$^5$ and by Garscadden and his collaborators$^{72,73}$, where negative ions appear to control the stability of the discharge at low E/N. The results obtained here are consistent with the observation$^5$ that additions of CO to CO$_2$ lasers stabilize the discharge through electron detachment reactions with the negative ionic species.

**The role of atomic oxygen in the discharge**

As mentioned earlier in this section, at higher O$_2$ partial pressures the laser output power is found to decrease and the neutral temperature increase. Our calculations indicate that both of these effects are due to the formation of O atoms in the plasma. The cross sections for electron impact excitation of predissociative O$_2$ electronic states are large. This leads to large production
rates of oxygen atoms (reactions 14 and 17) and, consequently, large O concentrations in the discharge. The calculated time development of neutral oxygen species is shown in Figure V-5.

For small concentrations of $O_2$ as an additive to CO lasers the dissociation into O atoms has little effect upon laser performance. Above some threshold $O_2$ concentrations, however, vibrational-translational energy transfer collisions between CO and O (reaction 59) is expected to become the dominant deexcitation mechanism for high CO vibrational levels. Since it is the higher vibrational levels that dominate the laser output spectrum, the presence of O atoms will degrade the laser output. Examples of vibrational deexcitation rate coefficients for CO ($v=1$) and CO ($v=12$) are shown in Table V-4. For low vibrational states ($v=1$ to $v=8$) superelastic collision with electrons is the primary deexcitation process. In the absence of oxygen, radiation (reaction 76) and VT collision with He (reaction 75) are primarily responsible for CO vibrational deexcitation. The radiative rate per CO ($v=12$) molecule is given by the Einstein A coefficient in Table V-4. The deactivation rate per CO ($v=12$) by collision with He is $k_{VT}[He] = 262 \text{ sec}^{-1}$ for 18 torr of He. This is approximately the same as the radiation rate. Using the superelastic rate coefficient for $v = 1+0$, which is probably too large for the $v = 12+11$ transition, and an electron density of $10^{-10}$ gives a deexcitation rate of $10 - 100 \text{ sec}^{-1}$. Hence
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<td>239.9 sec$^{-1}$</td>
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<td>$1.7 \times 10^{-17}$ cm$^3$/sec</td>
<td>$9.0 \times 10^{-16}$ cm$^3$/sec</td>
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<tr>
<td>$V-T$ with O$^{67}$, $\gamma$</td>
<td>$5.9 \times 10^{-15}$</td>
<td>$\geq 2.9 \times 10^{-13}$ $^+$</td>
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<td>$V-T$ with O$_2$ $^{74}$, $\nu$</td>
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<td>$V-T$ with CO$_2$ $^{74}$, $\nu$</td>
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<tr>
<td>Superelastic</td>
<td>$10^{-9}$</td>
<td>$10^{-8}$ $^{\dagger}$</td>
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<tr>
<td>with e,$\gamma$</td>
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$^+$The value shown is computed assuming the same scaling with $\nu$ as the CO-He V-T process.

$^{\dagger}$The rate coefficient is typically in this range with its exact value depending upon the electron energy distribution function.

Table V-4: Deexcitation of CO vibrational levels.
radiation and He V-T exchange are likely to be the dominant deexcitation mechanisms.

When O atoms are present, even in small concentrations, they may strongly affect vibrational relaxation since the CO-O V-T rate coefficient is more than one hundred times larger than that for CO-He. If the same scaling with v is assumed for V-T relaxation by O atoms as exists for the He V-T process, an O partial pressure of 52 m-torr would be needed for CO-O V-T to be equal to the radiation or the CO-He V-T processes. Laser performance will be degraded when the contribution of the CO-O V-T rates is non-negligible in comparison to the fixed radiation and CO-He V-T rates. The scaling of vibrational relaxation rate coefficients with increasing vibrational level is, in general, uncertain. However, the collision system of \( \text{O}(^{3}p) + \text{CO}(^{1}Σ, ν') \), which correlates with the triplet state of \( \text{CO}_{2} \), offers the possibility of a strong "chemical" interaction through curve crossing to the \( \text{CO}_{2}(^{1}Σ) \) state and the enhanced energy transfer possibilities associated with a short lived triatomic complex.

Although these arguments are qualitative in nature, it is entirely plausible that the partial pressure of O\(_{2}\) at which the laser output is seriously degraded (i.e., 100 m-torr) yields a 20% dissociation to O (i.e., 40 m-torr since each O\(_{2}\) yields 2 O atoms) and the CO-O V-T process begins to relax the vibrationally excited CO leading to reduced laser output.
It can be seen from the rate coefficients in Table V-4 that vibrational relaxation by $O_2$ will be unimportant for the concentrations being discussed here. The same will be true for small concentrations of $CO_2$, which is formed primarily by reactions (21) and (23), $O^- + CO \rightarrow CO_2 + e^-$ (21); $CO^* + CO \rightarrow C + CO_2$ (23). The density of $CO_2$ is still increasing, however (Figure V-6), at the end of the calculation indicating that there may be a large buildup of this species in closed CO systems. In flowing discharges with a residence time of .1 -.5 sec this may not be a problem but in a sealed system $CO_2$ may be present in large enough concentrations to be a major source of vibrational deexcitation.

Additional discussion of CO laser chemistry

Carbon in the CO laser is formed primarily by reaction (23). Reactions (22) and (23)

\[ CO^* + CO \rightarrow CO^+ + CO \] (22)
\[ CO^* + CO \rightarrow C + CO_2 \] (23)

Correspond to two channels for deexcitation of $CO^*$ by CO. The total rate coefficient is known\(^{54}\), but the branching ratio is not. It has been assumed in these calculations that 10% of the $CO^* + CO$ reactions follow the $C + CO_2$ branch. The C production rate is critically dependent upon this branching ratio and there is, unfortunately, no information on the branching ratio or even on the carbon concentrations found in CO discharges. The carbon is
readily removed by reaction (44)

\[ C + O_2 + CO^\dagger + O^* \]  \hspace{1cm} (44)

with \( O_2 \). This is a satisfactory explanation of the observation that the addition of \( O_2 \) to a CO discharge reduces the quantity of carbon deposited in the system. The products of this reaction have been assumed to be \( CO^\dagger \) and \( O(1D) \) as these are spin allowed and energetically accessible.

Finally, mention should be made of the possible role of \( O(1D) \) in the discharge. It is rapidly formed by reactions (17) and (28):

\[ O_2 + e^- \rightarrow \Theta + O^* + e^- \]  \hspace{1cm} (17)

\[ O_2^+ + e^- \rightarrow O + O^* \]  \hspace{1cm} (28)

and, perhaps, (44) as discussed above. The \( O^* \) is then rapidly removed in reactions (57) and (58).

\[ O^* + CO \rightarrow O + CO^\dagger \]  \hspace{1cm} (57)

\[ O^* + CO \rightarrow O + CO \]  \hspace{1cm} (58)

Although \( O^* \) has little effect upon the chemistry of the system it may, in this way, be an important source for heating the gas.

