ASSESSMENT OF EXCITATION MECHANISMS AND TEMPORAL DEPENDENCIES OF INFRARED RADIATION FROM VIBRATIONALLY EXCITED CARBON MONOXIDE AND OZONE IN EXCEDE EXPERIMENTS

by

C.E. Kolb, M.S. Zahniser, and R.B. Lyons

Center for Chemical and Environmental Physics
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821

The work reported herein was performed under subcontract to Center for Space Engineering
Utah State University
Logan, UT 84322-4140

Scientific Report No. 22

11 March 1987

Approved for public release; distribution unlimited.

Prepared for:

AIR FORCE GEOPHYSICS LABORATORY
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
HANSCOM AIR FORCE BASE, MA 01731

DTIC
DECLASSIFIED JUL 2 2 1987


### Assessment of Excitation Mechanisms (cont.)

A goal of the EXCEDE artificial aurora experiment is to quantify upper atmospheric infrared emission mechanisms for disturbed atmospheric conditions.

In this report sources and vibrational excitation mechanisms relevant to electron beam induced infrared emission from carbon monoxide and ozone in the 90-130 km altitude range are reviewed and assessed. Estimates of vibrational excitation deposition fractions ratioed to the ion pair creation energy deposition level are presented along with predicted energy deposition and decay rates for each mechanism. Mechanisms considered for CO(v) production include direct electron impact on ambient CO, dissociative excitation of CO$_2$, V-V exchange with vibrationally excited N$_2$, O$_2$ and O, and infrared chemiluminescence from the reaction of CO$_2$ with O$^+$. The conclusions are that the initial production of CO(v).

<table>
<thead>
<tr>
<th>FIELD</th>
<th>GROUP</th>
<th>SUB. GR.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Abstract Security Classification

Unclassified
and Temporal Dependencies of Infrared Radiation from Vibrationally Excited Carbon Monoxide and Ozone in EXCEDE experiments

Continued Block 19: Is dominated by direct electron impact on ambient CO which represents a fraction of $4.5 \times 10^{-5}$ of the ion pair production energy at 100 km altitude and decays with a radiative time constant of 28.3 ms. On a longer time scale of 0.1 to 100 s after electron beam termination, energy transfer from $N_2(A)$ and the $O_2(A',c)$ metastable states and from vibrationally excited $N_2(v)$ may contribute to CO(v) production.

Potentially the strongest production mechanisms for vibrationally excited O$_3$ are the two body reactions of $O_2(A,A',c)$ metastable states with ambient O$_2$. These would occur on a time scale of 5 to 50 s and could account for up to 1% of the beam energy. Direct excitation of ambient O$_3$ by electron impact or by $O_2(b \,^1\Sigma)$ quenching may contribute to prompt emission of O$_3(v_3)$ 9.6 $\mu$m radiation below 100 km.
EXCEDE is a Defense Nuclear Agency/Air Force Geophysics Laboratory (DNA/AFGL) program which promotes the study of atmospheric radiative processes resulting from the controlled deposition of energetic electrons. A major goal of the EXCEDE experimental series is to generate a quantitative understanding of electron impact-induced infrared processes. In the experiments, rocket-borne electron accelerators introduce artificial auroral conditions into the upper mesosphere and lower thermosphere. The accompanying payload instrumentation then gathers and records the ultraviolet, visible, and infrared atmospheric emission data.

EXCEDE:SPECTRAL, the most recent EXCEDE mission, flew on 19 October 1979 into a dark, clear and aurorally inactive night atmosphere from Poker Flat, Alaska. EXCEDE:SPECTRAL, in contrast to previous EXCEDE missions, provided a higher irradiation rate, and incorporated more payload instruments. The payload optical and infrared spectral instruments recorded detailed band profiles.

The Center for Space Engineering (CSE) at Utah State University awarded Subcontract No. 83-035 to Aerodyne Research, Incorporated authorizing them to analyze data from EXCEDE:SPECTRAL. More specifically, they analyzed the 4.7μm carbon monoxide emission and ozone emissions ranging from 9.1 to 14.1μm. Aerodyne scientists completed their work under the subcontract and submitted their final report to CSE in December, 1984. This scientific report is based on Aerodyne's final report. It discusses direct excitation of CO and Aerodyne's temporal predictions for CO. This report also discusses the production mechanisms for vibrationally-excited ozone.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foreword</td>
<td>111</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>v</td>
</tr>
<tr>
<td>List of Figures</td>
<td>vii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>vii</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Infrared Emission From Carbon Monoxide</td>
<td>3</td>
</tr>
<tr>
<td>2.1 Direct Excitation of CO/Analysis of EXCEDE SPECTRAL Observations</td>
<td>3</td>
</tr>
<tr>
<td>2.2 Temporal Predictions for CO 4.7 µm Radiation</td>
<td>10</td>
</tr>
<tr>
<td>2.2.1 Direct Electron Impact Excitation of CO</td>
<td>14</td>
</tr>
<tr>
<td>2.2.2 Dissociative Excitation of Carbon Dioxide</td>
<td>15</td>
</tr>
<tr>
<td>2.2.3 Vibrational Exchange with N2(v)</td>
<td>18</td>
</tr>
<tr>
<td>2.2.4 Quenching of Metastable Electronic States</td>
<td>20</td>
</tr>
<tr>
<td>2.2.5 Chemiluminescent Reaction Sources of CO(v)</td>
<td>27</td>
</tr>
<tr>
<td>3. Production Mechanisms for Vibrationally-Excited Ozone</td>
<td>31</td>
</tr>
<tr>
<td>3.1 Review of Ozone Properties</td>
<td>31</td>
</tr>
<tr>
<td>3.2 Excitation of Ambient O3</td>
<td>32</td>
</tr>
<tr>
<td>3.2.1 Electron Impact Excitation of Ozone</td>
<td>32</td>
</tr>
<tr>
<td>3.2.2 E+V Excitation of Ozone</td>
<td>33</td>
</tr>
<tr>
<td>3.2.3 V+V Excitation of O3(v)</td>
<td>36</td>
</tr>
<tr>
<td>3.3 Chemical production of O3(v)</td>
<td>36</td>
</tr>
<tr>
<td>4. Conclusions</td>
<td>39</td>
</tr>
<tr>
<td>References</td>
<td>41</td>
</tr>
</tbody>
</table>
This page intentionally left blank.
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CO and CO$_2$ Mixing Ratios, Comparison of Model and Measurements</td>
<td>4</td>
</tr>
<tr>
<td>2. Atmospheric Concentration Profiles</td>
<td>5</td>
</tr>
<tr>
<td>3. Vibrational Excitation Cross Sections for CO Vibrational Levels and for N$_2$(Σv)</td>
<td>7</td>
</tr>
<tr>
<td>4. 4.7μm/N$_2^+$ (3914) Intensity Ratio and CO Mixing Ratios</td>
<td>8</td>
</tr>
</tbody>
</table>

LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Excitation Mechanisms for CO(v)</td>
<td>12</td>
</tr>
<tr>
<td>2. Electronically Metastable Reservoir Species</td>
<td>13</td>
</tr>
</tbody>
</table>
This page intentionally left blank.
1. INTRODUCTION

The EXCEDE series of experiments conducted for the Defense Nuclear Agency by the Air Force Geophysics Laboratory is designed to identify and quantify radiation producing mechanisms operative in the upper mesosphere and lower thermosphere during disturbances initiated by the deposition of high energy electrons.

During the EXCEDE experiments rocket borne electron accelerators deposit bursts of energetic (~3 kV) primary electrons at altitudes ranging from roughly 70 to 130 km. Ultraviolet, visible and infrared atmospheric emissions induced by these electron bursts are recorded by ground based, aircraft based and/or on-board (rocket based) spectrometers, radiometers and cameras.

A major goal of the EXCEDE experimental series is to generate a quantitative understanding of electron impact induced infrared processes. These processes, which, due to atmospheric transmission characteristics, must generally be observed by in situ instrumentation, were a major target of the EXCEDE:SPECTRAL mission flown in October, 1979. While many of the infrared spectral features observed on this flight were anticipated, several infrared features observed by the EXCEDE:SPECTRAL flight were unexpected, including a distinct feature at 4.7 μm. In addition, the EXCEDE:SPECTRAL on-board instruments did not cover the spectral range between 6.8 and 12 μm.

The field data gathered by the initial EXCEDE:SPECTRAL flight were rich in detail and subsequent analyses have highlighted the desirability of additional EXCEDE missions. For instance, an analysis effort at Aerodyne Research, Inc. identified the source of the unexpected 4.7 μm feature as direct excitation of ambient thermospheric carbon monoxide.

Furthermore, additional analyses of the long-lived visible spectral glow observed during the PRECEDE portion of the EXCEDE experimental series has
identified the 4.5-5.0 eV states (A $^{3}Σ^{+}$, A' $^{3}Δ$ and c $^{1}Σ^{-}$) of O$_2$ as an important reservoir of electron deposition energy.\textsuperscript{4,5} Quite recently, laboratory experiments involving these highly excited molecular oxygen states have strongly indicated that they can be a source of vibrationally excited ozone,\textsuperscript{6} thus possibly producing strong infrared radiation in the 9.0 to 10.5 \textmu m region not covered in the EXCEDE:SPECTRAL experiment.

