EVALUATION OF CO RELEASES TO DETERMINE ATMOSPHERIC N₂ VIBRATIONAL POPULATION

Morton Camac
Utah State University

Prepared for:
Air Force Cambridge Research Laboratories
Defense Advanced Research Projects Agency
April 1973
EVALUATION OF CO RELEASES TO DETERMINE
ATMOSPHERIC N₂ VIBRATIONAL POPULATION

by

Morton Camac*

Electro-Dynamics Laboratory
Utah State University
Logan, Utah 84321

Contract No. F19628-70-C-0289
Project No. 8692

Special Scientific Report
April 1973

* Aerodyne Research, Inc.
Northwest Industrial Park
Burlington, Massachusetts 01803

Contract Monitor: Dean F. Kimball
Optical Physics Laboratory

Approved for public release; distribution unlimited.

Sponsored by
Defense Advanced Research Projects Agency
ARPA Order No. 1365

Monitored by
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS 01730

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield, VA 22151
ARPA Order No. 1366
Program Code No. 2E50
Contractor: Utah State University
Effective Date of Contract: 1 June 1970

Contract No. F19628-70-C-0289.
Principal Investigator and Phone No.
Dr. Doran J. Baker/801 752-4100
AFCRL Project Scientist and Phone No.
Dean F. Kimball/617 861-3204
Contract Expiration Date: 30 April 1974

Qualified requestors may obtain additional copies from the Defense Documentation Center. All others should apply to the National Technical Information Service.
EVALUATION OF CO RELEASES TO DETERMINE ATMOSPHERIC N₂ VIBRATIONAL POPULATION

This paper evaluates the use of gaseous CO releases at high altitudes to determine the atmospheric N₂ vibrational temperature. Since vibrational energy transfer from N₂ to CO leads to CO infrared emission in the 4.7-micron fundamental band and 2.4-micron overtone band, CO infrared intensity measurements might be used to obtain the vibrational temperature.

One result of these predictions is that CO emission intensity in the 2.4-micron band will be low due to radiation cooling of the first CO vibration level. The second CO vibration level (the main 2.4-micron source) can be populated by either one or two collisions with vibrationally excited N₂. The two-collision process populates the first and then the second CO vibrational level. The transfer to the second level in two-collision processes is suppressed due to 4.7-micron radiation from the first level. Excitation of the second level is predominantly by the weaker single-step process involving a two-vibration quantum transfer from N₂ to CO. The slow rate for the two-quantum transfer process makes observation of the overtone radiation emission difficult.

Emission in the 4.7-micron band is not affected by radiation cooling. However, for a ground-based platform, 4.7-micron radiation is severely attenuated by the atmosphere. Since this attenuation becomes negligible above about 12 km, an airborne platform should be used to make observations of the 4.7-micron radiation.

This experiment would be severely limited by additional CO emission that is excited by other sources, particularly sun and earthshine. Emission due to sunshine sets the daytime lower limit to the detectable N₂ transfer rate to CO. Earthshine sets the nighttime lower limit. N₂ transfer rate measurements are marginal at the predicted N₂ vibrational temperature.
<table>
<thead>
<tr>
<th>KEY WORDS</th>
<th>LINK A</th>
<th>LINK B</th>
<th>LINK C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Atmosphere Chemistry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO-N₂ Vibration Coupling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO Infrared Atmospheric Transmission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂ Vibrational Energy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper Atmospheric Gaseous Release</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ABSTRACT

This paper evaluates the use of gaseous CO releases at high altitudes to determine the atmospheric $N_2$ vibrational temperature. Since vibrational energy transfer from $N_2$ to CO leads to CO infrared emission in the 4.7-micron fundamental band and 2.4-micron overtone band, CO infrared intensity measurements might be used to obtain the vibrational temperature.

One result of these predictions is that CO emission intensity in the 2.4-micron band will be low due to radiation cooling of the first CO vibration level. The second CO vibration level (the main 2.4-micron source) can be populated by either one or two collisions with vibrationally excited $N_2$. The two-collision process populates the first and then the second CO vibrational level. The transfer to the second level in two-collision processes is suppressed due to 4.7-micron radiation from the first level. Excitation of the second level is predominantly by the weaker single-step process involving a two-vibration quantum transfer from $N_2$ to CO. The slow rate for the two-quantum transfer process makes observation of the overtone radiation emission difficult.

Emission in the 4.7-micron band is not affected by radiation cooling. However, for a ground-based platform, 4.7-micron radiation is severely attenuated by the atmosphere. Since this attenuation becomes negligible above about 12 km, an airborne platform should be used to make observations of the 4.7-micron radiation.