Using the reaction rates for both \( O(1D) \) quenching into translational energy (reaction 58) and relaxation of \( CO^\dagger \) into translational energy (reaction 59) as given in Table V-5, the total energy flux from these reactions is
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Table V-5: Rate Constants and Rates of Individual Reactions† at t = 0.1 sec
Table V-5, continued

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<td>1.69^{08}</td>
</tr>
<tr>
<td>66</td>
<td>1.00^{-09}</td>
<td>2.05^{09}</td>
</tr>
<tr>
<td>67</td>
<td>1.00^{-07}</td>
<td>9.67^{07}</td>
</tr>
<tr>
<td>68</td>
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<td>1.93^{08}</td>
</tr>
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<tr>
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<td>1.75^{09}</td>
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<tr>
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<td>1.00^{-31}</td>
<td>1.43^{11}</td>
</tr>
<tr>
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<td>2.00^{07}</td>
</tr>
<tr>
<td>74</td>
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75. 1.70^{-17}, 3.09^{16}
76. 3.36^{+01}, 2.11^{17}
77. 1.60^{-15}, 1.19^{15}
78. 1.11^{-07}, 3.05^{09}
79. 2.00^{-27}, 1.11^{09}

†See Table V-2 for a listing of the reactions
sufficient to explain the observed\textsuperscript{37} gas temperature increase with increasing $O_2$ pressure beyond the optimum pressure for laser output.
VI. Conclusion

This report has outlined the theory and methodology behind modeling the steady state plasma of a molecular laser system incorporating both the inelastic and superelastic processes appropriate to a given laser mix. Sample calculations on the CO/N₂ laser system have confirmed the non-Boltzmann character of the electron energy distribution function in substantial agreement with the earlier work of Nighan⁴ and Rockwood⁵. The effect of added N₂ is shown to increase the density of electrons in the energy range for maximum coupling to CO vibrational energy but detailed calculations on excitation rates indicate that this shift is essentially compensated for by the decrease in CO partial pressure required to maintain a constant total molecular density (constant E/N). If superelastic processes are included in the CO/N₂ mixture case, further support is given to pure CO being the optimum mixture for coupling the electron energy into CO.

The laser plasma code discussed in this report is very efficient and is easily extended to any number of molecular or atomic constituents for which cross section information is available. The results of the plasma calculations presented here are in substantial agreement with the results of other workers as well as measured drift velocities for N₂ and CO. There are, however, clear indications from the results of the calculations presented in
this report that reliable cross section information is critical to the understanding and optimization of laser plasma performance.

We have presented results of calculations on the chemical kinetics of the CO laser with O_2 as an additive. We have shown that vibrational temperature is an important parameter in the evaluation of ionization and recombination rate coefficients, and, in these calculations, have used rate coefficients for excitation and ionization computed from an electron energy distribution that includes the effects of gas composition and vibrational temperature. These calculations have demonstrated that O_2^+ is the dominant ion in CO-O_2 systems as a consequence of charge transfer reactions with CO^+ and C_2O_2^+. In a current regulated discharge this results in a lowering of the E/N leading to more efficient pumping of the CO vibrational levels. We have also found, from these calculations, that O atoms, formed by electron impact dissociation of O_2, have a deleterious effect upon CO laser performance for large concentrations of O_2 as an additive. This is due to relaxation of the CO laser levels by vibrational translational energy exchange in CO^+-O collisions.

These results suggest that Xe and Hg, which are known to enhance laser output even if present in very small concentrations\textsuperscript{36} may affect the plasma chemistry of the CO laser in a similar manner to O_2 as the Xe^+ and Hg^+ ions can be expected to recombine much more slowly than O_2^+. In
addition, due to their low ionization potentials, they may enhance ionization rates. With knowledge of the fundamental processes occurring in laser discharges and the ability to perform plasma and kinetics calculations such as those presented in this work, one should be able to search systematically for additives that affect the plasma chemistry in such a way as to produce desired laser performance characteristics.
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PART II

CALCULATION OF THE RELATIVISTIC FORM FACTOR FOR ELECTRON IMPACT IONIZATION OF ARGON
1. Introduction

This work arose out of an effort to model the physical processes involved in pumping high pressure gas lasers using a relativistic electron beam.\textsuperscript{1} In these systems, the energetic electrons in the incident beam produce many low energy secondary electrons as a result of ionizing collisions with the target laser gas. The secondary electrons are then responsible for most of the subsequent excitation processes in the gas.

As a specific example, energy loss calculations for a relativistic electron beam in argon depend upon a knowledge of the ionization cross-section differential in energy loss $d\sigma/dW$. Large discrepancies were found at relativistic energies between the total cross-section computed from the semi-empirical analytic form for $d\sigma/dW$ based on the Bethe-Born approximation, as given by Peterson and Allen\textsuperscript{2}, and the experimental cross sections\textsuperscript{3}. The Peterson and Allen total cross sections have the correct non-relativistic $A\ln E/E + B/E$ energy dependence, where $E$ is the incident electron energy, but it incorrectly retains this energy dependence for larger relativistic impact energies (i.e., above about $10^5$ eV). Since the experimental $\sigma(E)$ starts to level off at about $10^5$ eV and even rises at higher energy, due to relativistic effects that will be discussed later,
the Peterson and Allen total ionization cross section is too small at relativistic impact energies. It is, for example, approximately a factor of five too small at $10^6$ eV and is even worse at higher energy.

Although the reason for this was the use of the non-relativistic Bethe-Born approximation by Peterson and Allen, the problem stimulated interest in doing a completely relativistic calculation of the so-called Bethe surface for the ionization of argon within the framework of the Bethe-Born approximation. This is what is attempted in the presentation that follows.

Although this problem is now far removed from the laser studies mentioned above, and, in fact, is much more detailed and involved than is necessary for the laser modelling work, it does have merit in its own right. It serves as a test of the relativistic Bethe-Born approximation and is, to my knowledge, the first time that a proper calculation of the relativistic Bethe surface using relativistic self-consistent atomic wave functions has been attempted.

In the discussion that follows, cgs units have been used except for energy, which is given in electron volts. In analyses taken from other authors, their units, whatever they may be, have been converted to the cgs-eV system for the sake of consistency.
II. The Bethe-Born Theory for Ionization of Atoms by Relativistic Electrons

As shown by Bethe\(^4\),\(^5\), the relativistic form of the differential cross section for ionization by electron impact is given, in first order perturbation theory, by

\[
\frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{4\pi^2} \frac{E_i E_f k_f}{\hbar^4 c^4 k_i} |U|^2 \text{ cm}^2/\text{eV/sr}
\]  

(1)

where \( E_i \) and \( E_f \) are, respectively, the initial and final total energy of the incident electron,

\[
E_i = (m^2 c^4 + c^2 \hbar^2 k_i^2)^{1/2}
\]

\[
E_f = (m^2 c^4 + c^2 \hbar^2 k_f^2)^{1/2} = E_i - W
\]

\( W \) is the energy loss, \( k_i \) and \( k_f \) are the initial and final propagation vectors \((\vec{k} = \vec{p}/\hbar)\), and \( d\Omega \) is the element of solid angle for the scattered electron.

The matrix element \( U \) is proportional to the interaction energy between the incident electron and the atom, and is given by

\[
U = \int \psi_f^* (\vec{r}) V(\vec{r}) \psi_i (\vec{r}) \ d\vec{r}
\]  

(2)

where \( V(\vec{r}) \) = the potential energy of the incident electron and the atom;

\( \psi_i (\vec{r}) \) = the initial wavefunction of the system of incident electron + atom;

\( \psi_f (\vec{r}) \) = the final wavefunction of the system.

In the first Born approximation, the wavefunctions of the incident electron and of the atom are assumed to be
independent and thus the wavefunction of the system is describable as a product of the electron wavefunction, $\phi(\hat{r})$, and the atom wavefunction, $\psi(\hat{r}_1)$ for the $i$th atomic electron. If the atom has $z$ electrons, the matrix element (2) becomes

$$ U = \int \phi_f^*(\hat{r}) \psi_f^*(\hat{r}_1, \ldots, \hat{r}_z) V(\hat{r}; \hat{r}_1, \ldots, \hat{r}_z) \phi_i(\hat{r}) \psi_i(\hat{r}_1, \ldots, \hat{r}_z) \, d\hat{r}_1 \ldots d\hat{r}_z d\hat{r} \quad (3) $$

In the Born approximation, the electron wavefunctions $\phi(\hat{r})$ are taken to be plane wavefunctions, $e^{i\hat{r} \cdot \hat{\tau}}$ in non-relativistic theory, and $u(\hat{p})e^{i\hat{p} \cdot \hat{\tau}}$ in the relativistic case. The Dirac plane wavefunctions will be discussed in a later section.