The purpose of this report is to assess sources and vibrational excitation mechanisms for carbon monoxide and ozone in the disturbed atmosphere at altitudes (100-130 km) where the EXCEDE experimental arrangement functions best. Estimates of the source strength, spectral extent and temporal dependence of infrared radiation from vibrationally excited CO and O$_3$ induced by the EXCEDE electron impact source are presented along with suggestions on how future EXCEDE experiments might best be configured to observe the predicted infrared emission features.
2. INFRARED EMISSION FROM CARBON MONOXIDE

2.1 Direct Excitation of CO/Analysis of EXCEDE Spectral Observations

As reported in Reference 3, the 4.7\(\mu\)m emission feature measured by the EXCEDE:SPECTRAL experiment has been identified as arising from electron impact excited carbon monoxide. This identification was based on the shape of the spectral profile as measured by the on-board CVF spectrometer and on the close match between the magnitude of the observed radiance in the 4.7\(\mu\)m feature and that calculated using a thermospheric CO abundance predicted by Allen et al., known direct electron impact cross sections for CO, and an energy deposition computer model devised by J. Winnick of AFGL.

The predicted carbon monoxide mixing ratio used in the model calculation is based on a photochemical model driven by the photodissociation of CO\(_2\) above 90 km and the reaction of CO with OH to reform CO\(_2\) below 90 km. The resulting calculated CO and CO\(_2\) profiles from Reference 7 are shown in Figure 2-1 along with a comparison to available CO measurements in the 50 to 80 km range and measured CO\(_2\) profiles in the 80 to 120 km range. The good agreement in the CO\(_2\) mixing ratio fall off above 90 km gives added weight to the predicted CO profile in the 90 to 120 km range.

The resulting CO and CO\(_2\) profiles of Allen et al are also plotted in Figure 2-2 along with the other atmospheric constituents considered in the report. Major species profiles are adopted from the model of Keneshea et al. The apparent variability in atomic oxygen in this altitude region is illustrated with data from several recent measurements. The Ar, O\(_3\), and NO profiles are taken from References 16-18.

The direct excitation of carbon monoxide vibrational states by secondary electrons occurs principally through a negative ion shape resonance in the 1 to 3 eV energy range. The peak excitation energies for the first four vibrational levels lie just below the energy range for the 2 to 4 eV shape
Figure 2-1. CO and CO₂ Mixing Ratios, Comparison of Model and Measurements. (Heavy and light dashed lines are model CO and CO₂ profiles respectively for CO, ... and data profiles are reproduced from Ref. 7, — — — from Ref. 9 and — — from Ref. 10, CO₂ profiles are from Ref. 11)
Figure 2.2 Atmospheric Concentration Profiles. Dashed lines for $N_2$, $O_2$, and $Ar$ are model calculations from Keneshea et al. (Ref. 17). Solid lines for $O_2$ are measurements from Refs. 14-15. Other species are $Ar$ (Ref. 16), $CO$, and to (Ref. 19, 16, 23).
resonance excitation curves for \( N_2 \) and are thus "uncovered" by the dominant \( N_2 \) excitation process. Vibrational levels of CO higher than \( v = 4 \) will not be excited due to their overlap with the larger cross sections for the far more abundant \( N_2 \).

Measured electron impact cross sections for excitation to specific CO vibrational levels as presented in Reference 8 are plotted in Figure 2-3. Also presented for comparison is the total cross section for \( N_2 \) vibrational excitation from Reference 20.

The quantitative result of our modeling effort at 100 km was that \( 6 \times 10^{-3} \) quanta of CO vibrational excitation would be created per ion pair with 84% of the excited CO created in \( v = 1 \), 10% in \( v = 2 \), 4% in \( v = 3 \), and 2% in \( v = 4 \). This distribution arises from calculated vibrational energy distributions, \( N_v \), ratios of \( 1.5 \times 10^{-3} \), with a CO mixing ratio of \( 5 \times 10^{-5} \). It should be noted that spectral fitting routines assuming \( N_v \) quite similar to these calculated values provide an excellent fit to the EXCEDE:SPECTRAL CVF data feature at \( 4.7 \) \( \mu \)m.

The \( 6 \times 10^{-3} \) quanta/ion pair is derived as follows:

Given the fact that higher vibrational levels of CO have radiative lifetimes approximated by \( \tau(1-v) \), the immediate \( 4.7 \) \( \mu \)m output for the calculated 100 km \( N_v \) distribution is close to \( \sum_{v=1}^{4} v N_v \), or \( 1.5 \) times the \( v = 1 \) emission rate. Since the CO\((v = 1)\) production rate was calculated to be \( 1 \times 10^{-3} \) quanta per ion pair at 100 km, \(^3\) and since the steady state production and emission rates are equal, when correction is made for the faster radiative lifetimes of \( v = 2, 3, \) and \( 4 \), the "apparent" calculated emission rate is \( 1.5 \) times higher or \( 6 \times 10^{-3} \) per ion pair.

The Winick model was also used to predict a 3914A band production/emission rate from \( N_2^+ \) of \( 6 \times 10^{-2} \) quanta per ion pair, resulting in a predicted ratio of CO \((4.7 \mu m)\) to \( N_2^+ \) (3914A) steady state emission rate of \( 0.006/0.06 \) or \( .1 \). A plot of this ratio from the EXCEDE spectral data is shown as the open circles in Figure 2-4. Although there is
Figure 2-3. Vibrational Excitation Cross Sections for CO vibrational levels and for $N_2(\Sigma v)$.
considerable scatter in the data, the two points nearest 100 km give I (4.7 \( \mu \)m)/I (3914A) ratios of about 0.15 and 0.28 in good agreement with the calculated value of 0.1 given the considerable uncertainties in the model and its inputs.

Furthermore, given the model assumption that both CO vibrational excitation and \( \text{N}_2^+ \) (3914A) production are direct electron impact processes we expect the altitude dependence of the I (4.7 \( \mu \)m)/I (3914A) steady state emission to follow the CO mixing ratio profile which, in turn, is proportional to the CO/N\(_2\) ratio. As illustrated in Figure 2-4 given the data scatter the CO mixing ratio is a good indicator of the I (4.7 \( \mu \)m)/I (3914A) emission particularly between 95 and 110 km.

Thus, the spectral shape, absolute emission level and altitude profile of the EXCEDE:SPECTRAL 4.7 \( \mu \)m feature are all well explained by direct electron impact excitation of ambient CO. This unexpected result has been recently supported by the observation of high resolution CO spectra measured by the rocket borne Field Widened Interferometer experiment.\(^{22}\)

In summary, as first presented in Reference 3, the steady state beam-on production of 4.7 \( \mu \)m radiation is well explained by invoking the direct excitation of CO by secondary electrons in the 1 to 2 eV range. Since the production rate of CO vibrational quanta is \( \approx 6 \times 10^{-3} \) quanta per ion pair at 100 km, and since each quanta is about 0.26 eV, the fraction of beam energy deposited in CO vibration at 100 km is \( \approx 6 \times 10^{-3} \times 0.26 \text{ eV}/35 \text{ eV} \approx 4.5 \times 10^{-5} \) of the major energy deposition mechanism. As indicated by Figure 2-4, this energy deposition ratio probably rises by a factor of 2-3 in the 105 to 120 km range. The ratio of deposition energy to ion pair production energy will be a key indicator in the discussion of the temporal evolution of CO 4.7 \( \mu \)m radiation discussed in the following subsection.
2.2 Temporal Predictions for CO 4.7 μm Radiation

Infrared observations from the EXCEDE spectral mission were limited to a region of active electron beam irradiated atmosphere interspersed with nonirradiated regions as the electron beam switched on and off. This experimental geometry favors "prompt" emitters which are directly excited by the incident electron flux and have radiative lifetimes shorter than the observation time as the onboard instruments' fields of view pass through the irradiated volume (-10 ms). It has been recognized that radiation due to secondary excitation processes (e.g., metastable E+V exchange or infrared chemiluminescence) and/or longer lived emitters could be better analyzed if future EXCEDE missions were designed to view post-irradiated regions where prompt emissions are decaying at a faster rate than radiation from secondary processes or even long-lived promptly excited states.

The following subsections are an attempt to review all relevant prompt and secondary CO vibrational excitation mechanisms, in terms of their strength (the ratio of expected deposition energy into CO vibrational states to the energy deposited into ion pair production) and characteristic production and decay times. This review is intended to identify the major CO(v) production mechanisms and their inherent time scales as an aid to predicting 4.7 μm radiation characteristics available for observation by future EXCEDE missions.

The potential CO(v) excitation mechanisms reviewed in this effort are listed in Table 2-1. The mechanisms reviewed include two direct processes: secondary electron excitation of ambient CO and dissociative excitation of ambient CO₂; and nine indirect processes, including intermolecular E+V quenching of the electronic metastable species N₂(A), O(¹S), O(¹D), O₂(b¹Σ), O₂(a¹Δ), and the 4.5 eV states of O₂, E+V quenching of N₂(A) followed by secondary intramolecular E+V quenching of CO(a³π), V+V quenching of N₂(v) and infrared chemiluminescence in the reaction of O⁺ with CO₂.

