

THE VARIABILITY OF ATMOSPHERIC CO<sub>2</sub>

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by

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THE VARIABILITY OF ATMOSPHERIC CO<sub>2</sub>

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PREVIEW

## ABSTRACT

SIR-A Satellite radiance measurements and correlated radiosonde temperature and dew point temperature profiles were used to estimate the variability of atmospheric  $\text{CO}_2$  by asymptotic solution of the Ladenberg-Reiche equation for a single line. The 17 different sets of data used in these calculations were characterized by clear weather conditions and relatively low atmospheric water vapor content. For each case considered, the radiances for the  $15\mu$  band of  $\text{CO}_2$  were computed using, 1) the standard  $\text{CO}_2$  profile, 2) the radiosonde temperature profile, and 3) the water vapor absorption using the measured dewpoint temperature profile. The differences in the measured and computed radiances was attributed to the variability of  $\text{CO}_2$  in the atmosphere from the standard  $\text{CO}_2$  profile.

The computational technique is questionable in regions where the temperature profile is isothermal. The extent of possible sources of error in the results are examined.

## Table of Contents

	page
List of Tables-----	V1
List of Figures-----	VII
Chapter I-----	1
Introduction-----	1
Chapter II-----	5
Theory of Inverse Solutions of the Radiative Transfer Equation--	5
A. Radiative Transfer Equation (RTE)-----	5
B. Iterative Solutions-----	9
C. The Ladenberg-Reiche Approximation-----	11
Chapter III-----	15
The Data and Methods of Computation-----	15
A. Data-----	15
B. Methods of Computation-----	15
Chapter IV-----	23
Results and Error Analysis-----	23
A. Results-----	23
B. Sources of Error-----	23
Chapter V-----	57
Conclusions and Recommendations-----	57
List of references-----	59

## List of Tables

Table	page
I SIRS-A Radiances-----	24
II Values of ALPHA computed from the Ladenberg-Reiche approximation-----	25
III Re-computed values of ALPHA for temperature modifications-----	44
IV Re-computed values of ALPHA for ozone modifications-----	48
V Mean values of ALPHA with associated internal and external errors-----	56
VI Mean values for the mean deviation of ALPHA with associated internal and external errors-----	56

PREVIEW

## List of Figures

Figure	page
1. The derivative of the transmittance with respect to the logarithm of the pressure-----	14
2. U.S. Standard temperature profile-----	16
3. Int. Falls, Orbit 126-----	26
4. Green Bay, Orbit 66-----	27
5. Green Bay, Orbit 133-----	28
6. Green Bay, Orbit 495-----	29
7. Int. Falls, Orbit 59-----	30
8. Sault St. Marie, Orbit 133-----	31
9. Flint, Orbit 139-----	32
10. Rapid City, Orbit 46-----	33
11. Little Rock, Orbit 153-----	34
12. Brownsville, Orbit 133-----	35
13. Dodge City, Orbit 187-----	36
14. Dayton, Orbit 39-----	37
15. North Platte, Orbit 53-----	38
16. Little Rock, Orbit 133-----	39
17. Peoria, Orbit 133-----	40
18. Koror, Orbit 44-----	41
19. Truk, Orbit 97-----	42
20. Int. Falls, Orbit 126. Temperature modifications-----	45
21. Peoria, Orbit 133. Temperature modifications-----	46
22. Koror, Orbit 44. Temperature modifications-----	47
23. Int. Falls, Orbit 126. Ozone content modifications-----	49
24. Peoria, Orbit 133. Ozone content modifications-----	50
25. Koror, Orbit 44. Ozone content modifications-----	51



## Chapter I

### Introduction

All matter absorbs and re-emits electromagnetic radiation. The extent of absorption is determined by the frequency of the incident radiation and by the type and amount of matter absorbing the radiation. The emission processes are determined from the transition probabilities for spontaneous and stimulated emission for each species under consideration. Absorption and emission are characteristic properties of matter since no two atoms or molecules of different species have the same atomic or molecular structure. This interaction between radiation and matter is also temperature and pressure dependent through line broadening, excitation state distributions, etc.