In the Bethe-Born approximation we assume that the collision can be described as a binary collision between the incident electron and the atomic electron that is ejected as a result of the collision. Using this assumption and the Möller\textsuperscript{7,8} formula for the interaction between two relativistic electrons, the matrix element (3) becomes

$$ U = e^2 \int \int \frac{\phi_f^*(\hat{r}_1) \psi_f^*(\hat{r}_2) \left( 1 - \hat{a}_1 \cdot \hat{a}_2 \right)}{|\hat{r}_1 - \hat{r}_2|} e^{i\hat{p}_c \cdot (\hat{r}_1 - \hat{r}_2)} \phi_i(\hat{r}_1) \psi_i(\hat{r}_2) \, d\hat{r}_1 \, d\hat{r}_2 \quad (4) $$

where $|\hat{r}_1 - \hat{r}_2|$ is the distance between the two electrons and $\hat{a}_1$ and $\hat{a}_2$ are the Dirac operators. Here the $\hat{a}_1$ and
the $\hat{a}_2$ operate on the $\phi_i(\hat{r}_1)$ and $\psi_i(\hat{r}_2)$ respectively. The exponential is the retardation factor, which is due to the finiteness of the speed of light. The terms involving the $\hat{a}$'s arise from the magnetic interaction of the spins of the two electrons, electron spin being an intrinsic part of relativistic quantum theory. The Born approximation is used not only because it is a good approximation for high energy encounters\textsuperscript{4}, but also because it is about the only way of doing relativistic calculations since, in relativistic theory, there is no known general form for the many-body interaction energy in closed form.

The exchange matrix element is the same as (4) except with the final wavefunction given by $\phi_f(\hat{r}_2) \psi_f(\hat{r}_1)$. As shown by Mott and Massey\textsuperscript{40}, by Rudge\textsuperscript{41}, and, for relativistic interactions, by Perlman\textsuperscript{10}, the exchange matrix element is negligible for high (relative to the ionization energy) impact energies such as are being dealt with in this work. Hence it will be neglected here.

For the ionization calculation $\psi_i$ is a bound state wavefunction and $\psi_f$ is a continuum wavefunction. If the wavefunctions $\phi_i$ and $\phi_f$ are taken to be plane waves we have the Born approximation.

Let

$$\phi_i(\hat{r}_1) = u_i(\hat{p}_i)e^{i\hat{k}_1\cdot\hat{r}_1}$$

$$\phi_f(\hat{r}_1) = u_f(\hat{p}_f)e^{i\hat{k}_f\cdot\hat{r}_1}$$
then
\[
U = e^2 \int \frac{d}{d\tau_1} \left\{ e^{i\left( \mathbf{k}_1 \cdot \mathbf{r}_1 \right)} \mathcal{M}_1 \frac{e^{i\mathbf{W} \cdot \tau_1}}{i\mathbf{W} \cdot \tau_1} d\tau_1 \right\} \psi_f^*(\tau_2) (1-\alpha_1 \cdot \alpha_2) \psi_i (\tau_2) d\tau_2
\]

The integral over \( \tau_1 \) is
\[
\frac{4\pi}{K^2 - W^2 / (\hbar c)^2} e^{iK \cdot \tau_2}
\]

where \( K = k_1 = k_f \).

This gives for the cross section,
\[
\frac{d^2\sigma}{d\Omega d\omega} = \frac{4e^4}{\hbar^4 c^4} E_i E_f \left( \frac{k_f}{k_i} \right) \frac{1}{\left[ \frac{K^2 - W^2}{\hbar^2 c^2} \right]^2}
\]

The integral over \( \tau_2 \) is defined as the relativistic form factor \( \eta(W,K) \). The calculation of this quantity is the main object of this work and will be discussed later. The \( \sum \) represents a sum over all degenerate final states (angular momenta, electron spins, etc.) and an average over all degenerate initial states.

If the variable \( Q \) is defined as
\[
Q = \frac{1}{2m} \left( \hbar^2 K^2 - W^2 / c^2 \right)
\]

which is approximately the recoil kinetic energy of the ejected electron, then the element of solid angle, \( d\Omega \)
can be replaced by
\[ d\Omega = \frac{2\pi k_d k_f}{k_i k_f} = \frac{2\pi}{k^2} \frac{dQ}{k_i k_f} \]
and the cross section becomes
\[ \frac{d^2\sigma}{dWdQ} = \frac{2\pi e^4}{\beta^2 mc^2} \left( \frac{E_f}{E_i} \right) \left( \frac{1}{Q^2} \right) |\eta(W,Q)|^2 \]
where \( \beta^2 = \left( \frac{E_i^2 - m^2 c^4}{E_i^2} \right) \approx (v_i/c)^2 \). The total cross section is then
\[ \frac{(E_i + 1)}{2} \]
\[ \sigma = \frac{2\pi e^4}{\beta^2 mc^2} \int_{Q_{\text{min}}}^{Q_{\text{max}}} dW \left| \eta(W,Q) \right|^2 \frac{dQ}{Q^2} \]
where \( Q_{\text{min}} \) and \( Q_{\text{max}} \) are defined by \( k_{\text{min}} = k_i - k_f \) and \( k_{\text{max}} = k_i + k_f \). The factor of \( E_f/E_i \) has been neglected here as it is very close to unity.

As can be seen here, the important quantity in the theory of ionization is the form factor, \( \eta(W,Q) \). In non-relativistic theory this reduces to the familiar matrix element \( \langle W | e^{iK \cdot r} | 0 \rangle \). In atomic physics, the generalized oscillator strength,
\[ \frac{df(K,W)}{dW} = \frac{W}{R} \frac{1}{(a_{oK})^2} |\eta(W,K)|^2 \]
where \( R \) is the Rydberg energy (13.6 eV) and \( a_o \) is the Bohr radius, is generally used instead of the form factor.
Bethe surface, which is characteristic of the atom. As pointed out by Inokuti\(^4\), this is a useful generalization of the familiar optical dipole oscillator strength. In the limit of \(K \to 0\), for high primary electron energy, this goes into the optical oscillator strength, \(df_0/dW\)\(^{12}\).

For photoionization, the energy loss, \(W\), is equivalent to the photon energy, \(\hbar \omega\), and the cross section is given by\(^{13}\):

\[
\sigma(\omega) = \frac{2\pi^2 e^2 \hbar}{mc} \frac{df_0}{dW} = 1.098 \times 10^{-16} (\text{cm}^2\text{eV}) \frac{df_0}{dW}
\]

The existence of this limit allows some comparison\(^4\) to be made between electron impact data and photoionization data as will be shown later.
III. Calculation of the Relativistic Form Factor

As defined previously the relativistic form factor is given by

\[ \eta(W,K) = \int e^{i \cdot \vec{r}_2} u_f^* \psi_f(\vec{r}_2)(1-\vec{\alpha}_1 \cdot \vec{\alpha}_2) u_i \psi_i(\vec{r}_2) d\vec{r}_2 \]  

(1)

This is independent of the direction of \( \vec{K} \) because the coordinate system is chosen so that \( \vec{K} \) points along the z-axis which is also taken to be the quantization axis for the wavefunctions.