The bulk of the indirect processes considered involve the intermolecular E+V quenching of electronically excited species. A summary of the excitation energy and major excitation and quenching processes of these metastable
electronic energy reservoir species is shown in Table 2-2. Production and loss mechanisms of several reservoir species for EXCEDE experimental conditions have been deduced from analysis of the PRECEDE experiment. Other key excitation and loss mechanisms can be evaluated from the work of Torr and Torr. An analysis of the potential role of both electronically and vibrationally excited reservoir species in the production of \( \text{CO}(v) \) is presented below.
<table>
<thead>
<tr>
<th>PROCESS FORMULA</th>
<th>PROCESS TYPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) $e + \infty \rightarrow \infty(v) + e$</td>
<td>Direct electron impact</td>
</tr>
<tr>
<td>2) $e + \infty_2 \rightarrow \infty(v) + 0 + e$</td>
<td>Electron impact dissociative excitation</td>
</tr>
<tr>
<td>3) $N_2(v) + \infty \rightarrow \infty(v') + N_2(v-v')$</td>
<td>V-V exchange with $N_2$</td>
</tr>
<tr>
<td>4) $N_2(A) + \infty \rightarrow \infty(a,v) + N_2$</td>
<td>E-E exchange with $N_2(A)$ plus radiative or collisional quenching</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>5) $N_2(A) + \infty \rightarrow \infty(v) + M$</td>
<td>E-V exchange with $N_2(A)$</td>
</tr>
<tr>
<td>6) $0 (^1S) \rightarrow \infty + \infty(v) + 0 (^3P)$</td>
<td>E-V exchange with $0 (^1S)$</td>
</tr>
<tr>
<td>7) $0 (^1D) \rightarrow \infty + \infty(v) + 0 (^3P)$</td>
<td>E-V exchange with $0 (^1D)$</td>
</tr>
<tr>
<td>8) $O_2 (c,A,A') + \infty \rightarrow \infty(v) + O_2$</td>
<td>E-V exchange with $O_2^*$</td>
</tr>
<tr>
<td>9) $O_2 (b^1\Sigma) + \infty \rightarrow \infty(v) + O_2$</td>
<td>E-V exchange with $O_2^*$</td>
</tr>
<tr>
<td>10) $O_2 (a^1\Delta) + \infty \rightarrow \infty(v) + O_2$</td>
<td>E-V exchange with $O_2^*$</td>
</tr>
<tr>
<td>11) $\infty_2 + O^+ \rightarrow \infty(v) + O_2^+$</td>
<td>Infrared chemiluminescence</td>
</tr>
<tr>
<td>EXCITED SPECIES</td>
<td>EXCITATION ENERGY (eV)</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>N₂ (A^3Σ^+)</td>
<td>6.16</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>O(^1S)</td>
<td>4.19</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>O(^1D)</td>
<td>1.97</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ (A^3Σ^+</td>
<td>4.5-5.0</td>
</tr>
<tr>
<td>A' 3Δ_u</td>
<td></td>
</tr>
<tr>
<td>c 1Γ_u</td>
<td>5-50</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ (b ^1Σ^+</td>
<td>1.64</td>
</tr>
<tr>
<td>g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ (a ^1Δ_g)</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>CO (a ^3π)</td>
<td>6.01</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2.1 Direct Electron Impact Excitation of CO

As reviewed in Section 2-1 our previous analysis of the EXCEDE:SPECTRAL Mission identified direct electron impact on ambient CO as the predominant mechanism for the production of "prompt" CO(v). Our model analysis for the 100 km case (5 \times 10^{-5} mixing ratio for CO) predicted the amount of beam energy deposited in CO(v) was \( \approx 4.5 \times 10^{-5} \) of the ion pair creation energy.

The infrared emission time scale associated with this direct excitation mechanism is the intrinsic radiative lifetime of the CO(v) excited states. The radiative emission time scale dominates because the quenching of low CO(v) states by atmospheric species is very slow. For example the rate constant at 300°K for V = 1 state of CO to undergo V+V exchange with N\(_2\) is 5 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}, with O\(_2\) it is 9 \times 10^{-17} and the V+T/R rate constant for Ar is less than 3 \times 10^{-18}.25 For vibrational quenching to compete with radiative decay at 100 km where the N\(_2\) number density is 10^{13} \text{ cm}^{-3}, the quenching rate constant, K_Q, for N\(_2\) would have to exceed 3 \times 10^{-12} since:

\[ k_Q[M] \geq \frac{1}{\tau_{\text{rad}}} = 35 \text{ sec}^{-1}. \]

The V+T/R rate for atomic oxygen would have to exceed 3 \times 10^{-11}, and although room temperature rates are not available for this process it is unlikely that O is more than 10^7 times more effective than the upper limit for Ar.

A best estimate of the CO(v=1) radiative lifetime is 28.3 msec based on four recent determinations of the CO(1+0) integrated band absorption coefficient of 266.0,26 282.2,27 27928 and 27329 cm\(^{-2}\) atm\(^{-1}\) at standard temperature and pressure.

Averaging these four values gives an integrated band intensity, S, of 275 cm\(^{-2}\) atm\(^{-1}\) (STP). Using Penner's expression relating S\(_{\lambda u}\) with the radiative lifetime\(^{30}\) and a band center frequency, \( \nu_{\lambda u} \), of 2143 cm\(^{-1}\) or 6.42 \times 10^{13} \text{ sec}^{-1} \text{ yields:}
Thus the direct excitation of CO(v) by electron impact will decay after beam termination with a rate constant of $1/\tau_{\text{rad}} = A (1+0) = 35 \text{ sec}^{-1}$ for $v = 1$, with higher vibrational levels displaying a radiative decay rate approximately $v$ times $A (1+0)^{21}$ cascading to lower $v$'s. However, since we have calculated that for the 100 km case 84% of the excited CO will be created in $v = 1$ the 35 sec$^{-1}$ decay rate constant will dominate the 4.7 µm fall off from direct excitation.

In summary, for our 100 km benchmark altitude with a CO mixing ratio of $5 \times 10^{-5}$, we predict that about $4.5 \times 10^{-5}$ of the ion pair creation energy will be deposited by direct electron impact excitation into the CO vibrational manifold, with the great bulk of the excitation in $v = 1$. This radiative source will start coincident with the exciting electron deposition and the predominant component will decay after beam termination at the radiative decay rate of the $v = 1$ component with a decay rate constant of 35 sec$^{-1}$.

2.2.2 Dissociative Excitation of Carbon Dioxide

As shown in Figures 1-2 and 2-2 the ambient CO$_2$ concentration exceeds that of CO by about a factor of 3 at 100 km, equals the CO concentration near 108 km and falls below the CO concentration at altitudes above 108 km.

Since the O-CO bond energy in CO$_2$ is 5.5 eV, electrons with energy in excess of about 5.75 eV are capable of dissociating CO$_2$ and leaving the CO fragment vibrationally excited. If the dissociating electron attaches to the atomic oxygen, the energy dissociation threshold is lowered to 4.0 eV with $-4.25 \text{ eV}$ required for CO vibrational excitation.

There are no cross section measurements available which indicate the degree of CO vibrational excitation in direct dissociation or dissociative attachment electron impact cross sections for CO$_2$. However, in both neutral and ionic chemical reactions there is a general observation that vibrational
reaction energy is usually not present in a molecular fragment unless it is formed during the reaction. Thus for an exothermic reaction of the type

$$ABC + D \rightarrow AB + CD$$

the fragment $CD$ which is formed in the reactive process if far more likely to be excited than the $AB$ fragment.

By analogy, we might expect that the electron impact processes:

$$e + CO_2 \rightarrow CO + O^-$$
$$CO + 0 + e$$

might not be particularly effective means of producing vibrationally excited $CO$.

Cross sections are available for the dissociative attachment portion of the process noted above with the room temperature value displaying two narrow ($\approx 1 \text{ eV}$) peaks (with no observable vibrational structure) reaching $1.5 \times 10^{-19} \text{ cm}^2$ just above 4 eV and $4.5 \times 10^{-19}$ just above 8 eV. This can be compared with the total direct excitation cross section for $CO(v)$ (individual vibrational level cross sections are shown in Figure 2-3) which peaks above $8 \times 10^{-16} \text{ cm}^2$. Electron energy loss in the 4 and 8 eV ranges is dominated by momentum transfer to $N_2 (\sigma = 10^{-15} \text{ cm}^2)$ and possibly by electronic excitation of $O_2$ and $N_2$ respectively.

However, even the first mechanism, momentum transfer to $N_2$, would dominate $CO_2$ dissociation as an energy loss mechanism in the 4 and 8 eV ranges. This can be seen from a simple comparison of energy loss for the two processes. The momentum transfer energy loss fraction can be approximated by the ratio of the electron to $N_2$ mass of $2 \times 10^{-5}$ multiplied by the electron energy (4 or 8 eV, corresponding to the two peaks in the $CO_2$ dissociation cross section). Thus the 4 eV energy loss rate for momentum transfer to $N_2$ at 100 km can be approximated by:
\[ \frac{R_{N_2}}{R_{CO_2}} = \frac{v_e \sigma_{N_2}[N_2]}{v_e \sigma_{CO_2}[CO_2]} \Delta E \]

\[ = v_e \text{ cm sec}^{-1} \times (10^{-15} \text{ cm}^2) \times (10^{13} \text{ cm}^{-3}) \times (4 \text{ eV}) \times 1 \times 10^{-5} \]

\[ = 8 \times 10^{-7} (v_e) \text{ eV/sec} \]

while the comparable energy loss rate for CO \textsubscript{2} dissociation is

\[ \frac{R_{CO_2}}{R_{N_2}} = \frac{v_e \sigma_{CO_2}[CO_2]}{v_e \sigma_{N_2}[N_2]} \Delta E \]

\[ = v_e \text{ cm sec}^{-1} \times (1.5 \times 10^{-19} \text{ cm}^2) \times (3 \times 10^9 \text{ cm}^{-3}) \times (4 \text{ eV}) \]

\[ = 1.8 \times 10^{-9} (v_e) \text{ eV/sec} \]

Thus, the energy loss rate ratio for CO \textsubscript{2} dissociation and \(N_2\) momentum transfer at 4 eV is less than 1.8 x 10\(^{-9}\) \(v_e\) / 8 x 10\(^{-7}\) \(v_e\) or 1/400 of the loss rate for momentum transfer to \(N_2\). A similar fraction applies at the 8 eV resonance peak as well. Since we have argued that probably only a small fraction of the dissociative attachment events leave the CO fragment vibrationally excited, and since most of the energy loss in the CO \textsubscript{2} process is taken up in breaking the CO \textsubscript{2} bond not exciting CO(v), it seems probable that CO(v) production from CO \textsubscript{2} cannot compete with direct excitation of CO. This is particularly true of altitudes above 108 km where CO is more abundant than CO \textsubscript{2} to start with.