This experiment would be severely limited by additional CO emission that is excited by other sources, particularly sun and earthshine. Emission due to sunshine sets the daytime lower limit to the detectable $N_2$ transfer rate to CO. Earthshine sets the nighttime lower limit. $N_2$ transfer rate measurements are marginal at the predicted $N_2$ vibrational temperature.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2 THEORY OF EXPERIMENT</td>
<td>3</td>
</tr>
<tr>
<td>3 DEPENDENCE OF MEASURED INTENSITY ON SENSOR ALTITUDE</td>
<td>21</td>
</tr>
<tr>
<td>3.1 Atmospheric Absorption of CO Infrared Radiation</td>
<td>23</td>
</tr>
<tr>
<td>3.2 Signal-to-Noise Ratio for Airborne Optical System</td>
<td>24</td>
</tr>
<tr>
<td>4 SUMMARY</td>
<td>27</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>29</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS

Figure | Description                                                                 | Page
-------|-----------------------------------------------------------------------------|------
1      | THE NITROGEN VIBRATIONAL TEMPERATURE IN THE ATMOSPHERE                     | 2    
2      | CO CLOUD RELEASE                                                           | 4    
3      | ENERGY LEVEL DIAGRAM FOR CO MOLECULE SHOWING INFRARED BANDS                | 7    
4      | CO INFRARED EMISSION FROM CLOUD CENTER                                     | 12   
5      | TOTAL EMISSION FROM CLOUD                                                  | 13   
6      | RADIATION INTENSITY AT 110 KILOMETERS FROM CLOUD                           | 14   
7      | ATMOSPHERIC TEMPERATURE AND CONSTITUENTS                                   | 16   
8      | I(h) IS THE 4.7μ EMISSION FROM AN OPTICAL PATH THROUGH THE CLOUD. L0 IS THE CLOUD EMISSION AT 110 KM (ALTITUDE) AND 550°K (N2 VIBRATIONAL TEMPERATURE). L0=1.4 X 10^-13 AND 1.4 X 10^-22 WATTS/CM² FOR 10^-5 AND 10^-4 STERADIAN OPTICAL SYSTEMS, RESPECTIVELY, 110 KILOMETERS FROM THE CLOUD. | 17   
9      | CLOUD DIMENSIONS 100 SEC AFTER A 10 KG RELEASE AT 110 KM ALTITUDE. VIEWING GEOMETRY OF A 10^-5 OPTICAL SYSTEM | 22   
10     | ATMOSPHERIC CO CONCENTRATION AND MIXING RATIO, TAKEN FROM REF. 15.          | 25   
11     | ATMOSPHERIC TRANSMISSION OF CO4.7μ RADIATION VS. ROTATIONAL LINE FOR OBSERVER ON GROUND AND AT 12 KM. ROTATIONAL EMISSION SPECTRA [I(j)/ΣI(j)] FROM CLOUD AT 150 KM (700°K), 130 KM (500°K) AND 110 KM (230°K) ALTITUDE. | 26   
SECTION 1
INTRODUCTION

A variety of gaseous releases at high altitudes have been used to furnish information about the atmosphere. For example, the concentration of some atmospheric constituents,\(^1,\(^2\) electric fields,\(^3,\(^4\) and wind patterns\(^5\) have been determined. It has been suggested\(^6,\(^7\) that a gaseous CO release could be used to measure the \(N_2\) vibrational temperature in the upper atmosphere. Vibrationally excited nitrogen could provide a substantial source of latent energy, and its magnitude, therefore, is of considerable interest. \(N_2\) vibrational excitation could be of importance in E-layer chemistry. Figure 1 shows nitrogen vibrational temperature measurements made by O’Neil\(^8\) using rocket-borne electron-beam probes. Theoretical calculations of Breig, Brennan and McNeal are also shown.\(^9\) The measured nitrogen vibrational temperature is near the maximum theoretical curve. In a CO release, the CO would become excited in collisions with vibrationally excited atmospheric \(N_2\). Observations could be made of the fundamental at 4.7 microns and of the overtone at 2.4 microns.

In this report, the CO emission is calculated as a function of the nitrogen vibrational temperature. The major difference between laboratory measurements\(^10\) of CO 2.4-micron emission and the predictions for high-altitude atmospheric releases, at much lower pressures, is the severe collision-limiting effect. For example, at 110 km, the pressure is approximately \(10^{-4}\) torr and the CO infrared lifetime is much shorter than the collisional transfer times. It is predicted that the 2.4-micron emission will be reduced by several orders of magnitude from the equilibrium level.

Collision limiting reduces the emission from the overtone radiation at high altitudes. This effect (illustrated for CO in this report) would also exist for other infrared harmonic radiation.
FIGURE 1. THE NITROGEN VIBRATIONAL TEMPERATURE IN THE ATMOSPHERE.

Solid curves: maximum and minimum theoretical temperatures.  
Dashed curve: upper limit measurement.
SECTION 2
THEORY OF EXPERIMENT

The proposed CO release experiment should determine the N$_2$ vibrational temperature. To evaluate the feasibility of determining the N$_2$ vibrational temperature, several factors must be considered. These include: (1) CO storage and rapid release, (2) the drop in CO temperature during the expansion to low pressure, (3) the interdiffusion of CO and the atmosphere, (4) vibration transfer processes leading to CO infrared emission, (5) sun and earthshine excitation of CO emission, and (6) atmospheric transmission. A detailed analysis and calculation is beyond the scope of this study. Our objective is to evaluate the importance of each of these items and to estimate the CO signal levels from the various excitation modes.

