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SCIENCE SUPPORT FOR THE ATMOSPHERIC TRACE MOLECULE SPECTROSCOPY (ATMOS) EXPERIMENT

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1.0 Introduction

The Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment is a satellite solar occultation interferometer spectrometer experiment under development for flight on Spacelab 3. Launch is expected in March 1985. ATMOS will provide high spectral resolution (0.02 cm^{-1}) and high spatial resolution (2 km from Shuttle altitude) data over the spectral range from 2 µm to 16 µm. This region of the spectrum is rich in absorption features of major and minor trace gases which are critical to our understanding of the chemistry and physics of the Earth's upper atmosphere. The broad objectives of the ATMOS experiment are to:

- Improve our understanding of the composition and physical processes in the upper atmosphere.
- Identify and measure, on a global scale, the volume mixing ratios to levels of 10^{-12} of known and newly discovered molecular species.
- Determine vertical profiles for these species.
- Provide spectral data on the atmosphere for use in optimizing the design of future instruments to monitor specific gases.

This report describes work done in collaboration with Dr. James M. Russell, III, who is an ATMOS Co-Investigator. The guidance for these research activities has been provided by Dr. Russell in order to ensure that the research performed complements efforts of other ATMOS science team members and that is is in accord with his assigned team responsibilities. The research reported was perfomed by the balloon spectroscopy group of NASA Langley and the College of William and Mary (Drs. James M. Russell, III, Jae H. Park, Mary Ann H. Smith, D. Chris Benner, and Curtis P. Rinsland). Unless noted as otherwise in the text, the research activities described in the report were done in collaboration with William and Mary investigators under funding provided by NASA Research Cooperative Agreement NCC 1-3 and/or NASA Grant NSG-1484.

2.0 Summary of Research

2.1 Introduction

Our effort in the past 4 years has been focused on studies in the 2 μm to 5 μm spectral range where many important molecules have absorption features. The goal of these efforts has been to develop an independent capability for retrieval of these molecules (i.e., NO_2, HNO_3, $C\ell ONO_2$, $CH_3C\ell$, OCS, HF, and $HC\ell$) in keeping with the ATMOS team philosophy of providing some overlap with other team efforts in order to obtain better confidence in the final results. We have also developed the capability to do simultaneous pressure-temperature retrievals as part of this effort (Park et al., 1980 a, b; Park, 1982). Other areas of research have included examination of continuum absorption that can be studied with ATMOS, and development and implementation of retrieval algorithms for those molecules which are diurnally active (e.g., $C\ell O$, NO_2, NO).

Our approach has been to develop line-by-line spectral simulation routines which accurately represent atmospheric limb absorption, including the effect of refraction as a function of tangent height, and to test these routines using actual balloon observations taken with the JPL high resolution (0.18 cm^{-1}) interferometer in occultation. We have developed (a) interactive programs which access and display observed spectra; (b) spectral simulation and point-by-point ratio routines for use in calculating residuals which are useful for identification of simulation problems, line parameter errors, or unaccounted-for absorption; (c) two retrieval approaches for constituents, pressure, and temperature using the equivalent width and/or least squares techniques; (d) methods for removing "channeling" effects from observed spectra; and (e) a technique to simulate the effect of the vertical smearing of interferograms due to changing air mass during a solar occultation. A description of our display, simulation, and pressure-temperature retrieval studies is given in Appendix A. A necessary part of our work has been the compilation of adequate spectroscopic parameters to use in the simulations. This is also briefly described in Appendix A. The remainder of this section will provide highlights of important results from our algorithm development and balloon spectra studies.

2.2 Results of Balloon Spectra Analyses

As already indicated, we have been analyzing the JPL high resolution balloon data as a way of testing our algorithms for ATMOS. In addition, we have performed several scientific studies in the course of this work which are relevant not only to ATMOS, but also to other stratospheric remote sensing experiments. These studies are discussed in the next four subsections.

2.2.1 Retrieval of Gas Concentration Profiles

We have implemented two fundamental procedures for use of the transmittance data in the retrieval of gas concentration or pressure and temperature. The first of these is the conventional equivalent width method where the area under an observed line is measured at each tangent altitude and the same quantity is calculated in the simulation. This approach has the advantage of being fast and inexpensive to apply on the computer, and it is insensitive to errors in the instrument line shape function. However, the accuracy of the technique is very limited in cases where there are overlapping absorption lines, or where absorption by the line of interest is very weak. In these cases, it is not easy to determine a good background level to use for the area determination.

The second approach we have used is the nonlinear least squares technique (Chang et al., 1978; Niple et al., 1980). This method makes maximum use of the spectral information by interactive point-by-point fitting of the calculated and observed spectra through adjustment of key parameters. This technique is very accurate in most instances, including cases of overlapping absorption or where the background is difficult to assess. Our program performs the fit by adjusting line position, background level and slope, channeling parameters, spectral resolution, and gas mixing ratios. One or two gases can be retrieved simultaneously from spectral intervals up to 8 cm^{-1} wide. The program can handle up to 10 interfering gases and has provisions to simulate solar carbon monoxide lines. Corrections for diurnally varying gases can be included using the method of "asymmetry factors" introduced by Boughner et al., (1980). The least-squares method requires considerably more computer time than the equivalent width method due to the large number of points included in the fit and the number of parameters to be evaluated. It is also more sensitive to line position errors and requires accurate knowledge of the instrument line shape function.

The inversion algorithm approach we have adopted is the so-called "onion skin" method (Russell and Drayson, 1972; Russell et al., 1977). In this approach, we match either calculated equivalent width or spectral line shape to the observed quantities starting from the top of the atmosphere and working downward, adding on successively lower layers in the retrieval processes.

An example of measured and calculated balloon spectra using the least-squares method and onion skin inversion is shown in figure 1 for water vapor at a 22 km tangent height. In the spectral interval shown, 400 data points were used. RMS differences between the observed and calculated transmittances are on the order of 2 percent. The mean water vapor mixing ratio profile retrieved using the least-squares method is compared with results obtained by the equivalent width technique in figure 2. Twelve isolated water vapor lines in the 3-μm region were used in each case. Agreement between these results is very good at lower altitudes but degrades in upper regions. The accuracy of the equivalent width method is worse than that for least-squares at altitudes greater than 30 km due to the weakness of the water vapor signal. Clearly, the equivalent width and least-squares techniques are of use in analyzing high resolution atmospheric spectra. The choice of algorithm in retrievals will be governed by the specific nature of the absorption signal in the region of interest. Generally, unless lines are well isolated from other nearby features and the background level is well defined, we have used the equivalent width method to obtain a good first guess and then we relied on the least-squares method for more accurate retrievals.