If CO(v) production from CO \textsubscript{2} were comparable with direct excitation of CO, the 4.7 \(\mu\)m radiation feature observed in the EXCEDE:Spectral experiment should have followed the CO \textsubscript{2} mixing ratio profile, at least in the 90-105 km region where [CO \textsubscript{2}] > [CO] (see Figure 2-1). As illustrated in Figure 2-4 the 4.7 \(\mu\)m profile appears to closely follow the CO mixing ratio (sharply increasing between 90 and 100 km and constant in the 100-115 km range) not the monotonically decreasing CO \textsubscript{2} mixing ratio. This strongly corroborates our
argument that CO$_2$ dissociation is a minor source of CO(v) under EXCEDE conditions.

Of course any CO(v) created by impact dissociation of CO$_2$ would decay with the same radiative quenching rate characteristic of directly excited CO upon beam termination.

2.2.3 Vibrational Exchange with N$_2$(v)

As indicated by the large electron impact cross section for vibrational excitation of N$_2$ plotted in Figure 2-3 and the fact that N$_2$ is the dominant atmospheric species in the 90-120 km range as shown in Figure 2-2, the EXCEDE experiments can be expected to produce copious amounts of N$_2$(v). Since N$_2$(v) does not have an electric dipole moment it forms a long lived metastable energy source until collisionally quenched. The principal quenchant for N$_2$(v) by the altitude range of interest is atomic oxygen with a quenching rate constant of -2 x 10^{-15} cm$^3$ sec$^{-1}$ for N$_2$ (v = 1) at upper mesospheric and lower thermospheric temperatures.

Given an atomic oxygen density at 100 km of 8 x 10$^{10}$ to 8 x 10$^{11}$ cm$^{-3}$ from Figure 2-2 this corresponds to a N$_2$(v) quenching rate of between 1.5 x 10^{-4} and 1.6 x 10^{-3} sec$^{-1}$ or a quenching lifetime of greater than 625 sec. (or 10 minutes) at 100 km. Thus, for any time scale of interest to an on board or fly along EXCEDE experiment the N$_2$(v) pool will remain constant.

The rate constant for the production of CO (v = 1) from N$_2$ (v = 1) at temperatures characteristic of 100 km is about 8 x 10^{-15} cm$^3$ sec$^{-1}$. Thus, the time scale for the production of CO(v) from N$_2$(v) is also quite long. Assuming [CO] $\ll$ [N$_2$(v)] and a CO concentration of 5 x 10$^8$ at 100 km (from Figure 2-2) then the rate for the production of CO(v) is 8 x 10^{-15} cm$^3$ sec$^{-1} x 5 x 10^8$ cm$^{-3} = 4 x 10^{-6}$ sec$^{-1}$ giving a V-V exchange time scale 2.5 x 10$^5$ seconds or almost 3 days.

The fraction of the beam energy directly deposited into N$_2$(v) is probably well approximated by the -2.0 eV slice between -1.6 and 3.6 eV electron energy range which is dominated by the N$_2$ shape resonance plotted in
Figure 2-3. In this energy range $N_2(v)$ excitation dominates energy loss processes. This direct excitation also dominates total $N_2(v)$ production although some additional $N_2(v)$ production through $O^+$ and $O^-$ quenching will also occur. Since the electron energy loss per ion pair is 35 eV, each secondary electron loses roughly 2.35 or 6% of its energy to direct excitation of $N_2(v)$. This estimate is in agreement with Winnick's model at 700 cm which predicts that 8.7% of the ion pair creation energy is deposited in $N_2(v)$. If roughly $6 \times 10^{-4}$ of the ion pair formation energy is present as $N_2(v)$, then the fraction flowing into $CO(v)$ is limited by the ratio of $k_{CO}$ to $k_{O}$ quenching of $N_2(v)$ which at least for $N_2(v = 1)$ can be estimated.

If we take the $CO$ and $O$ at 700 cm to be $6 \times 10^{-7}$ and $4 \times 10^{-7}$ respectively then the ratio of their $N_2(v = 1)$ quenching rates is

$$k_{CO}[CO]/k_{O}[O] = (6 \times 10^{-7}) / (4 \times 10^{-7}) = 1.5 x 10^{-7}$$

Thus, the fraction of the ion pair creation energy deposited through $N_2(v)$ into $CO(v)$ can be estimated as $6 \times 10^{-7} x 1.5 x 10^{-7}$ or $9 \times 10^{-7}$.

This level of fractional energy transfer is about 4 times greater than the $4.5 \times 10^{-5}$ fraction calculated for direct CO excitation at 100 cm. However, it is important to remember that the deposition rate is very slow compared with the direct process. The direct process is fast enough to reach steady state when the beam is on and decays with the CO radiative lifetime of 15.1 msec. The $N_2(v)$ process pumps energy into $CO(v)$ with a time scale that is very long compared to the beam-on duration and decays with $N_2(v)$ quenching by O-atoms on a time scale of roughly 10 minutes.

By dividing total energy input fraction by the decay time constants for each process we can assess their initial relative radiative output rates.

$N_2(v): \frac{2.4 \times 10^{-7}}{625 \text{ sec}} = 3.8 \times 10^{-7}$
Thus, initially the direct excitation mechanism is a $4 \times 10^3$ stronger source of $\text{CO}(v)$ radiation; however, after $9$ radiative lifetimes (0.25 s) the direct source will decay to a point where the $\text{N}_2(v)$ source dominates. The $\text{N}_2(v)$ source will then dominate until the $\text{N}_2(v)$ is quenched, a process which will require several tens of minutes.

### 2.2.4 Quenching of Metastable Electronic States

Analysis of the first three $\text{CO}(v)$ excitation mechanisms listed in Table 2-1 has shown that process (1), the direct electron impact excitation of CO will be the dominate source of $\text{CO}(v)$ radiation while the beam is on and will decay exponentially until dominated after roughly 0.25 s by process 3, the V-V exchange with $\text{N}_2$.

The purpose of this subsection is to investigate processes 4 through 10 from Table 2-1, all of which involve the quenching of electronically metastable species which may be directly or secondarily created by electron impact. Key characteristics of these metastable states are summarized in Table 2-1.

Mechanisms 4 and 5 involve quenching of $\text{N}_2 (A)$. Under EXCEDE conditions the production of $\text{N}_2 (A)$ has been estimated to be equivalent to the ion pair production rate. Since each $\text{N}_2 (A)$ represents at least 5.16 eV of excitation energy, over 72% of the ion pair production energy appears to flow through this species. Mechanism 4 from Table 2-1 is a two step process whereby $\text{N}_2 (A)$ is quenched by $\text{O}$ to form the $\text{CO}(a_1)$ state in a near resonant E-E exchange process. $\text{X}(a_1)$ is then collisionally or radiatively quenched to yield $\text{CO}(v)$. Mechanism 5 involves direct E-V quenching by CO.

As indicated by Table 2-2, $\text{N}_2 (A)$ is rapidly reactively destroyed by $\text{O}$ and $\text{N}_2$ with $\text{N}_2 (A)$, with $v = 0$ rate constants of $3 \times 10^{-11}$ cm$^3$/sec$^{1/2}$ and $2 \times 10^{-12}$ respectively. If we take $[\text{O}]$ at 100 km to be $5 \times 10^{14}$ cm$^{-3}$ and $[\text{O}_2]$ as $4 \times$
\[ 10^{12} \text{ cm}^3 \text{ then the quenching rate for } N_2(A) \text{ is:} \]

\[ Q_0 + O_2 = k_0 [O] + k_{O_2} [O_2] = 3 \times 10^{-11} \times 5 \times 10^{11} + \]

\[ 2 \times 10^{-12} \times 2 \times 10^{12} = 19 \text{ sec}^{-1} \]

which is significantly faster than the compared radiative quenching rate of \(1/\tau_{\text{rad}} = 0.5 \text{ sec}^{-1}\).

The quenching rate constant for \(N_2(A), v = 0\) by CO is \(5 \times 10^{-12}\). For a \([CO]\) of \(5 \times 10^8\) at 100 km the CO quenching rate:

\[ Q_{CO} = k_{CO} [CO] = 5 \times 10^{-12} \times 5 \times 10^8 = 2.5 \times 10^{-3} \text{ sec}^{-1} \]

which is \(1.3 \times 10^{-4}\) of the combined \(O\) and \(O_2\) rate. The amount of \(N_2(A)\) energy eventually deposited in \(CO(v)\) when CO quenches \(N_2(A)\) is not known, but since most of the reaction passes through \(CO(a)\) which will radiatively decay at a rate of \(-140 \text{ sec}^{-1}\) it may be quite small. This fraction of the ion pair energy flowing into \(CO(v)\) via \(N_2(A)\) can be written as the fraction of the ion pair energy going to \(N_2(A)\) \((.17)\) times the fraction quenched by CO \((2 \times 10^{-4})\) times the fraction of the energy quenched ending up as \(CO(v)\). If we take this latter fraction, designated \(f_v(CO)\), as certainly 0.1 or less we then estimate that mechanisms 4 and 5 together cannot pump more than \(0.17 \times 2 \times 10^{-8} \times 0.1\) or \(3.4 \times 10^{-6}\) of the ion pair energy. This fraction is significantly less than the \(4.5 \times 10^{-5}\) calculated for direct excitation, but might play a role after a few radiative decays of the directly excited \(CO(v)\) - if \(f_v(CO)\) is as large as 0.1 for the combination of processes 4 and 5.