During a period of up to several seconds after the release, the CO aerodynamics is involved with pressure and rarefaction waves and it is difficult to describe the CO/air interface surface and temperature distribution. The temperature is required to calculate the vibrational excitation rates. Diffusion processes at the interface mix the air with the spherically-shaped CO cloud. Where CO and air mix, the dominant process is vibrational exchange between the vibrationally excited N$_2$ and CO. The diffusion rate increases with altitude, while the vibration transfer rate decreases with altitude. At low altitudes, the N$_2$/CO vibration transfer rate is faster than diffusion; that is, diffusion is the rate-limiting step. Vibrational energy transfer to CO takes place in the outer regions and there is no excited N$_2$ inside the shell. On the other hand, at high altitudes, the vibrational transfer rate is slower than the diffusion rate and vibrationally-excited N$_2$ can diffuse to the center of the CO cloud without appreciable deactivation. The crossover from diffusion to vibration-transfer limiting is between 110 to 120 km altitude for large CO releases.

In addition to vibrational excitation in collisions with N$_2$, CO can be excited by sun and earthshine absorption in the 4.7 and 2.4-micron bands. Similar CO infrared emission spectra would follow either excitation process, radiation absorption
or excitation by N₂. This severely limits the range of atmospheric conditions over which useful data on the N₂ vibrational excitation can be obtained.

Since this experiment has several limitations, a detailed analysis, including the CO expansion and followed by the coupled diffusion/vibrational processes, is not warranted. To identify the various processes that take place and evaluate their importance, a specific example, a low altitude release at 110 km, is chosen. The results are then extended to 180 km.

Consider a fairly large CO release experiment: 10 kg (2 x 10²⁶ molecules) of gaseous CO at 110 km altitude. Figure 2 shows the growth of the CO cloud as a function of time starting from an initial radius of approximately 0.27 km. After 100 seconds, approximately the time required for the atmospheric gases to diffuse through the CO and reach the center of the cloud, the cloud expands to a radius of 0.49 km. As the atmospheric gases mix with the CO, vibrational energy exchange between N₂ and CO occurs.

![Figure 2. CO Cloud Release](image-url)
The concentrations of the major atmospheric constituents at 110 km are:

\[
\begin{align*}
\left[H_2\right] &= 2 \times 10^{12} \text{ cm}^3 \\
\left[O_2\right] &= 4 \times 10^{11} \text{ cm}^3 \\
\left[O\right] &= 3 \times 10^{11} \text{ cm}^3 \\
\text{total density} &= 2.7 \times 10^{12} \text{ cm}^3
\end{align*}
\]  

The mean temperature is 270°K. If the \(2 \times 10^{26}\) CO molecules are distributed uniformly over a cloud of 1/2 km radius, the species concentration in the cloud becomes

\[
\begin{align*}
\left[N_2\right] &= 1.7 \times 10^{12} \text{ cm}^3 \\
\left[O_2\right] &= 3.4 \times 10^{11} \text{ cm}^3 \\
\left[CO\right] &= 4.0 \times 10^{11} \text{ cm}^3 \\
\left[O\right] &= 2.6 \times 10^{11} \text{ cm}^3 \\
\text{total density} &= 2.7 \times 10^{12} \text{ cm}^3
\end{align*}
\]

The four main reactions transferring vibrational energy from \(N_2\) to \(CO\) are:\textsuperscript{11,12}

\[
\begin{align*}
N_2(1) + CO(0) &\rightarrow N_2(0) + CO(1) & k_1 &= 3 \times 10^{-14} \text{ cm}^3/\text{sec} \\
N_2(1) + CO(1) &\rightarrow N_2(0) + CO(2) & k_2 &= 3 \times 10^{-14} \text{ cm}^3/\text{sec} \\
CO(1) + CO(1) &\rightarrow CO(0) + CO(2) & k_3 &= 3 \times 10^{-12} \text{ cm}^3/\text{sec} \\
N_2(2) + CO(0) &\rightarrow N_2(0) + CO(2) & k_4 &= 10^{-16} \text{ cm}^3/\text{sec}
\end{align*}
\]
\( N_2(0), N_2(1), N_2(2), \text{CO}(0), \text{CO}(1), \text{and CO}(2) \) indicate \( N_2 \) and CO molecules in
the ground, first, and second vibration levels. For an \( N_2 \) vibrational temperature, \( T_v \), the vibrational excitation is

\[
\frac{[N_2(1)]}{[N_2(0)]} = e^{-\frac{3300^{\circ}K}{T_v}},
\]

\[
\frac{[N_2(2)]}{[N_2(0)]} = e^{-\frac{6600^{\circ}K}{T_v}}.
\]