Here the initial four-vector Dirac wavefunctions, \( u_i \) and \( \psi_i \), of the incident and bound electron, respectively, are operated on by the Dirac matrices \( \vec{\alpha}_1 \) and \( \vec{\alpha}_2 \). The \( \vec{\alpha} \)'s have three components which are\(^6\)

\[ \alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad \alpha_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} \quad \alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \]

The components of \( \vec{\alpha} \) operating on a four-vector \( \phi = \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{pmatrix} \)

give the following:

\[ \alpha_x \phi = \begin{pmatrix} \phi_4 \\ \phi_3 \\ \phi_2 \\ \phi_1 \end{pmatrix} \quad \alpha_y \phi = \begin{pmatrix} \phi_4 \\ \phi_3 \\ -\phi_2 \\ \phi_1 \end{pmatrix} \quad \alpha_z \phi = \begin{pmatrix} \phi_3 \\ \phi_4 \\ \phi_1 \\ -\phi_2 \end{pmatrix} \]

The form factor, written in terms of components, is:

\[ \eta(W,K) = \int e^{i \cdot \vec{r}_2} \begin{pmatrix} u_f^* \psi_f(\vec{r}_2) & u_i^* \psi_i(\vec{r}_2) \\ -u_f^* \psi_f(\vec{r}_2) [\alpha_x u_i \alpha_x \psi_i(\vec{r}_2) + \alpha_y u_i \alpha_y \psi_i(\vec{r}_2)] & +\alpha_z u_i \alpha_z \psi_i(\vec{r}_2) \end{pmatrix} x d\vec{r}_2 \]  

(2)

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When all of the four-vector products are carried out this becomes a sum of sixty-four integrals, each of the form,

\[ u^*_f(\alpha) u^*_i(\beta) \int \frac{d\vec{r}_2}{r_2} e^{i\vec{k} \cdot \vec{r}_2} \Phi^*_f(\vec{r}_2) \psi^*_i(\vec{r}_2) \]

where the \( u^*_f(\alpha) \), \( u^*_i(\beta) \), \( \Phi^*_f(\vec{r}_2) \), \( \psi^*_i(\vec{r}_2) \) are each a component of the corresponding four-vector wavefunction. With cancellations the number of terms reduces to forty.

In computing the integrals (3) the well known expansion

\[ e^{i\vec{k} \cdot \vec{r}_2} = \sum_{n=0}^{\infty} i^{n(2n+1)} j_n(Kr_2) P_n(\cos \theta) \]

is used. Here \( j_n \) is the \( n^{th} \) spherical Bessel function, \( P_n \) is the Legendre polynomial of order \( n \), and \( \theta \) is the angle between \( \vec{k} \) and \( \vec{r}_2 \).

The wavefunction components \( \psi^{(i)} \) have the form,

\[ \psi^{(i)} = a^{(i)}(r_2)c^{\gamma} \gamma m \rho \rho \rho Y^{\gamma} Y^{\rho} \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \rho \ro
\[ u_f^*(\alpha) u_i (\beta) \sum_{n=0}^{\infty} i^n (2n+1) \]
\[ \left[ \int_a^b \frac{d\theta}{2\pi} J_n(K r) \right] \]
\[ \left[ \int_{\frac{1}{2}}^n Y^*_\ell \gamma \ell m \frac{d\ell}{\ell} \right] \]

Using the following relations \^{14,15}:

\[ Y_n (\theta, \phi) = \frac{1}{2\pi} \sum_{m=0}^{n} Y_n^m \gamma \ell m \left( \frac{2n+1}{4\pi} \right)^{1/2} P_n (\cos \theta) \]

the angular integral in equations (4) becomes

\[ (-1)^m Y^\ell, -m \]

where the \( \alpha \beta \gamma \) are Wigner 3-j symbols. \^{15} Since the 3-j symbol vanishes unless \( \alpha + \beta + \gamma = 0 \), we have the selection rule that \( m_{f, i} = m_{f, i} \). In addition, the 3-j symbol with \( \alpha = \beta = \gamma = 0 \) vanishes unless \( a + b + c \) is even. This means that in the sum, \( n \) takes on only even values such that

\[ |\ell_{f, i} - \ell_{i, i}| < n < \ell_{f, i} + \ell_{i, i}|. \]

The series then is finite.

With these simplifying features, the integral (4) becomes,
\[ u^*(a) u(b) \left( \frac{1}{2} (2\ell_f + 1) \right)^{1/2} \left( \frac{1}{2} \ell_i + 1 \right)^{1/2} \]

\[ C_{\ell_f \ell_i}^{\ell_i \ell_f} \left( \begin{array}{c} \ell_f + \ell_i \\ \ell_i \end{array} \right) \left\{ \begin{array}{c} n \\ \ell_f \\ \ell_i \end{array} \right\} i_n(2n+1) \left| \begin{array}{c} \ell_f - \ell_i \\ \ell_i \\ 0 \\ 0 \\ 0 \\ 0 \end{array} \right\} \]

This is now complete, except for the need to average over initial electron spin polarizations and initial \( m \) values and sum over final electron spin polarizations, final \( m \) values, and final angular momentum quantum numbers of the ejected electron. These sums and averages are taken on the matrix element squared. The sum and average over \( m \) gives a factor of \( 1/(2j_i+1) \). In summing over the final angular momentum quantum numbers of the ejected electron the number of \( j \) values required to achieve convergence to five per cent or better varied from a minimum of four for small momentum transfer to as many as ten for large momentum transfer and large energy loss. The sum and average over electron spin polarizations is discussed in the section on wavefunctions. The sum of the forty terms, each of the form (6) is then the relativistic form factor \( \eta(W, K) \).
IV. The Calculation of Wavefunctions

The calculation of the wavefunctions used in the scattering integral involves the solution of the time independent Dirac equation \(^6,7^\),

\[
(-i\hbar c \gamma^\dagger + \gamma^0 \gamma^2 + V)\psi = E\psi \tag{1}
\]

where \(\gamma^\dagger = \begin{pmatrix} 0 & \sigma^1 \\ \sigma^3 & 0 \end{pmatrix}\), the \(\sigma^i\) representing the Pauli spin matrices, and \(\gamma^0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\) with \(I\) being the 2x2 identity matrix. Since the Dirac equation applies only to a spin \(1/2\) particle in an external field (there exists no general formulation for a system of mutually interacting particles in relativistic quantum theory), the independent particle model must be used in its application to atomic systems. That is, each atomic electron is considered to be orbiting in an external field due to all of the other atomic electrons.

The wavefunction \(\psi\) is a four component spinor that can be written in the following form \(^7,16\),

\[
\psi_{jm}^{(r)} = \begin{cases}
  ig_{j\ell}^{(r)} \left( \frac{\ell + m + 1/2}{2\ell + 1} \right)^{1/2} Y_{m-1/2}^{\ell-1/2} \\
  ig_{j\ell}^{(r)} \left( \frac{\ell - m + 1/2}{2\ell + 1} \right)^{1/2} Y_{m+1/2}^{\ell+1/2} \\
  -f_{j\ell}^{(r)} \left( \frac{\ell' - m + 1/2}{2\ell' + 1} \right)^{1/2} Y_{m-1/2}^{\ell+1/2} \\
  f_{j\ell}^{(r)} \left( \frac{\ell' + m + 1/2}{2\ell' + 1} \right)^{1/2} Y_{m+1/2}^{\ell+1/2}
\end{cases}
\tag{2a}
\]

where \(\ell' = \ell + 1\).
For \( j = \frac{1}{2} - 1/2 \),

\[
\psi_{jm}(r) = \begin{pmatrix}
-ig_{J_{1}}(r) \left( \frac{\mathbb{1}_{-m+1/2}}{2L+1} \right)^{1/2} \gamma^{m-1/2} \gamma^{j+1/2} \\
ig_{J_{2}}(r) \left( \frac{\mathbb{1}_{m+1/2}}{2L+1} \right)^{1/2} \gamma^{m+1/2} \gamma^{j+1/2} \\
-f_{J_{e}}(r) \left( \frac{\mathbb{1}_{'-m+1/2}}{2L'+1} \right)^{1/2} \gamma^{m-1/2} \gamma^{j-1/2} \\
f_{J_{e}}(r) \left( \frac{\mathbb{1}_{'-m+1/2}}{2L'+1} \right)^{1/2} \gamma^{m+1/2} \gamma^{j-1/2}
\end{pmatrix}
\]  

(2b)

where \( \mathbb{1}' = \mathbb{1} - 1 \).