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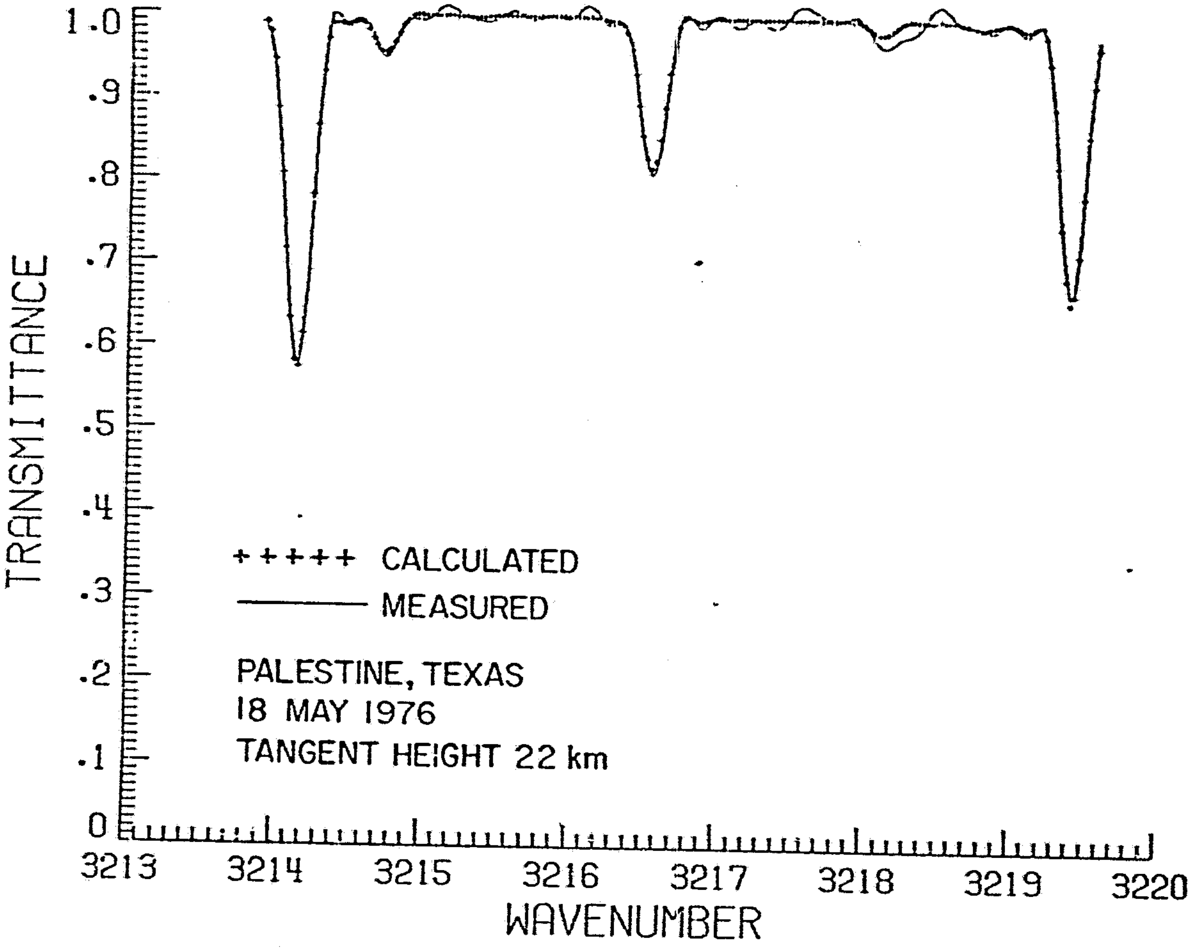

Figure 1: Sample results from a least-squares H_2O retrieval. Observed spectrum is given by the solid curve. Calculated spectrum, denoted by crosses, is based on the H_2O mixing ratio profile resulting from the least squares retrieval. All of the absorption features shown here are due to H_2O.

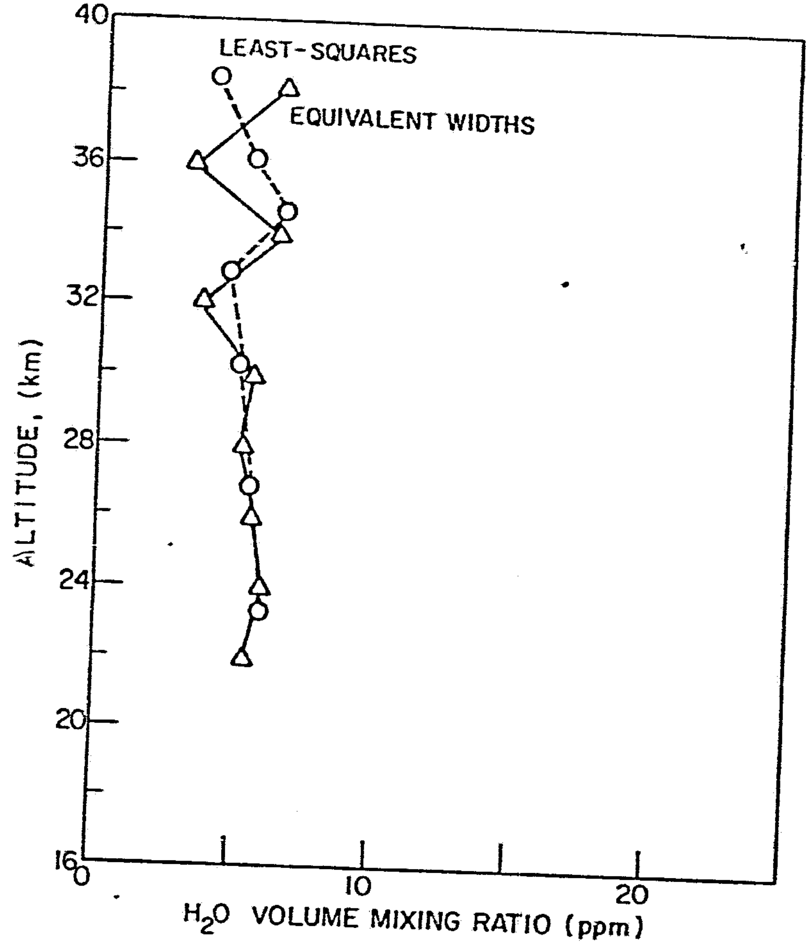

Figure 2: Comparison of H_2O profiles for Palestine, Texas, 18 May 1976, retrieved from the same set of balloon-flight spectra by the equivalent width and non-linear least squares techniques.

As a test of our least-squares retrieval program in the case of overlapping absorption by multiple gases, we have carried out a CO_2 retrieval near 3500 cm^{-1} (fig. 3) where there is interfering absorption by H_2O and N_2O. Although the agreement between observed and calculated spectra was excellent in our initial comparison, the retrieved CO_2 mixing ratio was about a factor of two off from the currently accepted value. In order to study the reason for such a large discrepancy, we collected new laboratory spectra using the Langley high-resolution Fourier transform spectrometer (maximum resolution = 0.06 cm^{-1}). Figure 4 shows our nonlinear least-squares calculated fit to a measured carbon dioxide absorption line in this interval. Our subsequent analysis on this and other lines indicates that the line intensities for the $(10^{0}1)_{II} - (00^{0}0)$ band of $^{13}CO_2$ on the AFGL tape are overestimated by about 78 percent. The revised line intensities yield CO_2 mixing ratios that are near the nominal stratospheric value. When we analyze a CO_2 band whose line parameters are well known, a mixing ratio close to 325 ppm is obtained. These results verify the validity of our retrieval algorithms. The effect of interferogram smearing should be incorporated in the final analysis of the spectrum, which will be discussed in section 2.2.4.