The higher vibration levels are not included here, as they are not important. The radiation emissions at 4.7 and 2.4 microns are

\[
I_{4.7 \mu} = \frac{[\text{CO}(1)]}{\tau_{4.7}} + 2 \frac{[\text{CO}(2)]}{\tau_{4.7}} \quad \tau_{4.7} = 0.033 \text{ sec}
\]

\[
I_{2.4 \mu} = \frac{[\text{CO}(2)]}{\tau_{2.4}} \quad \tau_{2.4} = 0.7 \text{ sec}
\]

These radiative transitions are shown schematically in Figure 3. The radiation lifetimes for the 4.7 and 2.4 micron bands are 0.033 and 0.7 seconds, respectively. These lifetimes differ by a factor of 20 which reduces the 2.4 micron radiation as shown below. The time \( \tau_{N_2} \) to remove a substantial amount of vibrational energy from the air via reaction (3a) is

\[
\tau_{N_2} = - \frac{[N_2(1)]}{\frac{d[N_2(1)]}{dt}} = \frac{1}{k_1[\text{CO}]} = \frac{1}{(3 \times 10^{-14}) (4 \times 10^1)}
\]

\( = 83 \text{ Seconds} \).
Note that the \( N_2 \) depletion time is comparable to the 100 second diffusion time.

In order to evaluate the depletion of \( N_2 \) vibration under these conditions, a calculation coupling the diffusion and vibrational processes is required. The radial concentration profiles would be gaussian instead of the square shape specified in Equation (2). It is estimated that the \( N_2 \) vibration depletion is less than a factor of two over the entire cloud. The depletion is much less at higher altitudes and is neglected in this approximate analysis.

The kinetics for the production of CO(1) and CO(2) are

\[
d[\text{CO}(1)] / dt = k_1 [N_2(1)] [\text{CO}(0)] - \frac{[\text{CO}(1)]}{\tau_{4.7}}
- k_2 [N_2(1)] [\text{CO}(1)] - k_3 [\text{CO}(1)]^2
\]  

(8)
and

\[
\frac{d [CO(2)]}{dt} = k_2 [N_2(1)] [CO(1)] + k_3 [CO(1)]^2 \]

\[
+ k_4 [N_2(2)] [CO(0)] - k_3 [CO(2)] [CO(0)] - \frac{2 [CO(2)]_s s}{\tau_{4.7}} - \frac{[CO(2)]_s s}{\tau_{2.4}}.
\]  

(9)

The concentrations of CO(1) and CO(2) increase and reach steady-state levels on the order of the fastest loss time, which is \(\tau_{4.7} = 0.033\) second. Equations (8) and (9) can be solved easily in the steady-state approximation. Equation (8) becomes

\[
\frac{d [CO(1)]_{ss}}{dt} = 0 = k_1 [N_2(1)] [CO(0)] - [CO(1)]_{ss}/\tau_{4.7}.
\]  

(10)

The third and fourth terms in Equation (8) were neglected in this approximation since their values are less than 1% of the other terms in Equation (10). The steady-state approximation for CO(2) is obtained from Equation (9).

\[
\frac{d [CO(2)]_{ss}}{dt} = 0 = k_2 [N_2(1)] [CO(1)]_{ss} + k_3 [CO(1)]_{ss}^2 + 
\]

\[
+ k_4 [N_2(2)] [CO(0)] - 2 [CO(2)]_{ss}/\tau_{4.7}.
\]  

(11)

Substituting the expression for \([CO(1)]_{ss}\) into Equation (11) from Equation (10) and solving for \([CO(2)]_{ss}\)
\[
[\text{CO}(2)]_{ss} = \frac{1}{2} \tau_{4.7} \left( k_1 k_2 [\text{N}_2(1)]^2 [\text{CO}(0)] \tau_{4.7} +
\right.
\]
\[
+ k_3 k_1^2 [\text{N}_2(1)]^2 [\text{CO}(0)]^2 \tau_{4.7}^2 + k_4 [\text{N}_2(2)] [\text{CO}(0)] \right) .
\]

The CO radiation intensity in the 4.7 and 2.4 micron bands can be expressed in terms of the steady-state concentrations. Equations (5) and (6) become

\[
I_{4.7\mu} = \frac{[\text{CO}(1)]_{ss}}{\tau_{4.7}} = k_1 [\text{N}_2(0)] [\text{CO}(0)] e^{-3300^\circ K/T_v}
\]

\[
I_{2.4\mu} = \frac{[\text{CO}(2)]_{ss}}{\tau_{2.4}} = \frac{\tau_{4.7}}{2\tau_{2.4}} [\text{N}_2(0)] [\text{CO}(0)] .
\]

\[
. \left( k_1 k_2 [\text{N}_2(0)] \tau_{4.7} + k_3 k_1^2 [\text{N}_2(0)] [\text{CO}(0)] \tau_{4.7}^2 + k_4 \right) e^{-6600^\circ K/T_v}.
\]