If we let \( \kappa = \pm (j+1/2) \) for \( j = \pm 1/2 \) and let \( G(r) = \text{r} g(r) \), \( F(r) = \text{r} f(r) \) the equations for the radial wavefunctions are,

\[
\frac{dG(r)}{dr} = -\frac{\kappa}{r} G(r) - \left[ \frac{E + mc^2}{\hbar c} + \frac{\alpha Z(r)}{r} \right] F(r) \tag{3}
\]

\[
\frac{dF(r)}{dr} = \left[ \frac{E - mc^2}{\hbar c} + \frac{\alpha Z(r)}{r} \right] G(r) + \frac{\kappa}{r} F(r)
\]

Here \( E \) is the total relativistic energy of the electron, \( E = \left( c^2 p^2 + m^2 c^4 \right)^{1/2} / 2 \), and \( \alpha \) is the fine structure constant, \( \alpha = e^2 / \hbar c = 1/137.036 \). \( Z(r) \) is the screened atomic charge of the atom, varying from \( Z \) inside the innermost atomic shell to \( Z-N+1 \) at infinity, where \( N \) is the total number of atomic electrons \(^8\). \( G(r) \) is known as the large component of the wavefunction and reduces to the solution of the Schrödinger equation in the non-relativistic limit. These wavefunctions are normalized such that

\[
\int_{r=0}^{\infty} \left( |G|^2 + |F|^2 \right) dr = 1.
\]
We need to solve these radial equations under the independent particle and central field assumptions for the wavefunction $G(r)$ and $F(r)$ and for the quantity $Z(r)$. The approach taken is to solve the radial equations for the neutral atom using the Hartree-Fock-Slater Self-Consistent Field method to obtain the bound state wavefunctions and the screened charge, $Z(r)$. The radial equations are then again solved using $Z(r)$ for the continuum wavefunctions which, when $Z(r)$ is given, are functions only of the angular momentum (via kappa) and the energy of the ejected electron. The calculation of continuum wavefunctions will be discussed later.

**Self-Consistent-Field Calculations**

The computer code for the calculation of SCF solutions to the radial Dirac equation was obtained from Dr. Chien-ping Lin. Detailed discussion of the SCF method can be found in references 18, 19, and 20. Discussion of the method applied to the Dirac equation is given in references 21 through 24.

In these calculations the wavefunction for the system is represented as a product of one-electron wavefunctions. Each electron is assumed to move independently of all the other electrons in a time-averaged, central, electrostatic field produced by the nucleus and all the other electrons. Minimization of the average energy of the system in this representation gives variational equations for the wave-
functions. These equations, the Hartree-Fock equations, contain exchange terms that account for statistical correlation in the motion of pairs of electrons of like spin. In the Hartree-Fock-Slater method used here, the exchange terms in the Hartree-Fock equations are simplified by use of the approximate Slater free electron exchange potential,

\[ v_{\text{exch}}(\rho) = -6 \left[ \frac{3}{8\pi} |\rho| \right]^{1/3} \text{ Rydberg} \]

where \( \rho \) is the total electron density. This is simply a means, based on the relationship between the potential and charge density in a free electron gas, of replacing the individual exchange potentials for different orbitals by a single average exchange potential depending only upon the local electronic charge density. The equations are then solved by iteration until the desired degree of consistency is achieved.

The Dirac-Hartree-Fock-Slater bound state wavefunctions for the argon M_{III} shell are shown in Figure IV-1. The screened charge \( Z(r) \) is shown in Figure IV-2. In Table IV-1 are displayed the shell energies for argon computed using this DHFS program, those computed by Herman and Skillman\(^{20}\), and some obtained from x-ray data\(^{25}\). A diagram of the shell structure of argon is shown in Figure IV-3.

**Continuum Wavefunctions**

The radial continuum wavefunctions are obtained by integrating the radial equations (3) from \( r=0 \) to large \( r \).
Figure IV-1: DHFS Wavefunctions for M_{III} Shell of Argon.
Figure IV-2: Screened Charge, $A(r)$, Computed for Argon by DHFS Method.
<table>
<thead>
<tr>
<th>Shell</th>
<th>This Calculation</th>
<th>Herman and Skillman</th>
<th>Herman and Skillman with Relativistic Corrections</th>
<th>X-ray Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_I(1'S_{1/2})$</td>
<td>3177.45</td>
<td>3163.68</td>
<td>3181.53</td>
<td>3202.86</td>
</tr>
<tr>
<td>$L_I(2^2S_{1/2})$</td>
<td>313.43</td>
<td>311.08</td>
<td>314.43</td>
<td>319.99</td>
</tr>
<tr>
<td>$L_{II}(2^2P_{1/2})$</td>
<td>249.43</td>
<td></td>
<td>248.23</td>
<td>247.37</td>
</tr>
<tr>
<td>$L_{III}(2^2P_{3/2})$</td>
<td>247.06</td>
<td>247.70</td>
<td>245.16</td>
<td></td>
</tr>
<tr>
<td>$M_I(3^2S_{1/2})$</td>
<td>28.92</td>
<td>28.66</td>
<td>29.08</td>
<td></td>
</tr>
<tr>
<td>$M_{II}(3^2P_{1/2})$</td>
<td>14.62</td>
<td></td>
<td>14.49</td>
<td>14.56</td>
</tr>
<tr>
<td>$M_{III}(3^2P_{3/2})$</td>
<td>14.42</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure IV-3: Grotrian Diagram of the Energy Level Structure of Argon.
using the screened charge, \( Z(r) \), obtained from the DHFS calculation. In these calculations a fourth order Runge-Kutta scheme with variable step size is used for the integration. The computed radial wavefunctions are normalized per unit energy by matching them to the analytic asymptotic continuum solutions for an electron in the field of a nuclear charge \( Z_a = Z - N + 1 \). These solutions are shown by Akheiser and Berestetskii to be:

\[
\begin{align*}
\mathbf{iG}(r) &= \left( \frac{m}{\pi \hbar p} \right)^{1/2} \left( 1 + \frac{E}{\hbar c^2} \right)^{1/2} \sin \left( \frac{pr}{h} - \frac{\pi}{2} + \delta + \nu \ln \frac{2pr}{h} \right) \\
\mathbf{F}(r) &= (\mathbf{-1})^{\mathbf{-1}} \left( \frac{m}{\pi \hbar p} \right)^{1/2} \left( \frac{E}{\hbar c^2} - 1 \right)^{1/2} \\
&\quad \sin \left( \frac{pr}{h} - \frac{\pi}{2} + \delta + \nu \ln \frac{2pr}{h} \right)
\end{align*}
\]

where

\[
\begin{align*}
\nu &= \frac{Z_a \alpha}{\beta} (\beta = v/c) \\
\gamma &= (K^2 - Z_a^2 \alpha^2)^{1/2} \\
\delta &= \xi - \arg \Gamma(\gamma + \nu) - \frac{\pi}{2} (\gamma - 1)
\end{align*}
\]

and \( \xi \) is defined by,

\[
e^{2i\xi} = \frac{K - iZ_a \alpha}{\left( \frac{mc}{p} \right)} \left( -\gamma + iZ_a \alpha \left( \frac{E}{cp} \right) \right)
\]

The units of \( G \) and \( F \) are \((\text{energy} \cdot \text{length})^{-1/2}\). The exact solutions to the radial Dirac equations for the bound Coulomb problem are confluent hypergeometric functions of complex argument which reduce to these trigonometric functions in the asymptotic limit. Some examples of the wavefunctions computed for various values of kappa and electron
kinetic energy using the $Z(r)$ of Figure IV-2 are shown in Figures IV-4 through IV-6.