\(O(1S)\) quenching by CO is a second potential E-W source of \(CO(v)\). As shown in Table 2-2 \(O(1S)\) is produced by atomic oxygen quenching of \(N_2(A)\) and by dissociative neutralization of \(O_2^+\). Since we have shown above that (depending on \([O]\) assumed) roughly half of the \(N_2(A)\) at 100 km is quenched by
Recent measurements indicate that .75% of these quenching interactions result in \( \text{O}^{(1S)} \) production.\(^{35}\) Thus at 100 km roughly 0.4 \( \text{O}^{(1S)} \) per ion pair may be created through the \( \text{N}_2(A) \) channel. Analysis of the PRECEDE experiment indicated that this mechanism dominates \( \text{O}^{(1S)} \) production under EXCEDE-like conditions in the 100-116 km range with \( \text{O}_2^+ \) recombination dominating only below 96 km.\(^{23}\) Assuming the \( \text{N}_2(A) \) source is dominant at 100 km the fraction of the ion pair production energy flowing through \( \text{O}^{(1S)} \) is the \( \text{O}^{(1S)} \) energy as a fraction of the ion pair energy (4.19/35 eV) times 0.4 or ~0.05.

As shown in Table 2-2 the main deactivation mechanisms for \( \text{O}^{(1S)} \) are quenching by \( \text{O}_2 \) and radiative decay. Previous laboratory experiments indicating a fast quenching rate for \( \text{O}^{(3P)} \) have been discredited due to \( \text{O}_2(1A) \) contamination results obtained since the analysis of the PRECEDE experiment\(^{23}\) was published. The quenching rate constant for \( \text{O}_2 \) has been measured as 3.6 x 10\(^{-13} \) cm\(^3\) sec\(^{-1}\).\(^{36}\) For a 100 km \([\text{O}_2]\) of 4 x 10\(^{12} \) cm\(^{-3}\) this leads to a quenching rate of:

\[
Q_{\text{O}_2} = k_{\text{O}_2} [\text{O}_2] = 3.6 \times 10^{-13} \times 2 \times 10^{12} = 0.7 \text{ sec}^{-1}
\]

which is slightly slower than the radiative quenching of \( 1/\tau_{\text{rad}} = 1.1 \) sec\(^{-1}\). Taken together, the \( \text{O}_2 \) and radiative quenching rate can be estimated as ~1.8 sec\(^{-1}\) at 100 km. The quenching of \( \text{O}^{(1S)} \) by \( \text{CO} \) is an inefficient process with a measured rate constant of 4.9 x 10\(^{-15} \) cm\(^3\) sec\(^{-1}\).\(^{36}\) Assuming a \([\text{CO}]\) of 5 x 10\(^8 \) cm\(^{-3}\) leads to a \( \text{O}^{(1S)} \) quenching rate by \( \text{CO} \) of:

\[
Q_{\text{CO}} = k_{\text{CO}} [\text{CO}] = 5 \times 10^8 \times 4.9 \times 10^{-15} = 2.5 \times 10^{-6} \text{ sec}^{-1}
\]

Thus, at 100 km the \( \text{O}^{(1S)} \) quenching rate by \( \text{CO} \) is estimated to account for no more than 2.6 x 10\(^{-6} \) sec\(^{-1}\)/1.8 sec\(^{-1}\) = 1.4 x 10\(^{-6} \). Since \( \text{O}^{(1S)} \) represents 0.05 of the ion pair creation energy, the \( \text{O}^{(1S)} \) source can not channel more than a negligible ~7 x 10\(^{-8} \) of the ion pair production energy into \( \text{CO}(v) \).
The third possible source of CO(v) by E•V exchange from metastable electronic species is O(\(^1\)D). From Table 2-2 O(\(^1\)D) can be produced by dissociative recombination of O\(_2\) and NO\(^+\) and also by radiative quenching of O(\(^1\)S). Since the neutralization of both O\(_2^+\) and NO\(^+\) efficiently produce O(\(^1\)D) and since N\(_2^+\) produces either NO\(^+\) or O\(_2^+\) in interaction with O and O\(_2\) respectively the ion channel may produce nearly one O(\(^1\)D) per ion pair through dissociative neutralization.

For the O(\(^1\)S) channel, nearly 96% of the radiatively damped O(\(^1\)S) produces O(\(^1\)D)\(^\text{24}\) and since at 100 km we have estimated that ~44% of the O(\(^1\)S) quenches radiatively, then we expect roughly 0.96 x 0.44 x 0.4 = 0.17 O(\(^1\)D) per ion pair through the 0.4 O(\(^1\)S) per ion pair as observed in the PRECEDE experiment. Thus in total we expect ~1.17 O(\(^1\)D) per ion pair representing 1.17 x E(O(\(^1\)D))/E (Ion Pair) = 1.17 x 1.97/35 = 0.066 of the ion pair production energy.

The main quenching mechanism for O(\(^1\)D) at 100 km is quenching by N\(_2\) with a quenching rate constant of 2.3 x 10\(^{-11}\) cm\(^3\) sec\(^{-1}\)\(^\text{24}\) The rate constant for O\(_2\) quenching is a factor of 1.5 to 3 larger than that for N\(_2\),\(^\text{24}\) but the concentration of N\(_2\) is 5 to 10 times the O\(_2\) concentration at the altitudes of interest leaving N\(_2\) as the dominate quencher.

At 100 km, the combined N\(_2\) and O\(_2\) quenching rate can be calculated.
After choosing the laboratory measured rate for O\(_2\) quenching of 3.6 x 10\(^{-11}\) cm\(^3\) sec\(^{-1}\)\(^\text{24}\) we calculate:

\[
Q_{N_2 + O_2} = k_{N_2} [N_2] + k_{O_2} [O_2]
\]

\[
= 2.3 \times 10^{-11} \times 1 \times 10^{13} + 3.6 \times 10^{-11} \times 2 \times 10^{12}
\]

\[
= 300 \text{ sec}^{-1}
\]

The total rate constant for CO quenching of O(\(^1\)D) has been measured as 7.3 x 10\(^{-11}\) cm\(^3\) sec\(^{-1}\) with a vibrationally specific rate constants (ratioed to 1.0
for \( v = 1 \) of: 1.5, 1.0, 0.66, 0.50, 0.36, 0.25, 0.12, 0.011 for \( v = 0 \) to 7 respectively.\(^{37}\) This yields an average \( \text{CO}(v) \) of 1.7. The quenching rate of \( \text{O}(^1\text{D}) \) to \( \text{CO} \) at 100 km is then:

\[
Q_{\text{CO}} = k_{\text{CO}} \left[ \text{CO} \right] = 7.3 \times 10^{-11} \times 5 \times 10^8
\]

\[
= 3.7 \times 10^{-2} \, \text{sec}^{-1}
\]

When compared with the \( \text{N}_2 \) and \( \text{O}_2 \) rate of \( 3 \times 10^2 \) we predict that \( 1.2 \times 10^{-4} \) of the \( \text{O}(^1\text{D}) \) energy or \( 1.2 \times 10^{-4} \times 0.066 = 7.9 \times 10^{-6} \) of the ion pair production energy will be deposited in \( \text{CO} \) through \( \text{O}(^1\text{D}) \) quenching at 100 km. This \( \sim 8 \times 10^{-6} \) is fairly small (-1/6) compared to the \( 4.5 \times 10^{-5} \) calculated for direct electron impact excitation at 100 km and since the \( \text{O}(^1\text{D}) \) source is collisionally quenched with a time constant of \( 1/3.0 \times 10^2 \, \text{sec}^{-1} = 3 \, \text{msec} \) this source does not significantly outlast the direct excitation channel. However, within the uncertainties of the respective estimates it may noticeably enhance the direct electron impact excitation source.

The final metastable reservoir species to be considered are all electronically excited states of molecular oxygen. They include three highly excited states in the 4.5 to 5 eV range and the lower lying and better characterized \( b \, ^1\Sigma^+ \) and \( a \, ^1\Delta \) states. Key characteristics for these states are listed in Table 2-2.

Our previous analysis of the PRECEDE long lived visible and near ultraviolet 4.5 glow identified the three 4.5-5.0 eV \( \text{O}_2 \) states as probable important species under EXCEDE excitation conditions and reviewed apparent observations of these states in the natural aurora and airglow. The integrated strength of the long lived PRECEDE glow represents 5-6% of the beam deposition energy and represents an average \([\text{O}_2] \) in the irradiated volumes of order \( 10^7 - 10^8 \, \text{cm}^{-3} \).