Inserting numerical values for the concentrations at 110 km altitude and 100 seconds after the release, Equations (13) and (14) become

\[
I_{4.7\mu} = \left( 3 \times 10^{-14} \right) \left( 1.7 \times 10^{12} \right) \left( 4 \times 10^{11} \right) e^{-3300^\circ K/T_v}
\]

\[
= 2.0 \times 10^{10} \ e^{-3300^\circ K/T_v} \text{ photons/cc-sec}
\]
\[ I_{2.4\mu} = \frac{0.33}{2(0.66)} (1.7 \times 10^{12}) (4 \times 10^{11}) \]

\[ \cdot \left( 9 \times 10^{-28} \cdot 1.7 \times 10^{12} \cdot \frac{1}{30} + 9 \times 10^{-28} \times 3 \times 10^{-12} \times 1.7 \right. \]

\[ \times 10^{12} \times 4 \times 10^{11} \left( \frac{1}{30^2} + 10^{-16} \right) \]

\[ \times (-6600^oK/T_v)^{-1} \]  \hspace{1cm} (16)

\[ = (9.0 \times 10^5 + 3.5 \times 10^4 + 1.7 \times 10^6) e^{-6600^oK/T_v} \]

\[ = 2.6 \times 10^6 e^{-6600^oK/T_v} \] photons/cc-sec .

For the entire cloud of \( 2 \times 10^{26} \) CO molecules, the intensity becomes

at \( 4.7\mu \): \( \frac{3300^oK/T_v}{10^{25}} \) e photons/sec  \hspace{1cm} (17)

at \( 2.4\mu \): \( \frac{6600^oK/T_v}{10^{21}} \) e photons/sec  .

Total radiation from a cloud illuminating an area of one \( \text{cm}^2 \) at a distance of \( 110 \text{km} \), is

\[ S_{4.7} = I_{4.7} \left( 5 \times 10^{14} \right) \left( \frac{1.24/4.7}{1.1 \times 10^7} \right) \left( \frac{1.6 \times 10^{-19}}{4\pi} \right) \]

\[ = 2.8 \times 10^{-10} e^{-3300^oK/T_v} \text{ watts/cm}^2 \]  \hspace{1cm} (18)

\[ S_{2.4} = I_{2.4} \left( 5 \times 10^{14} \right) \left( \frac{1.24/2.4}{1.1 \times 10^7} \right) \left( \frac{1.6 \times 10^{-19}}{4\pi} \right) \]

\[ = 7.1 \times 10^{-14} e^{-6600^oK/T_v} \text{ watts/cm}^2 . \]
Figures 4, 5, and 6 present the emission intensity vs. temperature. Figure 4 shows the emission per cm$^3$ using Equations (15) and (16). Figure 5 shows the emission from the entire cloud using Equation (17). Figure 6 gives the illumination in watts/cm$^2$ at a distance of 110 km using Equation (18). It should be noted that the 4.7 micron emission is approximately five orders of magnitude greater than the 2.4 micron overtone radiation. This large difference is due to the nonequilibrium effect.

In equilibrium, the ratio of these two intensities becomes

$$\frac{I_{4.7}}{I_{2.4}}_{\text{equil}} = \frac{[CO(1)]_{\text{equil}}}{[CO(2)]_{\text{equil}}/I_{2.4}} = 20 \times \frac{3000^\circ K}{T_v}$$

which varies between 400 and 55 over the temperature range of 1000$^\circ$ to 3000$^\circ$K. The ratio including nonequilibrium effects is obtained from the ratio of Equations (13) and (14)

$$\frac{I_{4.7}}{I_{2.4}}_{\text{nonequil}} = \left(\frac{2k_1}{k_4}\right) e^{3300^\circ K/T_v} = 20 \times (600) \times e^{3300^\circ K/T_v}$$

The nonequilibrium radiation cooling effect reduces the overtone radiation by almost three orders of magnitude.

At 110 km, the main reaction contributing to the overtone radiation is the single step with a two-vibration-level jump, Reaction (3d). Thus the ratio of 4.7$\mu$ to 2.4$\mu$ intensities remains constant with altitude above about 110 km.