The quantity $e^2 Z(r)/r$ represents the screened central potential seen by any one of the $N$ independent electrons of the atom as it moves in the combined fields of the other $N-1$ electrons plus the nucleus. The use of the screened charge in the calculation of the continuum wavefunctions is commonly called the "frozen core" approximation in that during the collision process the wavefunctions of the other $N-1$ non-participating electrons remain unchanged. Hence the potential represents that of the unrelaxed atomic ion. This is, of course, strictly correct only for large $r$.

Further discussion on the use of screened charges and the calculation of continuum wavefunctions can be found in the articles by Cooper$^27$ and by Pratt, Ron, and Tseng$^28$.

**Dirac Plane Wavefunctions**

In the Born approximation being used for this scattering calculation the primary electron is treated as a plane wave before and after the collision. The relativistic plane wavefunctions for electrons of right (R) and left (L) handed helicity are given by$^6$:

$$\phi^{(R)}(P) = \frac{e^{iK \cdot P}}{\sqrt{[1 + \frac{E^2}{(E+mc^2)^2}]}^{1/2}} \begin{pmatrix} 1 \\ 0 \\ \frac{cP \cdot z_i}{E+mc^2} \\ \frac{c(P_x + iP_y)}{E+mc^2} \end{pmatrix} e^{-i\omega t} \quad \text{(5a)}$$
Figure IV-5: Argon Continuum Wavefunctions: Electron Energy = 5eV; Kappa = -3.
\[
\phi(L)(p) = \frac{e^{iK \cdot r}}{\sqrt{1+E^2 p^2/(E+mc^2)^2}} \left( \begin{array}{c}
0 \\
1 \\
C(p_x-ip_y)/(E+mc^2) \\
-Cp_z/(E+mc^2)
\end{array} \right) e^{-i\omega t} \quad (5b)
\]

where right and left handed helicities correspond to electron spin components +1/2 and -1/2 in the direction of travel \( \vec{p} \).

The calculation of the relativistic form factor involves an average over initial helicities and a sum over final helicities. If the primary electron is taken to be moving in the \( \vec{z} \)-direction initially, as shown in Figure IV-7, the momentum transfer \( \vec{P} \) is related to the initial and final primary electron momenta, \( \vec{p}_i \) and \( \vec{p}_f \), by the kinematical relation,

\[
p^2 = p_i^2 + p_p^2 - 2p_i p_f \cos \theta \quad (6)
\]

In relativistic theory momentum, \( \vec{p} \), is related to kinetic energy, \( T \), by the relation,

\[
c^2 p^2 = (T + mc^2)^2 - m^2 c^4 \quad (7)
\]

Given the momentum transfer and the energy loss, for electron impact ionization the scattering angle, \( \theta \), can be computed using relations (6) and (7).

Since the \( x \) and \( y \) components of the final momentum are not unique, but are needed in the post collision electron wavefunction, they are summed over the \( x-y \) plane in the calculation of \( |\vec{n}|^2 \).
Figure IV-7: Coordinates and Angles for Electron Scattering Calculation.
In non-relativistic theory, the components of momentum do not appear explicitly in the spinor multiplying exp $(i\mathbf{k} \cdot \mathbf{r} - i\omega t)$ in the plane wavefunction. This allows the square of the matrix element to be greatly simplified as shown by Manson\textsuperscript{17}. 
V. Photoionization Calculations

As pointed out in Section II, the electron impact ionization cross section calculated in the limit of small momentum transfer, that is, \( K \to 0 \), corresponds to the photoionization cross section. As a test of the computational technique and the computer program this calculation was performed for the \( M_{III} \) subshell of argon. The results are shown in Figure V-1 along with the experimental photoionization cross section data from Samson.\(^{31}\)

In the limit \( K \to 0 \), the \( e^{i \mathbf{k} \cdot \mathbf{r}} \) factor in the matrix element is, approximately,

\[
e^{i \mathbf{k} \cdot \mathbf{r}} \approx 1 + i \mathbf{k} \cdot \mathbf{r} + \ldots
\]

In principle, the first term will vanish due to the orthogonality of the initial and final electron wavefunctions leaving the \( \mathbf{k} \cdot \mathbf{r} \) "dipole" term. Since numerical wavefunctions are used in these calculations, however, the overlap integral \( \int \psi_f^* \psi_i \, d\mathbf{r} \) is, in general, not identically zero. This can lead to large errors in the calculation of the matrix element and hence, when \( |\mathbf{k}| \) is very small, in the computed photoionization cross section. Thus, the photoionization cross sections presented in Figure V-1 are computed from the matrix element of the quantity \( (e^{i \mathbf{k} \cdot \mathbf{r}} - 1) \).

These calculated photoionization cross sections are in good agreement with those computed by Cooper\(^{28,32}\) and by McGuire\(^{33}\) for argon using the non-relativistic dipole theory.
Figure V-1: Argon Photoionization Cross Section.
They are, however, very different from the measured cross sections, particularly at low energy. This is a well known characteristic of single electron models and has been discussed by a number of authors\textsuperscript{34, 35, 36, 37}. It is due to a neglect of many-body correlation effects that are most important at low energies. This is a problem that cannot be easily treated in relativistic theory, however, since, as has been mentioned previously, there is no relativistic quantum theory of many body interactions in closed form.

**Relativistic Electric Dipole Photoeffect Calculations**

Further photoionization calculations were performed using the formalism described by Grant\textsuperscript{38}. He computed the matrix element, $M_{\alpha\beta}$, for a radiative transition from $\beta$ to $\alpha$,

$$M_{\alpha\beta} = \left(\frac{\omega}{\pi c}\right)^{1/2} \int \psi_\alpha^*(\vec{r}) [\phi(\vec{r}) + c \vec{a} \cdot \vec{A}(\vec{r})] \psi_\beta(\vec{r}) d\vec{r}$$

using a multipole expansion of the vector potential. The reduction of this to radial matrix elements gives

$$M_{\alpha L}^e(G_L) = \bar{M}_{\alpha\beta}^e(0) + G_L \bar{M}_{\alpha\beta}^2$$

with

$$\bar{M}_{\alpha\beta}^e(0) = i^L \left\{ \left( \frac{L}{L+1} \right)^{1/2} \left[ (\kappa_\alpha - \kappa_\beta) I_{L+1}^+ + (L+1) I_{L+1}^- \right] 
- \left( \frac{L+1}{L} \right)^{1/2} \left[ (\kappa_\alpha - \kappa_\beta) I_{L-1}^+ - L I_{L-1}^- \right] \right\}$$

and

$$\bar{M}_{\alpha\beta}^L = i^L \left\{ (2L+1) J(L) + (\kappa_\alpha - \kappa_\beta) (I_{L+1}^+ + I_{L-1}^+) 
- L I_{L-1}^- + (L+1) I_{L+1}^- \right\}$$
The radial integrals are

\[ I_L^+(\omega) = -\int_0^\infty (G_\alpha F_\beta + F_\alpha G_\beta) j_L \left( \frac{\omega r}{c} \right) dr \]

\[ I_L^-(\omega) = -\int_0^\infty (G_\alpha F_\beta - F_\alpha G_\beta) j_L \left( \frac{\omega r}{c} \right) dr \]

\[ J^{(L)}_L(\omega) = \int_0^\infty (G_\alpha G_\beta + F_\alpha F_\beta) j_L \left( \frac{\omega r}{c} \right) dr \]

where \( \omega \) is the photon frequency.