Quenching data for the three 4.5-5 eV \( \text{O}_2 \) states is scarce, but recent studies by Kenner and Ogryzlo have yielded room temperature values of \( 9.3 \times 10^{-15}, 1.3 \times 10^{-11}, 1.3 \times 10^{-13}, 7 \times 10^{-13} \) and \( 7.2 \times 10^{-16} \) for \( \text{O}_2(A) \) quenching. 
by N₂, O, O₂, CO₂ and Ar respectively and 5.9 x 10⁻¹², 3 x 10⁻¹⁴, <6 x 10⁻¹⁴, and 6 x 10⁻¹⁶ for O₂(c) by O, O₂, CO₂ and Ar respectively. The O₂(A) values for O, O₂ and Ar are for the V = 2 state while other values are for the ground vibrational state. Except for the atomic oxygen values all of these rates are extremely slow and are consistent with our analysis of the PRECEDE data which indicates little quenching above 95 km. Atomic oxygen is probably the most serious quenchant above 95 km. If Kenner's and Ogryzlo's value of 5.9 x 10⁻¹² for k₀ is accepted for the O₂(c) state then the quenching rate at 100 km, assuming [O] of 5 x 10¹¹ cm⁻³, is:

\[ Q_0 = k_0 [O] = 5.9 \times 10^{-12} \times 5 \times 10^{11} = 3.0 \text{ sec}^{-1} \]

This compares with an expected radiative quenching rate of 1/τ_rad = 0.04 to 0.02 sec⁻¹ from Table 2-2. However, it is important to remember that, as indicated in Figure 2.2, the atomic oxygen concentration is quite uncertain in this altitude range and also that the quenching rate constants results by Kenner and Ogryzlo are difficult to measure and have not been confirmed by either additional laboratory or field measurements.

No quenching rates for the 4.5-5 eV O₂ states are available for CO, however the rates for the isoelectronic species N₂ or CO₂ should certainly be indicative. A value in the 10⁻¹³ to 10⁻¹⁴ range seems most likely from the available data. Assuming a k_CO of 10⁻¹³ for all three states and a [CO] of 5 x 10⁸ gives:

\[ Q_{CO} = k_{CO} [CO] = 10^{-13} \times 5 \times 10^{8} = 5 \times 10^{-5} \text{ sec}^{-1} \]

Comparing this number with the radiative quenching rates of 5.5, 0.2-0.02 and 0.04-0.02 for the A, A' and c states respectively indicates that no more than 10⁻⁵, 2.5 x 10⁻² to 3 and 2.5-1.2 x 10⁻² of each state can be transferred from O₂* to CO, this fraction is lessened by any collisional quenching of O₂* energy which is not transferred into CO vibration. Assuming that 6% of the
incident beam is deposited in $O_2^*$ allows probable upper bounds of CO(v) of $6 \times 10^{-7}$, $1.5 \times 10^{-3}$ to $6$, and $1.5$ to $0.7 \times 10^{-3}$ of the beam energy for the A, A', and c states respectively.

While these probable upper limits are large, it is important to note that upper bounds or probable upper bounds have been assumed for $k_{CO}$, the fraction of E-V energy transfer from $O_2^*$ to CO while lower bounds have been assumed for collisional quenching of $O_2$. All of these assumptions maximize the calculated limits on $O_2^*$ to CO(v) E-V transfer and each could contribute at least a factor of 10 to the overestimate.

If none of these parameters are poorly estimated then the A' and c states of $O_2$ might compete with $N_2(v)$ as a source of CO(v) decaying with a 5 to 50 second timescale (assuming radiative quenching predominates) compared with the 10 minute decay rate of $N_2(v)$. Due to its faster radiative and collisional quenching rate the $O_2(A)$ state is clearly a negligible source of CO(v).

The two lower lying $O_2$ metastable electronic states, $O_2(b^1\Sigma^+)$ and $O_2(a^1\Delta_g)$ at 1.64 and 0.98 eV of energy represent the lowest energy electronic metastables from Table 2-1. Both the collisional and radiative quenching of these states is very slow and have been reviewed by Davidson and Ogryzlo; the recommended quenching rate for $O_2(b)$ by $N_2$ is $2.2 \times 10^{-15}$ cm$^3$ sec$^{-1}$ and by CO is $3.3 \times 10^{-15}$. Since the $[CO]/[N_2]$ ratio is $[5 \times 10^8]/[10^{13}] = 5 \times 10^{-5}$ while the ratio of quenching rate constants is only $3.3 \times 10^{-15}/2.2 \times 10^{-15} = 1.5$ it is clear that less than $1.5 \times 5 \times 10^{-5} = 7.5 \times 10^{-5}$ of the energy in $O_2(b)$ can flow through CO. However, at 100 km even the $N_2$ quenching rate:

$$Q_{N_2} = k_{N_2} [N_2] = 2.2 \times 10^{-15} \times 10^{13} = 2.2 \times 10^{-2} \text{ sec}^{-1}$$

is slow compared to the radiative quenching rate $1/\tau_{\text{rad}} = 1/12 \text{ sec} = 8.3 \times 10^{-2} \text{ sec}$, so less than $7.5 \times 10^{-5}$ of the $O_2(1\Sigma)$ energy passes through CO.

Given the excitation mechanisms (direct excitation by electron impact and $O(1S)$ quenching by $O_2$ listed in Table 2-2) no more than 1% of the ion pair excitation energy can be expected to flow through $O_2(b)$. Thus, no more than
7.5 x 10^{-7} of the ion pair energy, a negligible amount, can reach CO(v) through this channel.

We also expect that O_2(a) represents a negligible source of CO(v). While there appears to be no direct measurement of the CO quenching rate constant of O_2(a), by analogy with O_2(b), it can be expected to be similar to that for N_2. Since the O_2 quenching rate constant for O_2 is ~24 times larger than that for N_2, CO will probably have to compete with O_2 quenching as well as N_2 (k_{O_2} = 2 \times 10^{-18}). Since the [CO]/[O_2] ratio at 100 km is ~ 5 \times 10^8 / 2 \times 10^{12} = 2.5 \times 10^{-4} and the rate constant ratio can be expected to be about 1/24, the fraction of O_2(a) quenched by CO compared with O_2 is about 10^{-5}. Given the sources of O_2(a) listed in Table 2-2 (direct electron impact excitation and radiative decay from the c, A' and b states of O_2 we would not expect more than a few percent of the ion pair creation energy to pass through O_2(a). Thus, the maximum energy fraction deposited into CO(v) by quenching of O_2(a) is of order 10^{-7} which is negligible compared to other long lived sources.

2.2.5 Chemiluminescent Reaction Sources of CO(v)

Infrared chemiluminescent processes are known to play an important role in the production of many vibrationally excited species in the upper atmosphere. Thus, a systematic evaluation of exothermic reactions to produce CO(v) was undertaken. Since there is no apparent source of atomic carbon to form CO by oxygen abstraction or recombination, the only apparent chemical pathways to CO involve the abstraction of an oxygen atom from CO_2.

However, as noted in subsection 2.2.1 the O-CO bond is strong and furthermore any reaction as simple as an O atom extraction from CO_2 may well leave the nonparticipating CO fragment vibrationally cold. One potential chemiluminescent reaction which does produce CO in an exothermic process was identified, the reaction of O^+ with CO_2:

O^+ + CO_2 + O_2^+ + CO
which is 1.5 eV exothermic and proceeds with a room temperature rate of $1.2 \times 10^{-9}$ cm$^3$ sec$^{-1}$.41

The major source of $O^+$ is expected to be dissociative ionization of $O_2$ by electron impact a process which has about 1/3 the total ionization cross section for $O_2$,20 thus about 1/3 of the $O_2$ ionized will form $O^+$.

Since $[O_2]$ is about 0.2 $[N_2]$ at 100 km and since the $O_2$ and $N_2$ total ionization cross sections are quite similar, we can estimate that $O^+$ is produced in about $(1/3 \times 1/6 = 1/18)$ or -5% of the total ion pair production rate.

In addition to reacting with $O_2$, the $O^+$ will react with $N_2$($k = 1.2 \times 10^{-12}$ cm$^3$ sec$^{-1}$) and $O_2$($k = 2.0 \times 10^{-11}$ cm$^3$ sec$^{-1}$).42 The total reaction rate with $N_2$ and $O_2$ at 100 km is:

$$k_{N_2 + O_2} = k_{N_2}[N_2] + k_{O_2}[O_2]$$

$$= 1.2 \times 10^{-12} \times 1 \times 10^{13} + 2.0 \times 10^{-11} \times 2 \times 10^{12}$$

$$= 52 \text{ sec}^{-1}$$

Thus, the decay rate of any $CO(v)$ produced by $O^+ + CO_2$ would decay on a 20 msec time scale. The $O^+$ plus $O_2$, $N_2$ reaction rates can be compared with the rate for $CO_2$ where, from Figure 2-2 we take $[CO_2]$ at 100 km as $2 \times 10^9$ cm$^{-3}$:

$$R_{CO_2} = k_{CO_2}[CO_2] = 1.2 \times 10^{-9} \times 2 \times 10^9 = 2.4 \text{ sec}^{-1}$$

representing $\sim 4.6 \times 10^{-2}$ of the $O_2+N_2$ rate.

If we assume that all 1.5 eV of the $O^+ + CO_2$ reaction exothermicity winds up in $CO(v)$, (something which is quite unlikely) then an upper bound for the fraction of the ion pair creation energy can be calculated from the ratio of $O^+$ to total ion production (0.05), the fraction of $O^+$ reacting with $CO_2$ (0.038) and the fraction of the ion pair production energy represented by the
exothermicity of the reaction (1.5/35 = 0.043). The resulting product (0.05 x 0.046 x 0.043) is \(1 \times 10^{-4}\) which is significant when compared with the \(4.5 \times 10^{-5}\) calculated for direct electron impact.