The variation of the 4.7 micron radiation emission as a function of altitude can be determined with the use of Equation (13). The $N_2$ concentration with
TIME AFTER RELEASE = 100 SECONDS
CO RELEASE = 10 KILOGRAMS
ALTITUDE = 110 KILOMETERS

FIGURE 4. CO INFRARED EMISSION FROM CLOUD CENTER
CO RELEASE = 16 KILOGRAMS
TIME AFTER RELEASE = 100 SECONDS
ALTITUDE = 110 KILOMETERS

FIGURE 5. TOTAL EMISSION FROM CLOUD
FIGURE 6. RADIATION INTENSITY AT 110 KILOMETERS FROM CLOUD
altitude is shown in Figure 7. Note that it drops by a factor of about 100 from 110 to 150 km altitude. The maximum intensity occurs when the CO concentration is comparable to the N₂, and at these conditions, the intensity varies with the square of the ambient density. This drop in intensity is compensated by the increase in N₂ vibrational temperature. For example, going from 550°K to 1500°K increases the fractional excited state population by a factor of 45. For a fixed number of molecules released, the optical path length is inversely proportional to the cube root of the ambient density. If the measurements are made when the N₂ and the CO concentrations are comparable, the 4.7 micron intensity has the following scaling law for the central portion of the cloud:

\[
\frac{I(h)}{I(110 \text{ km})} = \left( \frac{[N_2] \text{ at } h}{[N_2] \text{ at } 110 \text{ km}} \right)^{5/3} \exp \left( - \frac{3300°K}{T_v(h)} + \frac{3300°K}{T_v(110 \text{ km})} \right)
\]  

Equation (21) is plotted in Figure 8 as a function of altitude from 110 to 180 km using 550°K for the average T_v at 110 km and assuming unity atmospheric transmission. The two curves use predicted maximum and minimum T_v values (see Figure 1). There is a drop in intensity of about an order of magnitude between 110 and 150 km.

**CO Excitation by Absorbed Sun and Earthshine**

CO would absorb sun and earthshine in the 1.7 and 12.1 micron bands. An estimate of the amount of such excitation will be made and then compared to the N₂ excitation rate. The absorbed earthshine radiation per CO molecule, I_{es}, is given by the wavelength integral over the absorption band

\[
I_{es} = 2 \int_{\text{band}} I(\lambda) \mu(\lambda) \, d\lambda
\]

where I is the emission from the earth and \( \mu \) is the absorption coefficient. Since the wavelength interval over the band is small, Equation (22) can be approximated by the equation
FIGURE 7. ATMOSPHERIC TEMPERATURE AND CONSTITUENTS
FIGURE 8. \( I_0 \) is the 4.7\( \mu \)m emission from an optical path through the cloud. \( I_0 \) is the cloud emission at 110 km (altitude) and 5500 K (\( N_2 \) vibrational temperature). \( I_0 = 1.4 \times 10^{-13} \) and 1.4 \( \times 10^{-22} \) watts/cm\(^2\) for \( 10^{-5} \) and \( 10^{-4} \) steradian optical systems, respectively, 110 kilometers from the cloud (see Figure 6).
\[ I_{es} = 21 \int_{\text{band}} \mu(\lambda) \, d(\lambda) = 21S_0 \]  

Equation (23)

\( S_0 \), the integral band intensity, is \( 1.0 \times 10^{-17} \) and \( 6 \times 10^{-20} \) cm\(^2\)/cm-molecule for the 4.7 and 2.4 bands, respectively.\(^{13}\)

The earthshine intensity depends upon the temperature at the altitude from which the radiation arises, that is, from an optical depth into the atmosphere. In the 4.7\( \mu \) band, the atmosphere is opaque due to trace quantities of CO up to about 12 kilometers. In this altitude range the temperature of the atmosphere is around 230\(^{0}\)K. The atmosphere is transparent at 2.7\( \mu \) and the emission to the earth's surface is used. We shall assume an earth temperature of 275\(^{0}\)K. The corresponding black body emissions are \( 3 \times 10^{-5} \) and \( 8.5 \times 10^{-8} \) watts/cm\(^2\)-\( \mu \) at 4.7 and 2.4 microns, respectively. Inserting these values for \( I \) and \( S_0 \) into Equation (23), the CO excitation rates per molecule become

\[ \text{at } 4.7 \quad I_{es} = (2)(3 \times 10^{-5})(10^{-17})(\frac{(4.7)}{10^4})^2 \left( \frac{4.7}{1.24 \times 1.6 \times 10^{-19}} \right) \]

\[ = 3 \times 10^{-5} \text{ photons/sec-molecule} \]  

Equation (24)

\[ \text{at } 2.4 \quad I_{es} = (2)(8.5 \times 10^{-8})(6 \times 10^{-20}) \left( \frac{(2.4)}{10^4} \right)^2 \left( \frac{2.4}{1.24 \times 1.6 \times 10^{-19}} \right) \]

\[ = 6 \times 10^{-11} \text{ photons/sec-molecule} \]

The fourth bracket converts micron (wavelength) units to cm\(^{-1}\) (wave number) units, and the last bracket converts watts to photons per second.