On earth, the gross properties of the atmosphere are generally known to within one percent or better over the greater part of the globe. From laboratory measurements, the amount of absorptance by atmospheric gases is also well known (Wark and Flemming, 1966). Thus, by sounding the atmosphere at selected frequency intervals, the earth's vertical temperature profile can be inferred from these spectral measurements since the atmospheric gases attenuating the incident radiation are assumed known. Complications arise, however, in the interpretation of atmospheric spectra, mainly due to the lack of specific a priori knowledge of the relative abundances of the elements in the atmosphere. The distribution of the elements in the atmosphere, also, has an effect on the observed spectral transmittances.

Artificial satellites offer a unique opportunity to exploit the possibility of inferring either temperature or composition profiles from the earth's upwelling infrared radiation. The SIRS-A (Satellite Infrared

Spectrometer) instrument carried on board the Nimbus III satellite was designed to sound the earth's atmosphere at 8 selected spectral intervals or channels centered about the strong 15 micron absorption band of  $\text{CO}_2$ . Selection of this spectral interval as the sounding frequency for inferring temperature profiles was made under the assumption that  $\text{CO}_2$  is uniformly mixed at 320ppm and in local thermodynamic equilibrium (LTE) in the atmosphere to a height of about 70 km (Wark and Flemming, 1966). The validity of the former assumption is the subject of this thesis.

In the following few paragraphs, a summary of the available general knowledge on atmospheric  $\text{CO}_2$  is given. It appears that the observations indicate a variable  $\text{CO}_2$  content in the atmosphere.

Atmospheric carbon dioxide occupies about 0.03% of the atmosphere by volume and is increasing at a rate of .7ppm per year (Newell and Dopplick, 1970; Bolin and Bischof, 1970; Pales and Keeling, 1963; Brown and Keeling, 1963). Since the 1900's, the increased combustion of petroleum and fossil fuels has contributed to this increasing amount of atmospheric  $\text{CO}_2$ . If the total amount of  $\text{CO}_2$  released by combustion were to remain in the atmosphere, then the rate of increase is estimated to be about twice as much as the computed value of .7ppm, but the oceans and plant life serve as sinks for  $\text{CO}_2$ . Thus the amount of  $\text{CO}_2$  over any given locality strongly depends on the immediate environment.

In test conducted at Brookhaven, Long Island (Woodwell, et al, 1973) fluctuations in the  $\text{CO}_2$  content of the lower atmosphere were found to be greatest close to the ground and diminished substantially at a height of 125 meters. At low elevations, changes in  $\text{CO}_2$  concentrations of as much as 100ppm in less than one hour were common and at 125 meters, changes greater

than 20ppm in less than one hour were observed. These large fluctuations at low altitudes were also observed over cornfields, forests, and other large vegetation areas (Lieth, 1963).

In the years 1962-1968, numerous measurements in  $\text{CO}_2$  content were made by aircraft and commercial jet airliners over the northern hemisphere between the heights of one kilometer and the lower stratosphere (Bischof, 1970). The seasonal variations in  $\text{CO}_2$  computed from these measurements were found to have a maximum deviation from the annual mean of 320ppm during the months of March and August. The maximum concentrations of  $\text{CO}_2$  occurred during the latter parts of March and early April and the minimum concentrations during August. At 2 km, the deviations from the annual mean were greatest during April with an amplitude of 6.5ppm and least during August with an amplitude of -8.5ppm. At the tropopause, the amplitudes were 3.4ppm during March and -3.6ppm during August (Bolin and Bischof, 1970).

Eventhough numerous measurements on the  $\text{CO}_2$  content of the atmosphere have been made, the results are almost always reported as averages over long periods of time (either monthly or yearly). Some cases do exist in the literature, however, where daily  $\text{CO}_2$  measurements were reported. In flights conducted from South Carolina out over the Atlantic, measurements from the ground to about 200 meters indicate a decrease in  $\text{CO}_2$  concentration with height over the ocean. Over land mass, however, increases in  $\text{CO}_2$  concentration with height were observed close to 200 meters and again at 2000 meters (Bischof and Bolin, 1965).