2.2.2 Continuous Absorption by N_2 and CO_2 near 2400 cm^{-1}

A careful analysis of the Texas Mark I spectra near 2400 cm^{-1} has led to the identification of continuous absorption by N_2 and CO_2 in the lower stratosphere (Rinsland et al., 1981; Smith et al., 1981). We were able to detect and accurately measure the wavelength dependence of the continuum because of the long-path advantage gained in a solar

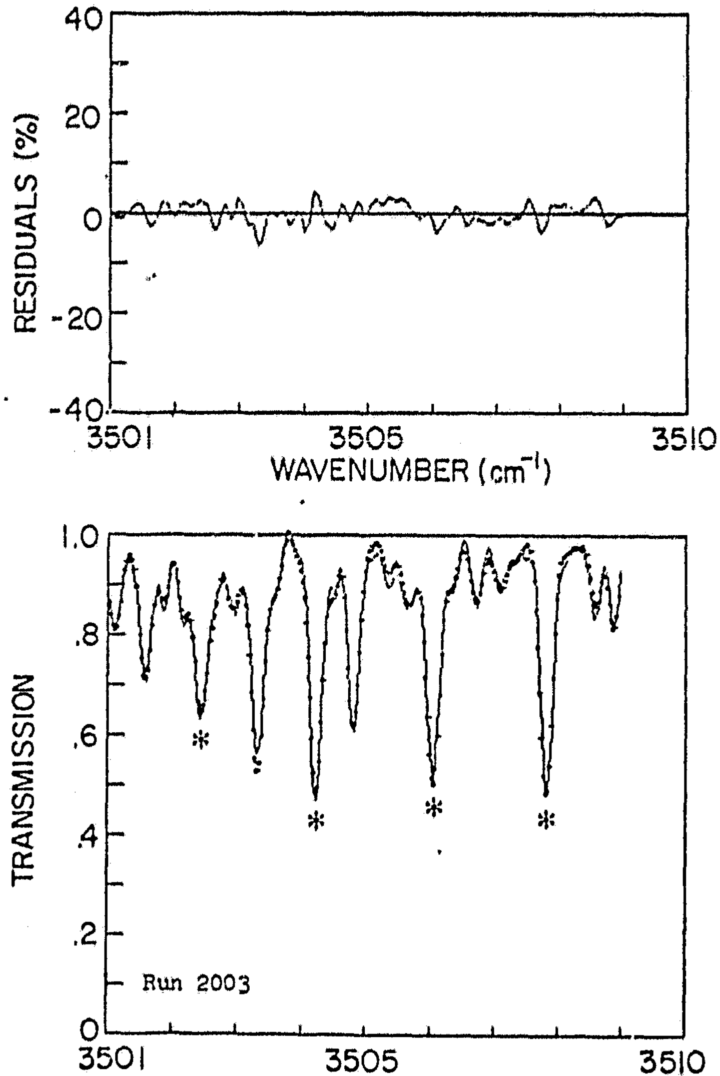

Figure 3: Least-squares CO_2 retrieval in the presence of interfering gases. In the lower panel, the solid curve represents a measured Mark I spectrum from May 1976, with a mean tangent altitude of 25.3 km. The crosses denote the simulated spectrum based on the retrieved CO_2 profile. The strongest CO_2 absorption features are marked by asterisks. The unmarked features are due to absorption by H_2O and N_2O as well as CO_2. In the calculations shown here, the profiles for the two interfering gases were taken from retrievals in other regions of the same spectra. Residuals are plotted in the upper panel.

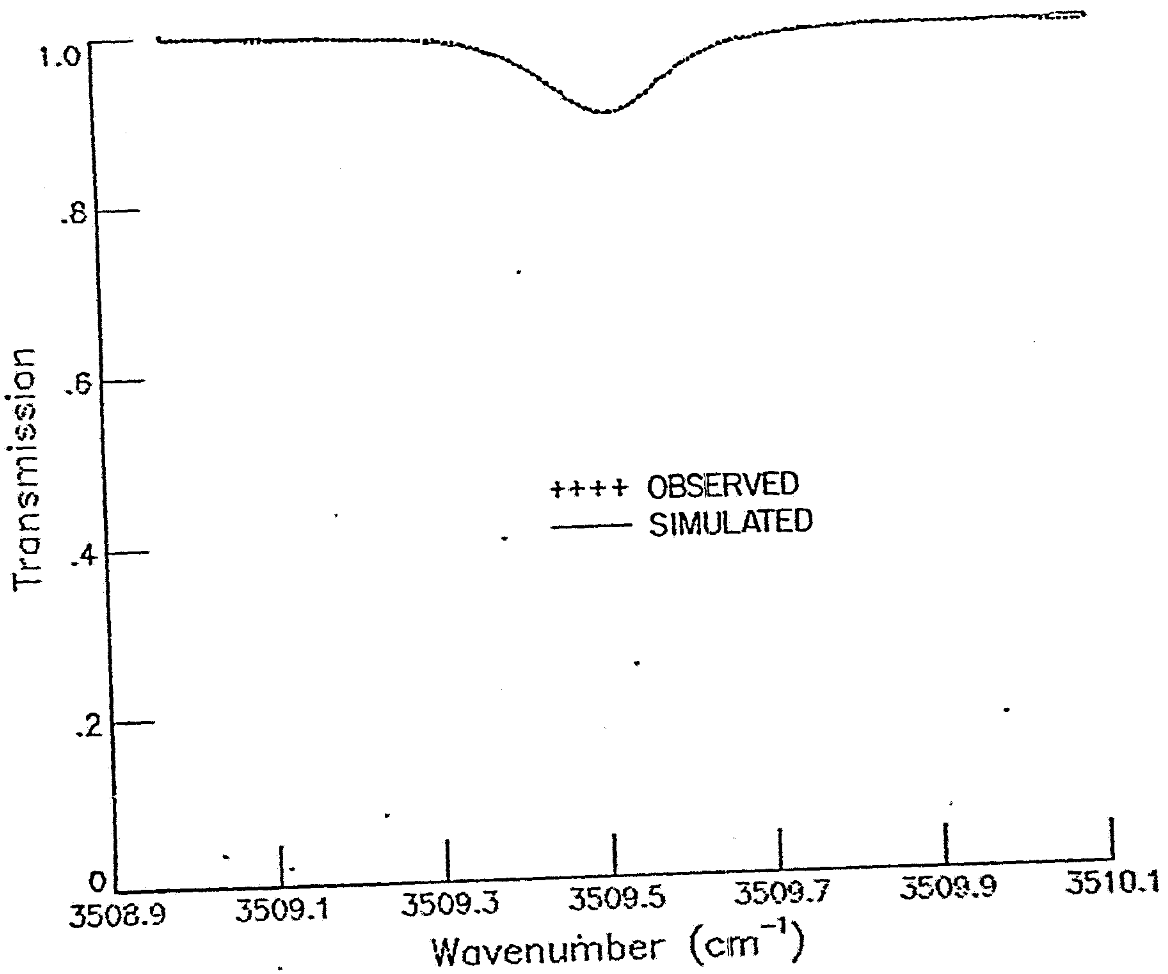

Figure 4: A carbon dioxide spectrum recorded with the Langley interferometer (+ symbols) and a non-linear least-squares fit to the data (solid curve).

occultation experiment and the capability to remove the wavelength dependence of the instrumental response and the solar flux by ratioing spectra at lower tangent altitudes to a high-Sun spectrum. An atmospheric transmittance spectrum is shown in figure 5 for the region 2380 to 2500 cm^{-1} (tangent altitude 21.8 km; float altitude 37.0 km). Continuous absorption increases in strength with decreasing wavenumber throughout this spectral region. For wavenumbers less than 2390 cm^{-1}, the continuum is masked by strong absorption by high-J lines of the ν_3 fundamental band of CO_2.

Continuum absorption in this spectral region arises from pressure-induced absorption in the fundamental band of N_2 and far-wing absorption by distant, intense lines of carbon dioxide. We have compared the stratospheric measurements to synthetic values based on laboratory measurements. The dashed curve in figure 5 was calculated for N_2 absorption only; the solid curves are calculated for different far-wing CO_2 line shapes and also include N_2 absorption. The observed and calculated curves are in fair agreement over most of the spectral region, although there is some suggestion that the N_2 absorption coefficients we used may overestimate the absorption at frequencies higher than 2450 cm^{-1}. Our calculations indicate that the continuum near 2400 cm^{-1} is sensitive to the far-wing CO_2 line shape. However, we feel that uncertainty in the N_2 contribution near the CO_2 band head precludes a determination of the air-broadened, far-wing CO_2 line shape using the stratospheric spectra at this time.