The absorbed sunshine per CO molecule, \( I_{ss} \), is given by the wavelength integral over the absorption band.
\[ I_{ss} = \int_{\text{band}} I_s(\lambda)\mu(\lambda) \, d\lambda = I_s^S \]  \hspace{1cm} (25)

Solar flux outside the atmosphere is \(4.5 \times 10^{-4}\) and \(6.0 \times 10^{-3}\) watts/cm\(^2\)-\(\mu\) at 4.7 and 2.4 microns, respectively. Inserting these values for \(I_s\) into Equation (25), the CO excitation rates per molecule become

\[ I_{ss} = 2 \times 10^{-4} \text{ photons/sec-molecule at 4.7}\mu \]

\[ I_{ss} = 2 \times 10^{-6} \text{ photons/sec-molecule at 2.3}\mu \]

A direct comparison of CO excitation by sun and earthshine to vibration transfer from \(N_2\) are given by the ratios

\[ \frac{I_{ss}}{I_{es}} = \frac{I_s^S}{k_1 \left[ \frac{n_{S}}{N_{S}}(1) \right]} = \frac{I_s^S}{k_1 \left[ \frac{n_{S}}{N_{S}}(1) \right] e^{-33000K/T_V}} \]

at 4.7\mu

\[ \frac{I_{ss}}{I_{es}} = \frac{I_s^S}{k_4 \left[ \frac{n_{S}}{N_{S}}(1) \right] e^{-66000K/T_V}} \]

at 2.3\mu

(26)

Numerical values for the ratios in Equation (26) are obtained with the use of Equations (2), (3), (24) and (25). At 110 km altitude, the ratio is unity in Equation (26) at \(T_V = 450^0\)K for night (earthshine only) for either the 4.7 or 2.4 micron bands. For daytime conditions the ratio is unity at \(T_V = 600^0\)K and 1500\(^0\)K for the 4.7 and 2.4 micron bands.

The sun and earthshine contributions to the CO emission is presented in Figure 8 for the 4.7\mu band. Note that the sunshine severely limits the proposed experiment at low vibrational temperatures. The best altitude for performing the release is around 120 km, but even there the experiment appears marginal for the predicted maximum \(N_2\) vibrational temperatures.
SECTION 3
DEPENDENCE OF MEASURED INTENSITY ON SENSOR ALTITUDE

The infrared emission from the CO release can be measured using either ground-based or airborne optical systems. Two effects which severely limit the radiation to these platforms are: (1) collision limiting, and (2) atmospheric absorption.

Equation (18) gives the radiation from the entire cloud. Optical systems, in which the solid angle subtends (1) the entire cloud and (2) a narrow column of the cloud, are considered. At 110 km, the cloud (100 seconds after release) subtends a 9 milliradian arc to an observer on the ground directly below the cloud. The geometry of the measurements for a $10^{-5}$ steradian optical system is shown in Figure 9. For a small angular aperture, the volume observed by the detector is a cylinder with a diameter of $d$ km and $h \approx 1$ km. (In Figure 9, $d = 0.35$ km.) The irradiance at the optical system is:

$$[4.7\mu\text{ flux}] = I_{4.7} \left( \frac{\pi d^2 h}{4} \right) \left( \frac{\Omega}{4\pi} \right) (h\nu) \ T_A$$

$$= I_{4.7} \left( \frac{\pi 10^{15} d^2}{4} \right) T_A \left( \frac{1.24 \times 1.6 \times 10^{-19}}{4.7 \times 4\pi \times 1.21 \times 10^{14}} \right)$$

or

$$= 4.4 \left( 10^{-10} \right) d^2 \ T_A \ e^{-3300^\circ K/T_v} \ \text{watts/cm}^2$$

$$[2.4\mu\text{ flux}] = I_{2.4} \left( \frac{\pi 10^{15} d^2}{4} \right) T_A \left( \frac{1.24 \times 1.6 \times 10^{-19}}{2.4 \times 4\pi \times 1.21 \times 10^{14}} \right)$$

$$= 1.1 \left( 10^{-13} \right) d^2 \ T_A \ e^{-6600^\circ K/T_v} \ \text{watts/cm}^2$$
FIGURE 9. CLOUD DIMENSIONS 100 SEC AFTER A 10 KG RELEASE AT 110 KM ALTITUDE. VIEWING GEOMETRY OF A $10^{-5}$ OPTICAL SYSTEM.
$T_A$ is the atmospheric transmission. Figure 6 presents the irradiance at the detector for a 3.2 mr angular aperture and from the entire cloud, neglecting the atmospheric absorption (i.e., for $T_A = 1$). The 2.4-micron signal is small and would require a very sensitive detector. On the other hand, the 4.7-micron intensity could be easily detectable when $T_A$ is near unity. For ground-based platforms, the 4.7-micron radiation is severely attenuated by the atmosphere, as shown below.