On June 22, 1955, the first recording of the near infrared solar spectrum from high altitudes were made with an infrared spectrograph

carried by balloon to an altitude of about 102,000 feet (Gates, et al 1958). The following statement concerning the uniformity of the CO<sub>2</sub> mixing ratio was made: "This result (uniform mixing ratio) is a consequence of the fact that the constants were evaluated on the basis of a constant mixing ratio and so the distribution obtained in this fashion (data smoothing) is redundant. If the unsmooth data were used for determining the CO<sub>2</sub> amount in the zenith above each level, values are found which might indicate that the CO<sub>2</sub> content of the atmosphere was far from uniform".

In addition to the above, unreported cryogenic sampling measurements at White Sands Missile Range indicate very large stratospheric CO<sub>2</sub> fluctuations (Ballard, 1973).

These variations and apparent conflicts indicate a need to utilize the satellite technique to estimate the variability of atmospheric CO<sub>2</sub>.

## Chapter II

### Theory of Inverse Solution of the Radiative Transfer Equation

In this chapter, the theory of radiative transfer is very briefly presented primarily for consistency in terminology and notation. For further details on the theory, the reader is referred to Goody, Atmospheric Physics; Theoretical Basis and to Chandrasekhar, Radiative Transfer.

#### A. Radiative Transfer Equation (RTE)

In atmospheric problems, the interaction between radiation and matter can be classed as either extinction or emission. If the temperature, pressure, and compositional structure of an atmospheric layer remains constant (homogeneous), then by Lambert's law, the extinction and emission processes are linear in the specific monochromatic intensity of radiation and in the amount of matter. When both extinction and emission processes occur, the total change in intensity can be expressed as

$$dI_{\nu}(P, \bar{s}) = e_{\nu} I_{\nu}(P, \bar{s}) da + e_{\nu} J_{\nu}(P, \bar{s}) da \quad (1)$$

where  $da$  is the amount of matter per unit area (equivalent differential column height),  $I_{\nu}$  is the specific intensity (or radiance) at a point  $P$  and in the direction  $\bar{s}$ .  $J_{\nu}$  is defined as the source function and the coefficient  $e_{\nu}$  is the emission or extinction coefficient where emission is defined as negative extinction. Equation 1 above is the equation of transfer for monochromatic radiation,  $\nu$ , and is the fundamental quantity in radiative transfer theory. This equation governs the radiation field in a medium which absorbs, emits, and scatters radiation. The application of the equation of transfer to atmospheric problems requires some knowl-

edge of the thermodynamics of the atmosphere, or strickly speaking, one must know the form of the source function  $J_\nu$ .

With respect to the distribution of molecular rotational states, the atmosphere is in local thermodynamic equilibrium and the source function can be fully described by the blackbody function

$$J_\nu = B_\nu(T) = \frac{2h\nu^3}{c^2 \{\exp(h\nu/kT) - 1\}} \quad (2)$$

where  $\nu$  is the frequency,  $c$  the speed of light,  $k$  the Boltzmann constant,  $T$  the temperature in degrees Kelvin, and  $h$  the Planck constant.

Describing the source function in terms of the blackbody function very necessarily imposes the assumption that the atmosphere is in thermodynamic equilibrium. Obviously, this is an oversimplified model of the atmosphere since the earth's vertical temperature profile is not isothermal. To avoid this oversimplification, the atmosphere is divided into a finite number of plane-parallel, homogeneous, isotropic stratifications each in LTE. When a system is in LTE, it is assumed that circumstances are such that we can define at each stratification a local temperature  $T$  and such that the emission coefficient,  $e_\nu$ , is given in terms of the absorption coefficient  $k_\nu$ , by the relation

$$e_\nu d\bar{s} = k_\nu \rho(P) d\bar{s} \quad (3)$$

where  $\rho(P)$  is the mass density at the point  $P$  and  $d\bar{s}$  is the direction of propagation of the radiation. Since the pressure,  $p$ , varies continuously with height in the atmposhere, it is convenient to express the height,  $z$ , in terms of the pressure by introducing the hydrostatic equation given