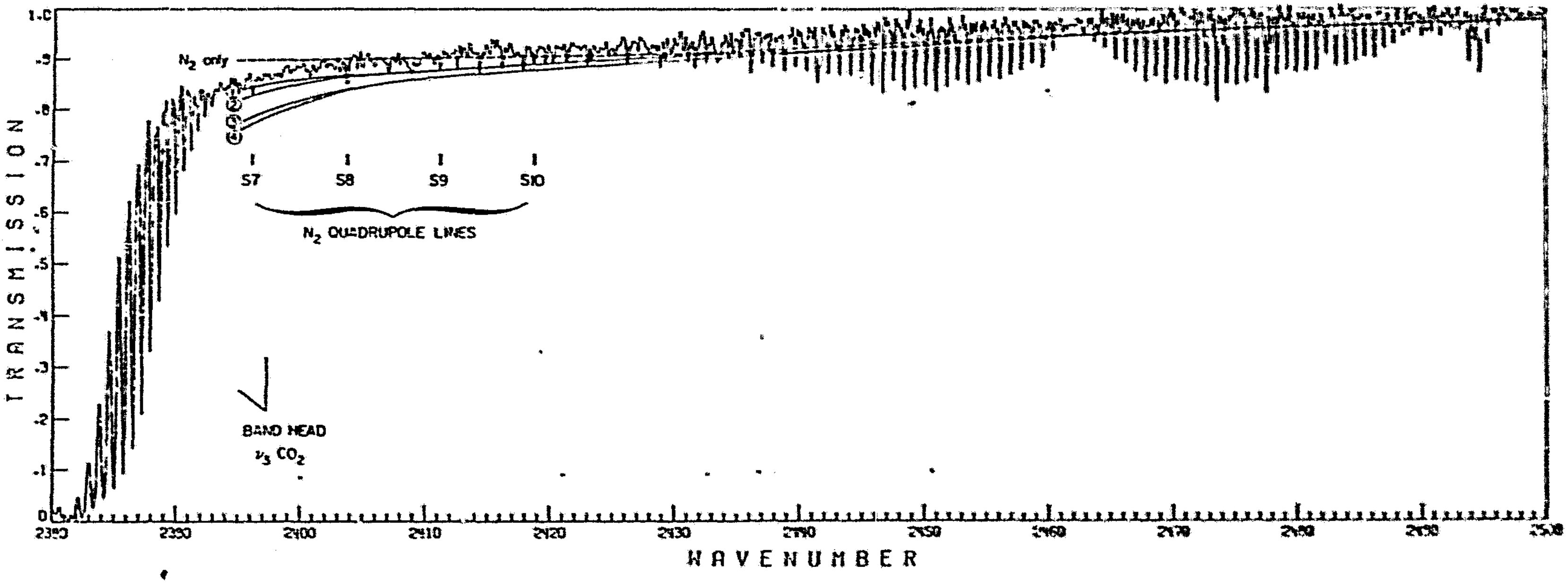

Figure 5: Comparison of a stratospheric transmittance spectrum obtained from balloon observations (float altitude 37 km) with synthetic monochromatic transmittances. The observed spectrum (resolution 0.18 cm^{-1}) was derived from the point-by-point ratio of a solar-occultation spectrum (geometric tangent altitude 21.8 km) to a high-Sun spectrum. The dashed curve represents transmittances calculated for N_2 absorption alone, while the heavy solid curves correspond to total $N_2 + CO_2$ absorption calculated for four sub-Lorentzian line shapes (1) Burch et al. (1969); (2) Susskind and Mo (1978); (3) Cann et al. (1980); (4) Winters et al. (1964). The location of the ν_3 CO_2 band head and several of the stronger lines of the S branch of the N_2 (1, 0) quadrupole band are marked.

The high-J absorption lines within the R branch of the ν_3 band head of CO_2 have been selected for our temperature sensing studies in the 4.3-μm region. It is clear from this study that this region is significantly affected by continuum absorption in the lower stratosphere. Since the optical depth of N_2 + CO_2 continuum absorption varies as the square of atmospheric pressure, the strength of the continuum will increase rapidly with decreasing tangent altitude. Also, because of the pressure squared dependence of the continuum, temperature retrievals will be sensitive to errors in the assumed atmospheric pressure profile. Therefore, it is most desirable to retrieve both pressure and temperature simultaneously. We have developed a technique for this type of retrieval (Park et al., 1980 a, b) and now include the N_2 + CO_2 continuum in our temperature-pressure retrieval studies (Park, 1982).

2.2.3 Search for Halocarbon Signatures in the 3.3-μm Region

The 3.3-μm region contains C-H stretch vibration-rotation bands belonging to a number of hydrocarbon and halocarbon species which may affect the chemistry of the stratosphere. Small halocarbons such as methyl chloride ($CH_3C\ell$), trichloroethylene ($CHC\ell = CC\ell_2$), and methyl chloroform ($CH_3CC\ell_3$) can act as sources of free chlorine atoms for the catalytic destruction of stratospheric ozone (Crutzen et al., 1978). On the other hand, nonmethane hydrocarbons such as acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_3H_6), and propane (C_3H_8) may act as sinks for $C\ell$ atoms, and may also play a role in the production of atmospheric CO (Chameides and Cicerone, 1978). All of the molecules mentioned above have been measured in stratospheric air samples by gas chromatographic techniques, with typical stratospheric concentrations ranging from 1 to several hundred parts per trillion (Cronn et al., 1977; Cronn and Robinson, 1979; Rudolph et al., 1981).

Since the concentration of methyl chloride is at least an order of magnitude higher than that of other chlorocarbons in the stratosphere, and $CH_3C\ell$ is one of our ATMOS assigned gases, a detailed analysis of the Mark I data was carried out for the 3-μm region to determine if absorption features belonging to the ν_4 fundamental of $CH_3C\ell$ were detectable in these spectra. From the Mark I spectra (resolution ≈ 0.18 cm^{-1}) it was not possible to identify the features of $CH_3C\ell$ absorptions. We are also attempting to obtain high-resolution spectra of halocarbons and hydrocarbons both from other laboratories and from our own measurements which will be useful for this analysis.

2.2.4 Effect of Altitude Smearing

Dr. Jae Park has studied the effect of the vertical smearing of interferograms which occurs due to the finite time required to complete a scan (Park, 1982). Infinite-resolution synthetic transmittance spectra were calculated for a series of tangent altitudes over a range corresponding to the start and stop times of a single interferometer scan. These synthetic spectra were then Fourier transformed, and the resulting series of interferograms were used to construct a single smeared interferogram. A new transmittance spectrum was obtained from the inverse Fourier transform of the simulated smeared interferogram.

Smearing was found to significantly modify the calculated spectrum. It was shown that the effective tangent altitude of the spectrum is the tangent altitude at which the center fringe of the interferogram is recorded and that the other components only define the instrument line shape. Interferogram [illegible] effectively creates strong sidelobes on absorption lines so that strong apodization is recommended for solar occultation experiments. This research was conducted by Dr. Park at the time he was a NASA employee.

2.3 Laboratory Studies

Historically, laboratory measurements of critical spectroscopic parameters and subsequent updating of the AFGL compilation, have usually not occurred until specific remote sensing requirements have been identified (Murcray and Alvarez, 1980). In the course of our Mark I analysis, we have identified a number of areas where existing spectroscopic parameters are inadequate. As a result, laboratory studies were initiated to collect needed data where obvious gaps exist in our knowledge of key parameters.