The Einstein coefficient in units of \( \tau_0 = \frac{n^3}{me^4} \) is given by

\[ A_{\beta+\alpha} = 2\alpha \frac{W}{2R_Y} \frac{2j_{\beta} + 1}{2L + 1} \left( \begin{array}{cc} j_{\beta} & L \\ j_{\alpha} & 0 \end{array} \right)^2 |W_{\alpha\beta}|^2 \]

and the oscillator strength is

\[ f_{\beta+\alpha} = \frac{A_{\beta+\alpha}}{2\alpha^3 \left( \frac{W}{2R_Y} \right)^2} \]

where \( R_Y \) is the Rydberg of energy.

For photoionization calculations we want 21

\[ f_{\alpha+\beta} = \frac{(2j_{\beta} + 1)}{(2j_{\alpha} + 1)} f_{\beta+\alpha} \]

For photoionization, this becomes the differential oscillator strength \( \frac{df}{dW} \) of section I as the continuum wavefunctions are normalized per unit energy.

In the above equations \( W_{\alpha\beta}^e \) represents the matrix element of the electric (transverse) vector potential and \( W_{\alpha\beta}^t \) is the matrix element of the longitudinal vector.
potential. \( G_L \) is the gauge parameter \( (L = \text{multipole quantum number}) \) defined such that the Coulomb gauge, for which the longitudinal component vanishes, corresponds to \( G_L = 0 \). Grant shows that \( M^{\alpha \beta}_\lambda \) should vanish for all pairs of states \( \alpha \) and \( \beta \) that are eigensolutions of the same Dirac hamiltonian since transition probabilities should be independent of gauge. He also shows that the matrix element in the Coulomb gauge reduces, in the non-relativistic limit, to the dipole-velocity form. He shows further that \( M^{\alpha \beta}_\lambda (G_L) \) reduces, for \( G_L = (L+1)^{1/2} / L \), to the non-relativistic dipole-length form.

Using this formalism the dipole \( (L = 1) \) photoionization cross section for argon \( M_{III} \) has been calculated in both gauges and the results are shown in Figure V-2. This calculation is in good agreement with the previous calculation. Although the longitudinal matrix element cannot be expected to vanish identically for the DHFS approximate wave functions, it should, at least, be substantially smaller than the transverse matrix element. This then serves as a test of the accuracy of the wave functions. For energies of about 60 eV both gauges give the same result with \( M^{\lambda \beta}_\alpha \) being, typically, less than one per cent of \( M^{e \beta}_\alpha \). This is not the case, however, at lower energies.

The problem here may be due to the use of the frozen core approximation in the calculation of continuum wave
Figure V-2: Argon $M_{\text{II}}$ Photoionization Cross Section Calculated from the Theory Given by Grant $^{38}$. 

$G_L = 0+$

(Coulomb gauge)

$G_L = \sqrt{\frac{L+1}{L}}$
functions. These wave functions should be more sensitive to the central atomic potential at low energy and at small radii so that the use of the potential of the unrelaxed ion should lead to inaccurate wave functions. Also, in these photoeffect calculations, the dominant contribution comes from the integrals $I_{L-1}^\pm(\omega)$ and $J^{(L)}$ containing spherical Bessel functions which weight the integrands toward small radii for small $\omega$ and $L = 1$. 
VI. Bethe Surface and Total Cross-Section Calculations

Low Energy Calculations

As a test of the computational technique and the computer code itself, calculations were made for electron impact ionization of argon in the non-relativistic limit. Cross sections differential in energy and angle were calculated for 4 keV electrons incident upon the M_{III} subshell of argon. These results and the experimental 4 keV data of Afrosimov, et al.\textsuperscript{39} are plotted in Figure VI-1. There is good agreement between the Bethe-Born calculation and the experiment for small energy loss and small scattering angle. This is a well known characteristic of Born approximations\textsuperscript{40, 41}. For larger values of energy loss (there are, unfortunately, no data for energy loss between 20 eV and 100 eV), the calculated cross sections have approximately the correct shape but are low by factors between two and three. This might be expected, however, because the computed cross section does not include contributions from the M_{II} shell, which has nearly the same ionization potential and wave function as the M_{III} shell. In addition, at energy loss greater than about 29 eV, there will be contributions from the M_{I} shell which, of course, have also been neglected.

It should also be noted that these calculations give approximately the same results as those obtained by Amus'ya, et al.\textsuperscript{42} in their calculations using the first Born approximation and the Herman-Skillman\textsuperscript{20} wave functions and
Figure VI-1: Differential Cross Sections for Ionization of Argon by 4 keV electrons; —— measured by Afrosimov, et al., —— calculated for M_{III} Shell of Argon.
potential.

High Energy Calculations

The Bethe surface computed using the theory presented previously is displayed in Figures VI-2 through VI-6 for primary electron energies of 4 keV, 10 keV, 100 keV, 1 MeV, and 10 MeV. Several characteristics common to all Bethe surfaces are apparent in Figure VI-2.

First, for large energy loss, each curve of $df/dW$ vs. $\ln(a_0 K)^2$ possesses a definite peak that moves to larger values of $K$ as $W$ increases. This peak, as a function of energy loss, is called the Bethe ridge. It corresponds to the scattering angle where, classically, momentum is conserved in the collision between the incident and atomic electron. At the Bethe ridge energy loss and momentum transfer are related by

$$ (a_0 K)^2 = W/Ry \quad \text{(non-relativistic)} \quad (1) $$

$$ (a_0 K)^2 = \left[ (W + mc^2)^2 - m^2 c^4 \right] 2Ry \cdot me^2 \quad \text{(relativistic)} $$

The finite width of the Bethe ridge is a quantum mechanical effect due to the binding of the struck electron. Because the momentum of the atomic electron is not well defined, collisions with momentum transfer different from that given by (1) do occur and thus give the oscillator strength as a function of momentum transfer a finite width around the Bethe ridge. The width of the peak is related to the binding energy, $B$, of the atomic electron by $^4$
Figure VII-2: Computed Argon M_{III} Bethe Surface for 4keV Electrons; each curve represents a constant energy loss in eV.
Figure VI-3: Electron Energy = 10 keV.
Figure VI-4: Electron Energy = 100 keV.
Figure VI-5: Electron Energy - 1 meV.
Figure VI-6: Electron Energy = 10 MeV.