However, our analysis of the EXCEDE Spectral data makes it unlikely that this mechanism produces the observed CO radiation – for the same reason we rejected dissociative electron impact on CO\(_2\). As noted in subsection 2.2.1 if this mechanism dominated CO(v) production, the observed radiation would follow the CO\(_2\) atmospheric profile rather than that for CO. Since the observed radiation matches the CO profile quite well, as demonstrated in Figure 2-4, we can rule out O\(^+\) + CO\(_2\) as the major source of CO(v). Again the major reason for the failure of this mechanism is expected to be that CO is produced with little or no vibrational excitation in this fast and presumably direct reaction.
This page intentionally left blank.
3. PRODUCTION MECHANISMS FOR VIBRATIONALLY EXCITED OZONE

3.1 Review of Ozone Properties

Ozone is a weakly bound species with an $O_2-O$ bond energy of $-1.0 \text{ eV}$. It is formed throughout the upper atmosphere by the three body reaction:

$$0 + O_2 + M ightarrow O_3 + M$$

with a termolecular rate constant of $6.0 \times 10^{-34} \text{ cm}^6 \text{ sec}^{-1} (T/300)^{-2.3}$ for $N_2$ and $O_2$ as dominant third bodies.$^{43}$

In the upper mesosphere and lower thermosphere $O_3$ is rapidly photolyzed during daylight. At night the formation reaction is balanced by reaction with atomic oxygen and atomic hydrogen

$$O + O_3 \rightarrow 2 O_2$$

$$H + O_3 \rightarrow OH + O_2$$

with rate constants of $8.0 \times 10^{-12} \exp^{-2060/T} \text{ cm}^3 \text{ sec}^{-1}$ and $1.4 \times 10^{-10} \exp^{-470/T}$ respectively,$^{43}$ leading to typical $O_3$ profiles as plotted in Figure 2-2. A major assessment of the aeronomy of $O_3$ in the undisturbed mesosphere and lower thermosphere has recently been published.$^{44}$

As illustrated in Figure 2-2, normal atmospheric $O_3$ profiles fall off rapidly above 95 km, leaving little ambient $O_3$ for vibrational excitation by electron impact or by $V+V$ or $E+V$ exchange processes above 100 km.

$O_3(v)$ is of interest to the EXCEDE program because of its strong $v_3$ vibrational mode centered in the long-wavelength infrared region at 1042 cm$^{-1}$ (9.6$\mu$m). The $v_3$ mode has a band strength measured to be in the range of...
324-355^45,46 cm^-2 atm^-1 at STP. Selecting the recent band strength measurement of 355 cm^-2 atm^-1^45 and utilizing Penner's expression^30 as illustrated for CO in subsection 2.2 leads to a radiative lifetime of 92.7 ms.

O_3 also has two other infrared active vibrational bands, \nu_1 centered at 1103 cm^-1 (9.1 \mu m) and \nu_2 at 701 cm^-1 (14.1 \mu m). However, both of these bands are much weaker than \nu_3 with reported band strengths of 9.65 and 17.9 cm^-2 atm^-1 at STP respectively.^44 These band strengths and frequencies correspond to radiative lifetimes of 3042 and 4059 ms. for \nu_1 and \nu_2 respectively.

3.2 Excitation of Ambient O_3

At night below 100 km sufficient ambient O_3 may be present to warrant consideration of mechanisms which would enhance its vibrational population.

Possible ambient excitation mechanisms include direct excitation by electron impact, E-V exchange with the metastable electronically excited species listed in Table 2-2 (N_2(A), O_2(a,b,A,A',c), O(1D, 1S) and V-V exchange with N_2(v) or O_2(v).

3.2.1 Electron Impact Excitation of Ozone

Direct electron impact excitation is difficult to assess. The complicating factor is that O_3 is subject to dissociative attachment:^6

\[ O_3 + e + 0^- + O_2 + 0.43 \text{ eV} \]

and

\[ O_3 + e + O_2^- + 0 - 0.6 \text{ eV} . \]

These are relatively efficient processes for thermal electrons with a rate constant of 8.9 \times 10^{-12} (T/300)^{3/2} cm^3 sec^-1 where T is the electron temperature.^4/ The dissociative attachment cross section is known to peak
between 1.0 and 1.5 eV for both the lowest energy (0⁻) and secondary (O₂⁻) processes with absolute cross sections estimated to be 10⁻¹³ to 10⁻¹⁷ cm² for each channel. While the electron temperature is not well defined under EXCEDE conditions, during the beam irradiation a thermal electron effective temperature of many thousand °K is probable, leading to a dissociative attachment rate constant as large as 10⁻⁹ cm³ sec⁻¹. With an average electron density, nₑ, of order 10⁶ cm⁻³ for EXCEDE beam on conditions at 100 km, ambient O₃ will not be destroyed during the beam duration since the rate for O₃ destruction can be estimated as:

\[ R_{O₃} = k [e] \times 10^{-9} \times 10^6 = 10^{-3} \text{ sec}^{-1} \]

However, since quantitative inelastic excitation cross sections for O₃ are not available the ratio of effective vibrational excitation to dissociative attachment cross sections is not known. Electron energy loss spectra for O₃ do show considerable structure in the 1.2 to 2.5 eV range which is predominantly associated with known O₃ excited electronic states; while electron transmission intensity derivative measurements have indicated clear vibrational structure for an O₃⁻ transition in the 0.9 to 1.8 eV range. Unfortunately none of these experiments give any measure of absolute vibrational excitation cross sections for inelastic electron scattering.

In summary there is some possibility that below 100 km, where night time ambient O₃ may exceed 10⁸ cm⁻³, sufficient O₃(v) may be excited by direct electron impact and survive dissociative excitation to be observable. However, in the absence of quantitative e/O₃ inelastic excitation cross section measurements it is difficult to predict the amount of O₃(v) which might be produced.

3.2.2 E-V Excitation of Ozone

Ambient O₃ vibrational excitation can also occur, in principle, with each of the metastable electronic species listed in Table 2-2. However, the
weakness of the O₂-O bond in O₃(-1 eV) compared to the excitation energy of these species leads to the prediction that their quenching by O₃ will generally result in O₃ dissociation:

\[ \text{O}_3 + M^* \rightarrow \text{O}_2 + O + M \]

rather than production of O₃(v). The energy mismatch between the metastable excitation energies of N₂(A), O(¹S), O(¹D), O₂(A,A' and c) and CO(a) are all clearly too large to expect O₃(v) production. Only O₂(b) with a total electronic energy of 1.64 eV (only 0.66 eV above O₂(a)) and O₂(a) at 0.98 eV may be capable of vibrationally exciting O₃ without dissociating it at the same time.

Laboratory investigations of O₃ quenching of O₂(b) and O₂(a) give some indication of the likelihood that these processes lead to O₃(v). Several measurements of the O₂(b) quenching rate constant by O₃ give values near 2 x 10⁻¹¹ cm³ sec⁻¹ [52-54] with an O₃ dissociation fraction in the range of 0.6 to 0.7 [53,54]. Thus, O₃ does effectively deactivate O₂(b) and about one third of the O₃ survives the collision.

The degree of O₃ vibrational excitation in the O₃ which survives O₂(b) quenching collisions is unknown. However, an upper limit, in terms of the ion pair creation energy can be estimated by noting that: 1) no more than 0.6 of the O₂(b) excitation energy can be transferred to O₃ without dissociating the receiving ozone, 2) that approximately one third of the O₃/O₂(b) collisions do not dissociate the O₃, 3) our estimate from subsection 2.2.4 that a limit to the fraction of the ion pair creation energy flowing through O₂(b) is -0.01 and again from subsection 2.2.4, that the O₂(b) dominant quenching process, radiative decay, has a rate of 8.3 x 10⁻² sec⁻¹ while quenching by N₂ at 100 km proceeds at a rate of 2.2 x 10⁻² sec⁻¹. From Figure 2-2 we estimate a 100 km O₃ abundance of 10⁸ cm⁻³, thus the O₃ quenching rate for O₂(b) at 100 km is:

\[ Q = k[O₃] = 2 \times 10^{-11} \times 10^8 = 2 \times 10^{-3} \text{ sec}^{-1} \]
or 2\% of the combined radiative and \text{N}_2 quenching decay rates at 100 km.

Thus, an upper limit for the fraction of the ion pair creation energy which can flow into \text{O}_3(v) at 100 km can be estimated as the \text{O}_2(b) energy fraction, times the percentage of \text{O}_2(b) quenched by \text{O}_3, times the fraction of quenching collisions in which \text{O}_3 survives, times the fraction of the \text{O}_2(b) excitation energy which can be deposited into \text{O}_3(v) without \text{O}_3 dissociation; or $0.01 \times 0.02 \times 0.67 \times 0.6 = 8 \times 10^{-5}$. This is a significant upper limit for \text{O}_3(v) production from \text{O}_2(b) and may well be observable. It will decay with a time scale characteristic of \text{O}_2(b) radiative decay rate plus collisional quenching by \text{N}_2. As noted above at 100 km this rate is $(8.3 + 2.2) \times 10^{-2}$ $= 0.1$ s$^{-1}$ giving it a characteristic time scale of 10 s at 100 km.