As part of our detailed analysis of the Mark I spectra for halocarbon absorption signatures (section 2.2.3), we have searched the literature to obtain laboratory high-resolution (better than 0.5 cm^{-1}) infrared spectra of halocarbon and hydrocarbon species of stratospheric importance. At least 18 different species have been measured at concentrations in the 1 to 1000 pptv range in the upper troposphere and lower stratosphere, and will probably be detectable in higher-resolution stratospheric spectra from future balloon experiments and from ATMOS. Unfortunately, only low-resolution laboratory spectra are available in the literature for a great number of these gases, and these data are of little use in the analysis of very detailed stratospheric spectra.

We initiated a program to systematically scan the spectra of important small halocarbons and hydrocarbons, using the Fourier transform interferometer at the Langley Research Center. Our goal has been to generate an atlas of high-resolution reference spectra for these molecules to be used in the identification of their absorption signatures in stratospheric spectra. The reference spectra recorded cover primarily the 2 to 5-μm region.

Since the methods selected for inferring upper atmospheric temperatures and pressures in both the ATMOS and HALOE experiments are based on the interpretation of the infrared spectrum of carbon dioxide, it is crucial to obtain CO_2 spectroscopic parameters to the highest possible degree of accuracy. Although assignments and line positions are satisfactory in most spectral regions, line strengths for many of the CO_2 bands important for pressure and temperature sensing have never been measured at high resolution in the laboratory. Line strengths based on low resolution measurements of total intensity in a given region were included in the original AFGL line parameter compilation (McClatchey et al., 1973), and these strengths have not been significantly changed in the updated compilation (Rothman, 1981). The errors of these calculated line strengths are not known well and may be quite large for many of the weaker bands. Our analyses of the Mark I spectra and of a single laboratory spectrum (section 2.2.1) have indicated that significant inconsistencies exist between the relative strengths of CO_2 bands in the observed spectra and those in the AFGL compilation. Clearly, a comprehensive program of high-resolution CO_2 line-strength measurements is needed so that reliable pressure and temperature profiles can be derived from the measurements of ATMOS, HALOE, and future infrared remote sensing experiments.

In support of ATMOS and HALOE, an analysis of the laboratory spectrum of $^{13}CO_2$ was made at high resolution (about 0.03 cm^{-1}) and elevated temperature (160°C) with a ^{13}C-enriched sample of carbon dioxide. The analysis was performed in cooperation with Dr. K. Narahari Rao of Ohio State University and Dr. Agostino Baldacci of the Institute of Organic Chemistry, Venice, Italy. The spectral region studied (3420 to 3680 cm^{-1}) overlaps the HALOE pressure-sensing channel, and the results of our anaysis were used to identify lines in the Mark I data.

Molecular constants were obtained for a total of 19 bands of $^{13}C^{16}O_2$ and two bands of $^{13}C^{16}O^{18}O$ (Rinsland et al., 1980, Baldacci et al., 1982). The transitions of $^{13}C^{16}O_2$ observed are illustrated in the energy level diagram in figure 6. The $^{13}CO_2$ spectrum in this region was last studied by Courtoy in 1959. Since our results were obtained with higher resolution and at elevated temperature, considerable refinement of a number of molecular constants was obtained. One of the strongest $^{13}C^{16}O_2$ bands is identified in the Mark I Texas data in figure 7.

In January 1982 an extensive set of carbon dioxide laboratory spectra were recorded at 0.01-cm^{-1} resolution with the Fourier transform spectrometer at Kitt Peak National Observatory. Data were obtained using normal and ^{13}C-enriched samples in the 1800 to 2600-cm^{-1} and 3400 to 4100-cm^{-1} regions. These spectra will provide important line parameters for ATMOS pressure-temperature retrieval studies. Preliminary analysis has shown that lines up to R108 of the ν_3 band are detectable

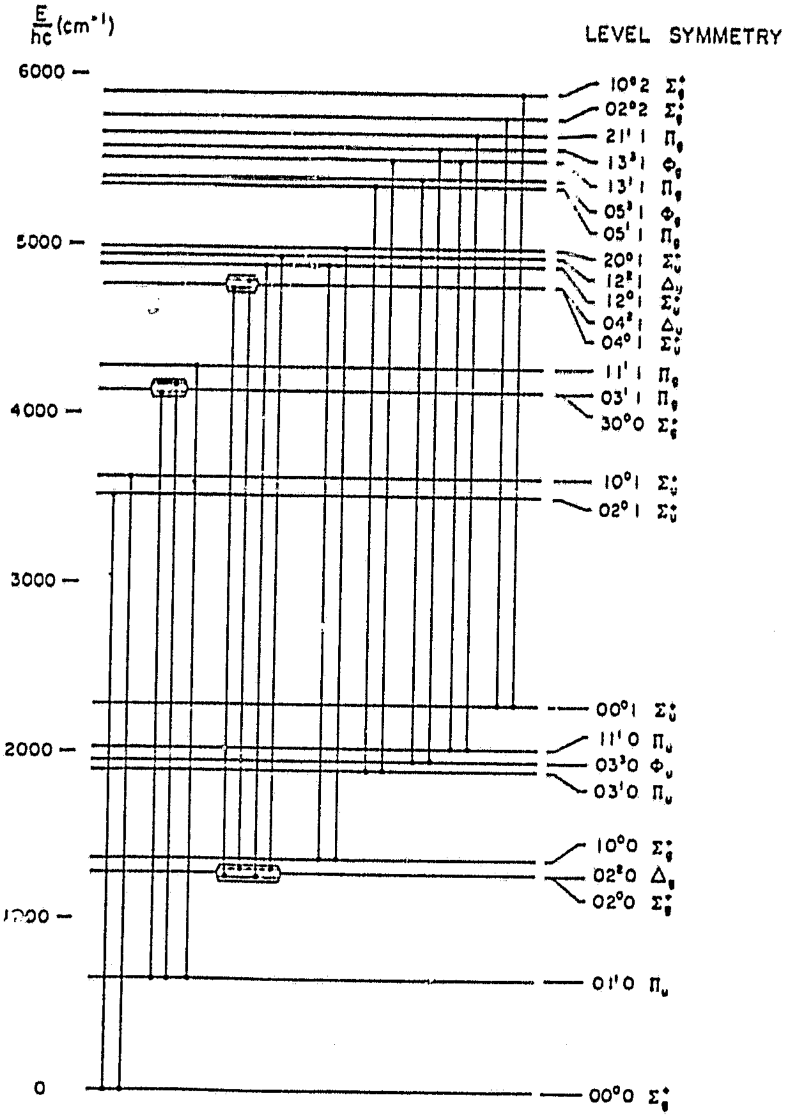

Figure 6: Energy level diagram for $^{13}C^{16}O_2$ showing transitions observed in the laboratory study at 2.8 μm (from Baldacci et al., 1981).