OSCIllATOR STRENGTH (N.EV)

(A0xK)*2

10^4

2

5

10

25

50

100
\[ \Delta[\ln(a_{o}K)^{2}] = \left( \frac{B}{W} \right)^{1/2} \]

For small energy loss, relative to the binding energy of the atomic electron, the Bethe ridge disappears and the oscillator strength becomes a much more sensitive function of the wavefunction of the atomic electron. Comparing Figures VI-2 through VI-6 it is apparent that the oscillator strength, and thus the total cross section, decreases with increasing incident electron energy. At about 1 MeV, however, this trend reverses and the oscillator strength increases again. This effect is called the "relativistic rise" and is due to the interaction between the incident electron and the atomic electron, through the emission and reabsorption of virtual photons. As shown by Fano\textsuperscript{48,44} and by Rose\textsuperscript{45}, the Coulomb interaction, a matrix element of \( e^2/|\vec{T}_1 - \vec{T}_2| \), exerts a force parallel to the momentum transfer vector, \( \vec{K} \), and hence is called longitudinal whereas the virtual photon interaction acts through "transverse" photon fields perpendicular to \( \vec{K} \). Emission of a photon of momentum \( \vec{K} \) by the incident electron and absorption of the same photon by the atomic electron is represented by the \( \vec{a}_1 \cdot \vec{a}_2 \) term in the Møller interaction described previously. In the region of the relativistic rise, the cross section does not continue to increase indefinitely, but, rather, starts to decrease again as the "density effect"\textsuperscript{43,46}, which involves the polarization by the electron of the atoms of the gas through which it is moving, becomes important.
The cross sections differential in energy, \( \frac{d\sigma}{dW} \), computed using these Bethe surfaces are shown in Figure VI-7. The total ionization cross sections are shown in Figure VI-8 along with the results of some other investigations. The experimental data shown are the non-relativistic results of Van der Wiel, et al.\textsuperscript{47}, and of Schram, et al.\textsuperscript{48}, and the relativistic absolute cross sections measured by Rieke and Prepejchal\textsuperscript{3}. The cross sections of Salop\textsuperscript{49} were computed using Bethe's relativistic formula\textsuperscript{6,14} and approximate non-relativistic matrix elements calculated with the projection operator method of Hahn and Watson\textsuperscript{50, 51}.

The low energy total cross sections calculated here agree very well with the experimental values, while the high energy cross sections differ somewhat from the experimental values. The computed total cross section for an incident electron energy of 10 MeV is \( 4.5 \times 10^{-17} \text{ cm}^2 \), which is about a factor of forty too large. The explanation for this involves the calculation of the relativistic form factor in the limit of small momentum transfer (photo-effect) and should be apparent in the following analysis due to Fano\textsuperscript{11}.

The total ionization cross section is given in terms of the relativistic form factor by equation (9) of Section II. As discussed by Bethe\textsuperscript{5}, the relativistic form factor can be approximately related to the non-relativistic form factor \( |F(W,Q)|^2 \) and the optical dipole matrix element
Figure VI-7: Calculated Cross Section Differential in Energy Loss for Ionization of Argon M_{III}.
Figure VI-8: Electron Impact Ionization Cross Sections for Argon.
squared, $|x(W)|^2$ by the following:

$$|\eta(W,Q)|^2 = |F(W,Q)|^2 - |X(W)|^2 \frac{W^2(1-\beta^2)}{2mc^2R_y}$$

(2)

where $R = 13.605$ eV, the Rydberg. The integration limits, which are functions of incident electron energy, can be taken as

$$Q_{\text{min}} = \frac{W^2(1-\beta^2)}{2mc^2R_y}$$

and

$$Q_{\text{max}} = \infty$$

For allowed electric dipole collisions ($Q < W$), $|F(W,Q)|^2$ has the form

$$|F(W,Q)|^2 = \frac{Q}{R_y} |X(W)|^2$$

If the integration of $|F(W,Q)|^2$ is split into two parts at $Q = \frac{W^2}{2mc^2} << W$ and the integrals over $Q$ of $|X(W)|^2$ are performed the following is obtained

$$\int_{Q_{\text{min}}}^{\infty} |\eta(W,Q)|^2 \frac{dQ}{Q^2} \approx \frac{|X(W)|^2}{R_y} [\ln \left(\frac{\beta^2}{1-\beta^2}\right)] - \beta^2$$

(3)

$$+ \int_{\frac{W^2}{2mc^2}}^{\infty} \frac{|F(W,Q)|^2}{Q^2} \frac{dQ}{Q^2}$$

The total cross section is then just $\frac{2\pi e^4}{\beta^2 mc^2}$ times the integral of (3) over energy loss, $W$. For low energy collisions, the dominant term in (3) is the integral involving the non-relativistic form factor. As $\beta$ increases toward the limiting value of unity, however, the contribution from the term involving the optical dipole matrix element.
increases and eventually becomes dominant. At relativistic energies, then, the total cross section becomes sensitive to the value of $|X(W)|^2$, which is proportional to the photoionization cross section. As we have seen, however, these form factor calculations are not very accurate in the small $K$ limit, particularly at the low values of energy loss that contribute most to the total cross section. This then explains the inaccuracies in the total cross section at relativistic energies and in particular at 10 MeV.

As a test of this explanation the total ionization cross section was calculated using equation (2) and the form factor for 4 keV electrons computed here and the optical dipole matrix elements squared from the photoionization cross section data given by Samson\textsuperscript{31}. The 4 keV form factor was used because it was available from the electron impact calculations presented above and because it is the most non-relativistic of the form factors calculated. The results, also shown on Figure VI-8, can be seen to be much better. The 10 MeV cross section computed in this manner is $1.2 \times 10^{-18}$ cm$^2$, a marked improvement over the $4.5 \times 10^{-17}$ cm$^2$ value computed previously. It thus appears that the best way to compute a relativistic ionization cross section is to calculate the non-relativistic form factor, obtain experimental photoionization data, and use the formalism of Fano presented above.
VII. Conclusion

As pointed out in the introduction, this is, to my knowledge, the first time that a complete relativistic electron impact ionization calculation has been performed using relativistic self-consistent atomic wavefunctions. The Bethe surface so computed reduces to the correct non-relativistic surface at low energy and exhibits the proper behavior due to relativistic effects at high energy. These effects which are due to electron-electron interactions via transverse virtual photons and are responsible for the rise in the cross section at high energy, are implicit in the relativistic theory. They are naturally included via the $\hat{\alpha} \cdot \hat{u}_1 \hat{\cdot} \hat{\psi}_1$ terms in the Möller interaction which mix large and small components of the wavefunctions. At relativistic energies the small components of plane wavefunctions are large enough for these terms to make a sizeable contribution to the interaction energy. These interactions are not present in the non-relativistic theory so that explicit multiplying factors involving electron velocity must be used when applying non-relativistic matrix elements to relativistic collisions, as in the Fano theory presented above. However, these calculations exhibit the correct relativistic effects qualitatively, but their quantitative accuracy suffers from the problems inherent in small momentum transfer (photoionization limit) calculations. A recent study by Robb et al.\textsuperscript{52} shows that even in the relatively simple case of helium,
correlation effects in both the initial and final states have a large effect on the photoionization cross-section. The correct treatment in this case, which would involve consideration of many body effects, is not a simple matter in the relativistic theory because, as has been pointed out previously, there is no known method of dealing with many body interactions in the relativistic quantum theory in closed form. In this sense, these calculations are difficult to improve upon. The relativistic calculation described here works reasonably well up to about 1 MeV incident electron energy, but then begins to break down due to an inadequate representation of the photoionization cross-section near threshold. The best approach above 1 MeV appears to be the semi-empirical method which incorporates the experimental photoionization cross section near the threshold as described at the end of the preceding section. They could be expanded, however, to investigate other relativistic effects such as spin flip by the incident electron due to the spin-orbit interaction, which is automatically included in the relativistic theory.

It would be interesting and useful to apply this scattering calculation to the ionization of, say, the K-shell of a heavy atom, where the relativistic nature of the inner shell atomic electron is particularly important. This calculation has never been performed, but as has been pointed out by others\textsuperscript{4,52}, would be desirable.
References


16. Note that the f(r) defined here is the negative of that used in reference (7).

17. Dr. Chien-ping Lin private communication.


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