On the other hand, the quenching rate for \text{O}_2(a) by \text{O}_3 is very slow, as it is for most other gases. At 300°K a quenching rate constant of $3 \times 10^{-15}$ cm$^3$ sec$^{-1}$ has been measured$^{55-57}$ but temperature dependent experiments$^{56-57}$ indicate that the appropriate rate to use for the 200°K temperature typically found at 100 km is $4 \times 10^{-17}$ cm$^3$ sec$^{-1}$, leading to a \text{O}_2(a) quenching rate by \text{O}_3 at 200 km of

$$Q_{03} = k_{03} [\text{O}_3] = 4 \times 10^{-17} \times 10^8 = 4 \times 10^{-9} \text{ sec}^{-1}$$

This compares with the \text{O}_2 quenching rate which is $10^3$ times faster:

$$Q_{02} = k_{02} [\text{O}_2] = 2 \times 10^{-18} \times 2 \times 10^{12} = 4 \times 10^{-6} \text{ sec}^{-1}$$

Furthermore, it is suspected that most of the measured \text{O}_2(a) quenching reactions with \text{O}_3 lead to dissociation of \text{O}_3.$^{55-57}$

In any event, since we concluded in subsection 2.2.4 that no more than a few percent of the ion pair creation energy can pass through \text{O}_2(a) and since only about $10^{-3}$ of the \text{O}_2(a) is quenched by \text{O}_3 we can conclude that the upper limit for \text{O}_3(v) creation in the quenching of \text{O}_2(a) is few times $10^{-5}$ of the
ion pair creation energy. When the fact that O₃ dissociation is believed to be the major product channel for O₂(a) quenching is added to the very slow transfer rate it is clear O₂(a) cannot produce observable O₃(v) under EXCEDE conditions.

3.2.3 V+V Excitation of O₃(v)

As explored in subsection 2.2.3, a considerable fraction, -2.4 × 10⁻⁴, of the ion pair creation energy is deposited in N₂(v) under EXCEDE conditions. However, since rate constants for even near resonant V-V transfer processes are small, this energy must be channeled into infrared active trace species vibrational modes like CO(v) and O₃(v) over very long time scales. A smaller fraction of the ion pair creation energy (<10⁻⁸) can be expected to be deposited in O₂(v).

Ozone is an unpleasant laboratory chemical, and very few laboratory vibrational quenching experiments have been reported for O₃ as a reactant. We are not aware of any V+V transfer measurements for either N₂(v) or O₂(v) by O₃. However, based on similar nonresonant systems such as O₂(v) transferring to CO₂(v) we doubt that V-V quenching rate constants for N₂(v) and O₂(v) by O₃ in the 200-300 K temperature range exceed 10⁻¹⁴ cm³ sec⁻¹. Assuming this 10⁻¹⁴ upper limit we can calculate the fastest time scales for V+V transfer from O₂(v) and N₂(v) to O₃ as = kV+V x [O₃] or 10⁻¹⁴ cm³ sec⁻¹ x 10⁸ cm⁻³ = 10⁻⁶ sec⁻¹ at 100 km. Thus, the transfer rate from N₂(v) or O₂(v) to O₃ has a probable time scale no shorter than 10⁶ seconds or 11.6 days. Thus, no observable enhancement of O₃(v) can be expected from V+V transfer under EXCEDE experimental conditions.

3.3 Chemical Production of O₃(v)

Above 100 km ambient O₃ drops to negligible levels and observable levels of O₃(v) must be formed in a chemical reaction.

The most common atmospheric source of O₃(v) is chemiluminescent production in the recombination formation reaction:
Numerous laboratory experiments have demonstrated that this reaction is an efficient source of \( O_3(v) \).\textsuperscript{58-60}

However, we do not expect this reaction to contribute to the \( O_3(v) \) spectrum under EXCEDE conditions because there is negligible enhancement of either \( O \) or \( O_2 \) caused by the electron irradiation process, and because the rate of \( O \) recombination with \( O_2 \) has an extremely long time scale, calculable from the \( O \) recombination rate at 100 km as:

\[
R_0 + O_2 + M = k_0 + O_2 + M [O_2] [M]
\]

\[
= 6.0 \times 10^{-3} \left( \frac{200}{300} \right)^{2.3} \text{ cm}^6 \text{ sec}^{-1} \times 2 \times 10^{12} \text{ cm}^3 \times 1.2 \times 10^{13} \text{ cm}^3
\]

\[
= 3.7 \times 10^{-8} \text{ sec}^{-1}
\]

Thus, the time scale for \( O \) atom recombination is over \( 10^7 \) sec. at 100 km.

Clearly if an infrared chemiluminescent source of \( O_3(v) \) is to be operative on EXCEDE experimental time scales it must involve a two body process. Any three body processes, involving either ground state or excited \( O \) and \( O_2 \) will have a time scale for too long to be observable under EXCEDE conditions.

We have identified one possible bimolecular source of \( O_3(v) \), the reaction of \( O_2 \) with the \( O_2^* \) 4.5-5 eV states:

\[
O_2^*(A, A' \text{ or } c) + O_2 + O_3(v) + 0
\]

As noted in the introduction, laboratory experiments reported by Kenner and Ogryzlo in Reference 6 strongly indicate that at least one of the \( O_2 \) 4.5-5 eV states can react with \( O_2 \) to produce \( O_3(v) \).
Also, as reported by us in References 4 and 5, analysis of PRECEDE data indicates that as much as 6% of the beam deposition energy may result in $O_2^*$ production. Furthermore, as discussed in subsection 2.2.4 both intrinsic radiative quenching and physical quenching of these states by atmospheric species is slow enough to allow them ample opportunity to react with ambient ground state $O_2$.

At the present time we have little quantitative rate information for this proposed source of $O_3(v)$, however the work reported in Reference 6 indicates a $O_2^* + O_2$ rate constant between $10^{-12}$ and $10^{-14}$ cm$^3$ sec$^{-1}$. Adopting a relatively small value of $3 \times 10^{-14}$ cm$^3$ sec$^{-1}$ gives an $O_3(v)$ production rate at 100 km of:

$$R_{O_2} = k_{O_2^*} \times [O_2] = 3 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1} \times 2 \times 10^{12} \text{ cm}^{-3} = 0.06 \text{ sec}^{-1}$$

Thus, $O_3(v)$ production rate is slower than the $O_2(A)$ radiative quenching rate by about a factor of 80 but comparable with the $O_2(A')$ or $O_2(c)$ radiative or collisional quenching rate. This rate estimate would give ~17 second time scale for the release of the copious $O_2^*$ energy into $O_3(v)$ which may well be observable by properly designed EXCEDE experiments. The choice of the $3 \times 10^{-14}$ cm$^3$ sec$^{-1}$ reaction rate constant for $O_2^*$ with $O_2$ is consistent with the measured quenching rate for $O_2(c)$ by $O_2$ and with our analysis identifying $O_2^*$ as the PRECEDE long lived visible radiator. However, it should be remembered that the $O_2^* + O_2$ rate constant is very uncertain and the actual time scale may be a factor of 10 or 100 faster. Up to 20% (-1 eV) of the $O_2^*$ energy can be transferred into $O_3(v)$, so that as much as $0.2 \times 0.06 = 1.2 \times 10^{-2}$ of the beam deposition energy could appear in $O_3(v)$ at 100 km.

It should also be noted that current photochemical theory badly under-predicts $O_3$ densities above 100 km and an additional $O_3$ production mechanism such as $O_2^* + O_2$ which is not included in current theory seems to be necessary to cure this deficiency.
4. CONCLUSIONS

4.1 CO(v) Production Yields and Time Scales

The initial production of CO(v) is dominated by direct electron impact on CO. At 100 km this source represents about 4.5 x 10^{-5} of the ion pair production energy and after beam termination decays with a time constant characteristic of the CO radiative decay (28.3 msec for v = 1). This source may be noticeably enhanced by additional prompt CO(v) created by O(D) quenching.

On the time scale of tenths of seconds to tens of seconds after beam termination it is possible that E+V transfer from N_2(A) and/or two of the O_2 4.5 - 5 eV states (A', c) may contribute to the CO(v) signal, however definitive predictions for these processes require better knowledge of CO(v) specific quenching cross sections for N_2(A) and O_2(A', c) by CO and for CO(a) by N_2, O_2, and O.

Finally, on the time scale of minutes to tens of minutes, a long-lived, low-level and slowly decaying (~10 minute) source of CO(v) will be produced from V+V exchange with N_2(v).

4.2 O_3 Excitation Mechanisms

Below 100 km, excitation of ambient O_3 either by direct electron impact or by O_2(b 1Σ) quenching may lead to observable O_3(v_3) emission on EXCEDE experimental time scales. These sources will be produced promptly and decay with the O_3(v) radiative v_3 lifetime of 92.7 msec.

A more important source of O_3(v) operative at all altitudes of interest is the reaction of electron-excited O_2* 4.5 - 5 eV states with ambient O_2. This source of O_3(v) may involve as much as one percent of the ion pair creation energy, it will most likely be created with a time constant of between 5 and 50 seconds and decay on a similar time scale.
This page intentionally left blank.
REFERENCES


35. L.G. Piper, "The Excitation of O($^1S$) in the Reaction Between N$_2$(A $^3\Sigma_u^+$) and O($^2P$)", J. Chem. Phys. 77, 2373 (1982).


37. R.G. Shortridge and M.C. Lin, "The Dynamics of the O($^1D_2$) + CO (x $^1\Sigma^+$, V = 0) Reaction", J. Chem. Phys. 64, 4076-4085 (1984).


39. R.D. Kenner and E.A. Ogryzlo, "Quenching of O$_2$ (c $^1\Sigma^-$) V = 0 by O($^3P$), O$_2$(a $^1\Delta g$) and Other Gases", Can. J. Chem. 61, 921-926 (1983).


54. T.G. Slanger and G. Black, "Interactions of $O_2(b^1\Delta_g)$ with $O(3\text{P})$ and $O_3$", J. Chem. Phys. 70, 3434-3438 (1979).


56. F.D. Findlay and D.R. Snelling, "Temperature Dependence of the Rate Constant for the Reaction $O_2(1\Delta_g) + O_3 \rightarrow 2O_2 + O$", J. Chem. Phys. 54, 2350-2355 (1971).