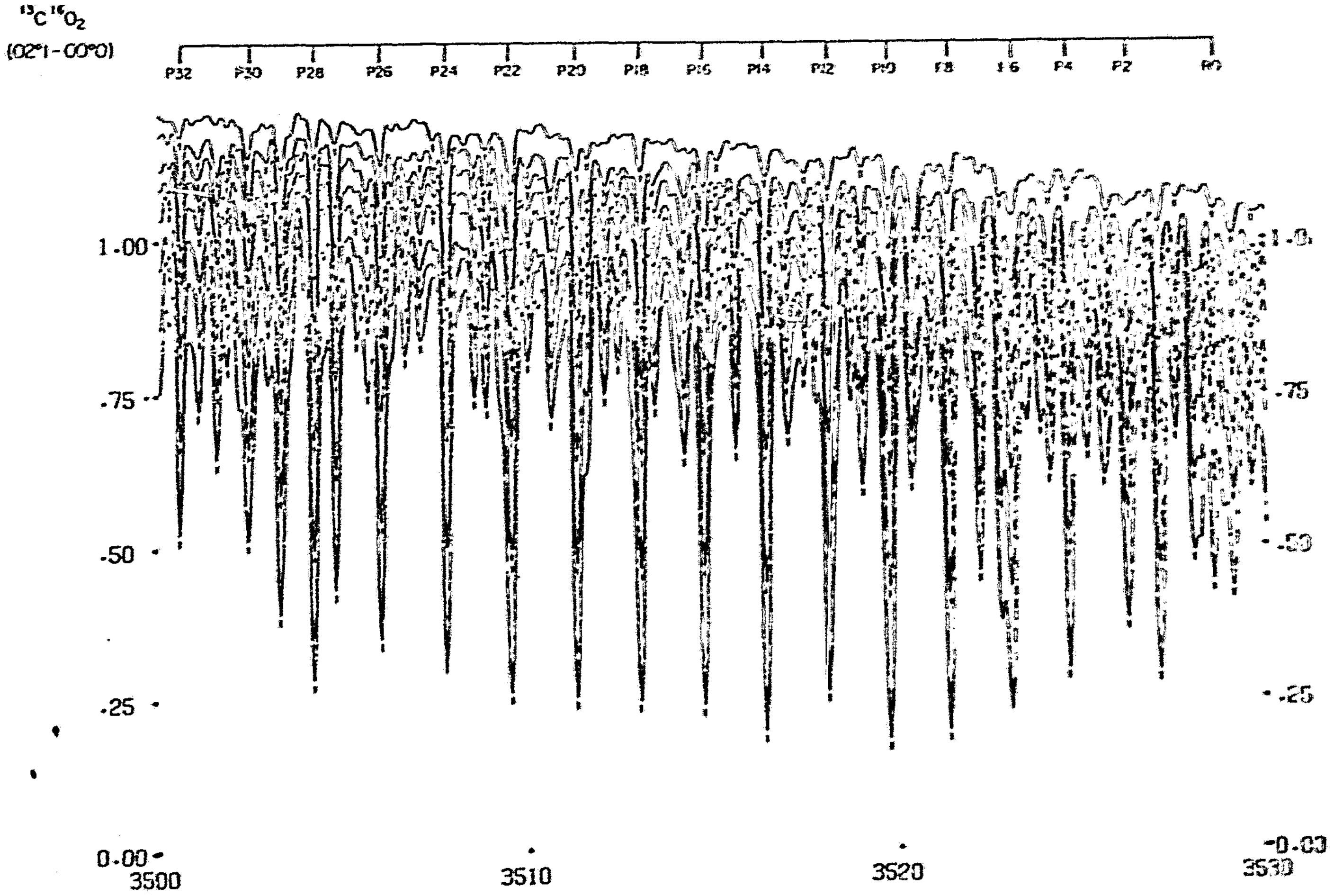

Figure 7: Short section of Mark I spectra obtained in May 1976 from a float altitude of 37 km near Palestine, Texas. Most of the absorption in this interval is from lines of $^{13}C^{16}O_2$. The strongest features are from the $2\nu_2 + \nu_3$ band and are identified above the spectra. Tic marks at each line peak are from the line-finding subroutine in the plot program.

in the data. This band is an important band for temperature sensing with ATMOS, and the accurate line stengths (± 3 percent) that can be derived from the data set will be used in ATMOS retrievals.

2.4 Applications to Design of Gas Specific Experiments

One of the stated goals of the ATMOS program is to provide comprehensive high resolution solar and atmospheric spectra which can be used in the design of gas specific experiments and in refining the software used to reduce data from these types of experiments. In this regard, for example, we have already made use of Mark I spectral date in studies related to the HALOE experiment. These data were very important to the selection of several HALOE channel locations (i.e., $HC\ell$, HF, CH_4, NO, and CO_2). Detailed spectral analysis and line identifications were carried out for the HF and $HC\ell$ filter regions in order to estimate the expected interference due to absorption by the major atmospheric species in each of the HALOE channels (Rinsland et al., 1982). An example of this work is shown in figure 8 where a section of a Mark I spectrum within the HALOE $HC\ell$ band pass is plotted along with a simulation based on the 1980 AFGL line parameters. Gas concentration profiles determined from the balloon spectra have also been provided to the HALOE science team for use in refinement of sensitivity studies.

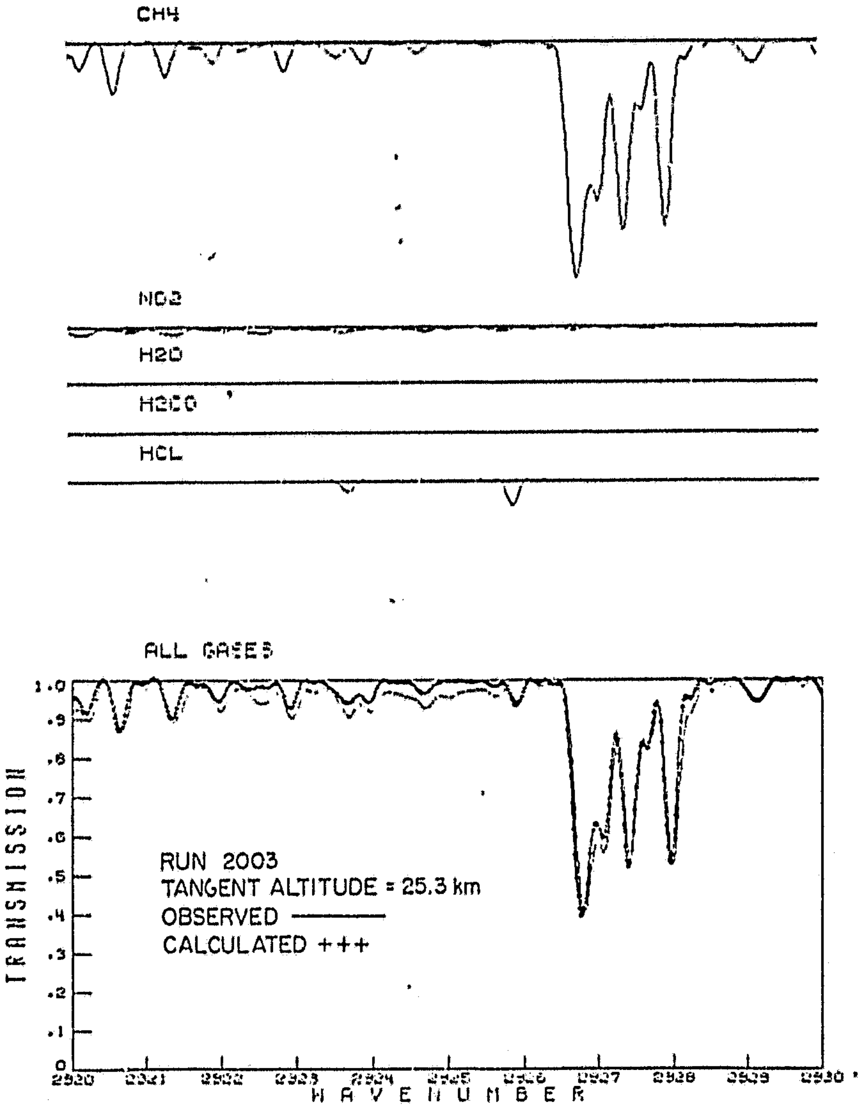

Figure 8: Measured Mark I Data and Simulated Spectra Using the 1980 AFGL Compilation in the HALOE HCℓ Filter Region.