3.1 Atmosphere Absorption of CO Infrared Radiation

The atmospheric absorption in the 4.7-micron band is mainly due to the atmospheric CO. Most of the absorption occurs at low altitudes where the spectral lines are collision broadened and have a Lorentz shape. The absorption coefficient at the center of each line becomes

$$
\mu = \left( \frac{S}{\alpha_0} \right) \left( \frac{T}{273^\circ K} \right)^{0.58}.
$$

(29)

where $S$ is the line strength; $\alpha_0$, the line width at sea level, is 0.05 cm$^{-1}$; and $T$ is the temperature in $^\circ$K. The line strength is dependent upon rotational population and is given by

$$
S = \Phi S_0 (1.44 B_e/T) (J + 1) \exp \left[ -1.44 B_e J (J + 1)/T \right].
$$

(30)

$B_e = 1.931$ cm$^{-1}$ is the rotational constant; $J$ is the rotation quantum number; and $\Phi$ is the mole fraction of CO. $S_0$ is equal to 261 cm$^{-2}$ atm$^{-1}$ for the 4.7 micron band and 1.65 cm$^{-2}$ atm$^{-1}$ for the 2.4-micron band. The absorption coefficient becomes

$$
\mu = \left( \frac{\Phi S_0}{\pi(0.05)} \right) \left( \frac{T}{273^\circ K} \right)^{0.58} \left( \frac{2.78^\circ K}{T} \right) (J + 1) \exp[-J(J+1)2.78^\circ K/T].
$$

(31)
The CO concentration in the atmosphere can vary from less than 50 to more than 100 parts per billion. Figure 10 presents a theoretical calculation of the CO concentration and mixing ratio as a function of altitude. $\phi$ is constant from sea level up to an altitude of 15 km. Above 15 km, two effects reduce the CO absorption at line center: $\phi$ decreases rapidly and $\mu$ (in Equation (29)) decreases due to doppler-broadening corrections.

The effect of atmospheric attenuation on the 4.7 micron radiation is illustrated in Figure 11. The attenuation affecting ground and aircraft observations is plotted as a function of the rotation quantum number, $J$. Also shown are the CO emission spectra at 110, 130, and 150 kilometers, at temperatures of 250°, 500°, and 700°K, respectively. The areas under the emission curves are normalized to unity. The 4.7 micron CO emission from the cloud can be observed from an aircraft above 12 km with essentially the signal levels shown in Figures 6 and 5, since atmospheric attenuation is less than a factor of 3.

### 3.2 Signal-to-Noise Ratio for Airborne Optical System

An aircraft-based optical system could have the following parameters:
- 20 cm diameter collection optics, detector sensitivity $D^* = 10^{11} \text{ cm}^{-2} \text{watt}^{-1} \text{sec}^{-1/2}$,
- detector area = 1 mm$^2$,
- and the system solid angles of $10^{-4}$ and $10^{-5}$ steradian.

For these parameters, the NEFD of the optical system is $1 \times 10^{-14}$ watts/cm$^2$.

A comparison of the system noise to the predicted CO radiation intensity at the observer is indicated in Figure 8; note the levels for signal-to-noise ratio of unity. Measurements of the $N_2$ vibrational temperature are marginal because of the significant sun and earthshine.
FIGURE 10. ATMOSPHERIC CO CONCENTRATION AND MIXING RATIO, TAKEN FROM REF. 15.
FIGURE 11. ATMOSPHERIC TRANSMISSION OF CO 4.7 μm RADIATION VS. ROTATIONAL LINK FOR OBSERVER ON GROUND AND AT 12 KM. ROTATIONAL EMISSION SPECTRA $[I(j)/\Sigma I(j)]$ FROM CLOUD AT 150 KM (7000 K), 130 KM (5000 K) AND 110 KM (2500 K) ALTITUDE.
In this paper, 10-kilogram releases of gaseous CO at altitudes above 110 km were considered and the CO infrared emission from the cloud was calculated. CO vibrational excitation requires mixing with the ambient N₂ and V-V transfer from the vibrationally excited N₂. Since the N₂ vibrational temperature is uncertain, it was left as a parameter.

Radiation in the 2.4 micron overtone band is suppressed due to collision-limiting effects in the two-step process transferring N₂ vibrational energy to the first and then to the second CO vibrational level. Radiation losses from the first level are so large that it is extremely difficult to populate the second level. Thus, the second level is predominantly excited by the weaker two-quantum transfer from N₂.

Observation of 4.7-micron radiation cannot be made by ground-based systems because of atmospheric attenuation. However, airborne-optical systems above approximately 12 km can observe 4.7-micron radiation, and this is the proper way to measure CO infrared emission. Present day optical systems have sufficient sensitivity to make the measurements. The major limitation to this experiment is the excitation of CO emission by sun and earthshine. CO excitation by N₂ vibration must be larger than excitation by radiation; this determines the minimum N₂ vibrational temperature that can be measured.

While this report treated collision-limiting effects for CO releases, in particular, this general effect holds for all overtone radiation at high altitudes. Collision-limiting occurs when the collision transfer rate is much slower than the radiative rate of the fundamental band. For example, molecules like CO, CO₂, and NO whose overtone radiations are in the 2- to 3-micron region have a very low emission, while molecules such as H₂O, HF, OH, and other hydrogen-containing molecules which have fundamental band radiation in this region are not affected by radiation cooling.
REFERENCES


7. Horn, K., Private Communication.