APPENDIX A

Display, Simulation, and Pressure-Temperature Studies

A-1 Manipulation and Display of Data

Twenty-seven complete spectra measured by the Mark I instrument in two different balloon experiments (Palestine, Texas, May 1976, and Broken Hill, Australia, September 1977) are stored in digital form on magnetic tape at NASA Langley Research Center. A spectral plotting program, derived from one developed at JPL, allows the display of the measured spectral data with a scale and degree of apodization chosen by the user (fig. A-1), and can also generate and plot the ratio of two spectra. A subroutine to find and mark the position of each spectral line has recently been added to this program. A line parameter plotting program based on that used to generate the Atlas of Absorption Lines from 0 to 17,900 cm^{-1} (Park et al., 1982) published at NASA Langley can display laboratory spectroscopic data on the same scale as the measured spectra (fig. A-2), making it possible to rapidly identify absorption features belonging to a number of infrared-active atmospheric constituents. We can also display the positions and strengths of solar carbon monoxide absorption lines.

A third utility program can plot a selected region of both a measured spectrum and a simulated spectrum on the same set of axes, then calculate and plot the point-by-point differences between the two spectra (observed minus calculated), as well as the residual transmittance (fig. A-3). The capability to obtain these differences and residuals is a very powerful tool which aids in the verification of the

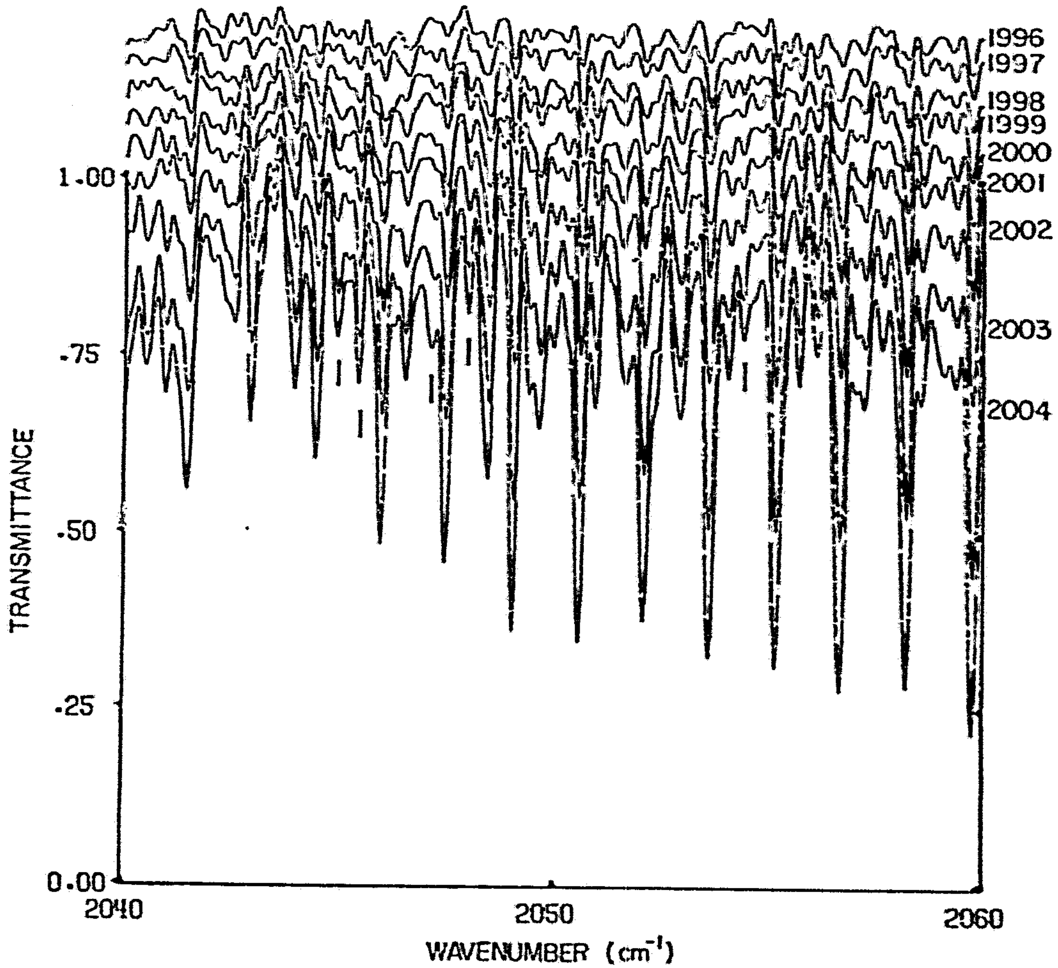

Figure A-1: Spectra measured by the Mark I interferometer in May 1976 on a balloon flight from Palestine, Texas, apodized to a resolution of 0.18 cm^{-1}. The spectra, in order of increasing zenith angle from top to bottom of the plot, are shifted along the vertical-axis for clarity. Each one has been ratioed to a high-Sun background spectrum.

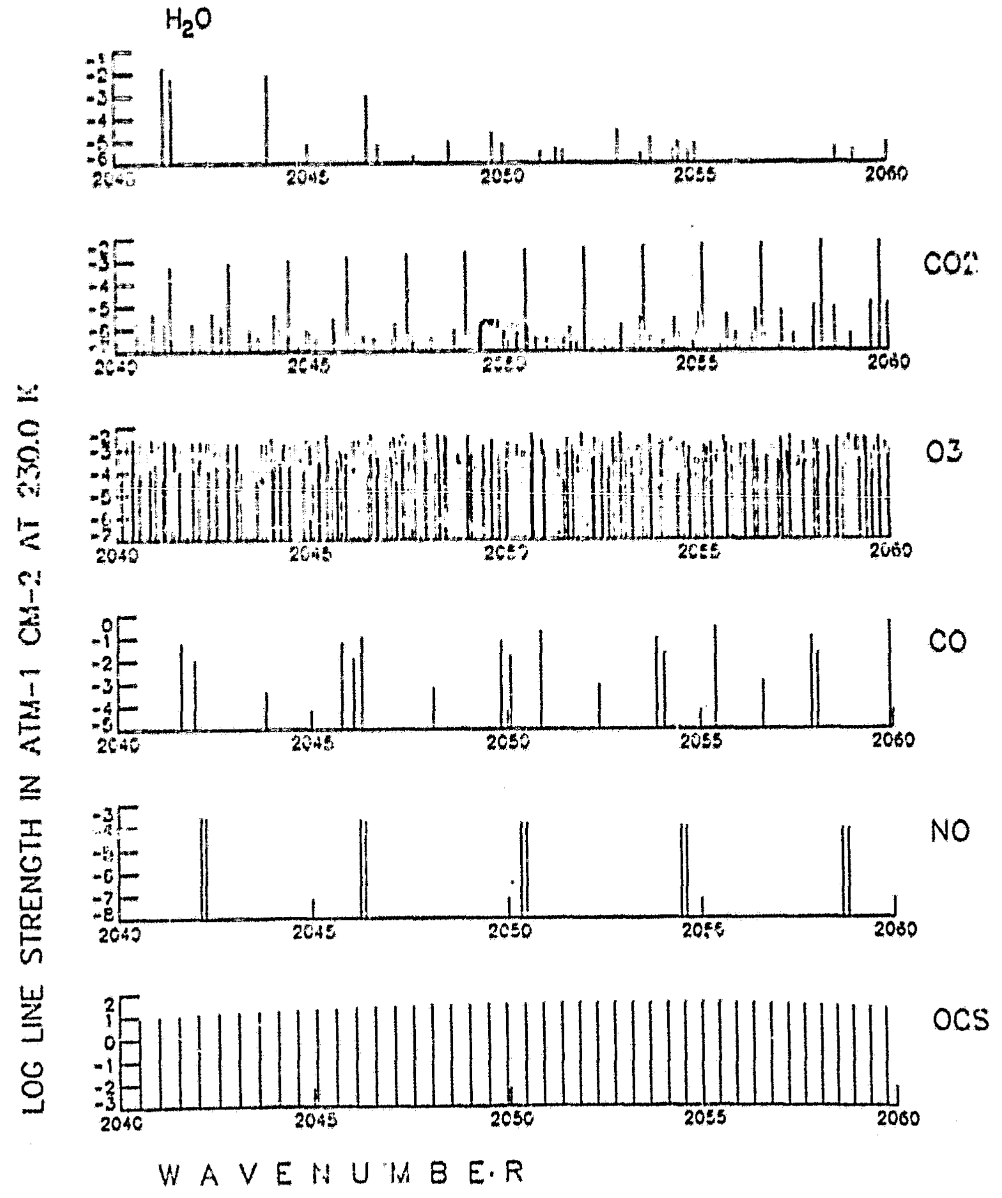

Figure A-2: Atlas plot of line positions and intensities for the spectral region shown in Figure 3-1. Data from the 1980 AFGL compilations (Rothman, 1981; Rothman et al., 1981) were used to calculate line strengths for a typical stratospheric temperature (230 K).

accuracy of spectroscopic parameters, retrieved gas concentration profiles, and of the assumed pressure-temperature profile. The differences and residuals will also allow us to readily determine the presence or absence of unaccounted for trace species. For example, in fig. A-3, the measured spectrum is compared to a simulation which takes into account absorption by only the three major gases, H_2O, CO_2, O_3. Absorption due to the ν_3 fundamental band of OCS also occurs in this spectral region. However, the differences and residuals in the figure do not show evidence of a detectable OCS absorption signal in the Mark I spectral (resolution 0.18 cm^{-1}). With the higher resolution of the second generation JPL interferometer (0.05 cm^{-1}), it is expected that the ratio residuals will clearly show the presence of OCS (Smith et al., 1980a). Nearly all of the absorption features in the residual absorption spectrum shown here can be related to weak absorption by CO, which was not included in the simulation, and to probable errors in line strengths given in the AFGL compilation for CO_2 lines and several of the O_3 lines.

A-2 Simulation of Spectra

Development of an accurate line-by-line simulation technique is a critical step in analysis of complex absorption spectra since the identification of new gas absorption features and subsequent determination of gas concentrations require an ability to completely characterize the contribution due to absorption by known gases. Simulation algorithms are not only used to study interfering absorption and to verify the results of retrievals, but they are also integral elements of the retrieval programs themselves.

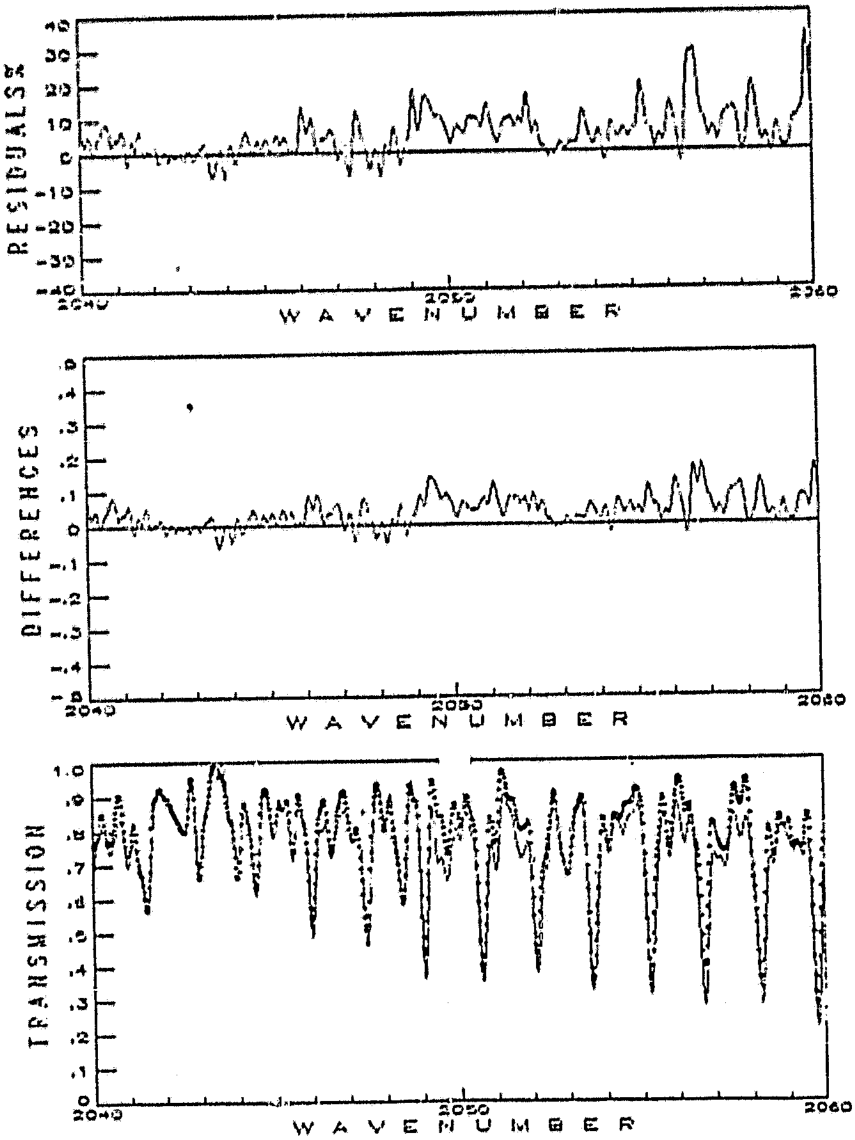

Figure A-3: Comparison of measured and simulated spectra. In the lower panel, the solid curve represents the measured spectrum, which is the same as the lowest curve in Figure 3-1 and corresponds to a geometric tangent altitude of 21.8 km. The crosses represent a simulation of the measured spectrum (see Figure A-4). The differences are plotted in the center panel, and the residuals are plotted in the upper panel.

A working simulation model, based on the algorithm of Drayson (1965), is used at the Langley Research Center to calculate simultaneous absorption by up to ten gases in a multi-layer atmosphere with realistic gas concentration, temperature, and pressure profiles. The model includes the effects of atmospheric refraction and the limb-viewing geometry. The simulated spectra are convolved with the appropriate instrument line shape function for the interferometer, allowing the choice of several degrees of apodization. Continuum absorption, solar carbon monoxide lines, and instrument effects such as channeling can also be included in the simulation at the user's option. Although the model is currently used to simulate portions of the Mark I spectra (fig. A-4), its parameters can be easily changed to simulate the higher-resolution Mark II and ATMOS data. As shown in this figure, we can simulate the contribution of each gas to the total spectrum. We have found such simulations very useful for the identification of individual features and for the selection of optimum features for retrieval. We generally obtain good agreement between the simulated and measured spectra (e.g., fig. A-3). Typical sources of discrepancies are uncertainties in the pressure, temperature, and gas concentration profiles assumed in the model; inaccurate modeling of filter effects and solar lines present in the measured spectra; and, in the majority of cases, missing or erroneous line parameters input to the simulation program.

A continuous effort has been made to improve the computational speed and efficiency of the line-by-line simulation algorithm discussed above. However, this technique becomes quite time-consuming and expensive when used to simulate spectral intervals larger than about

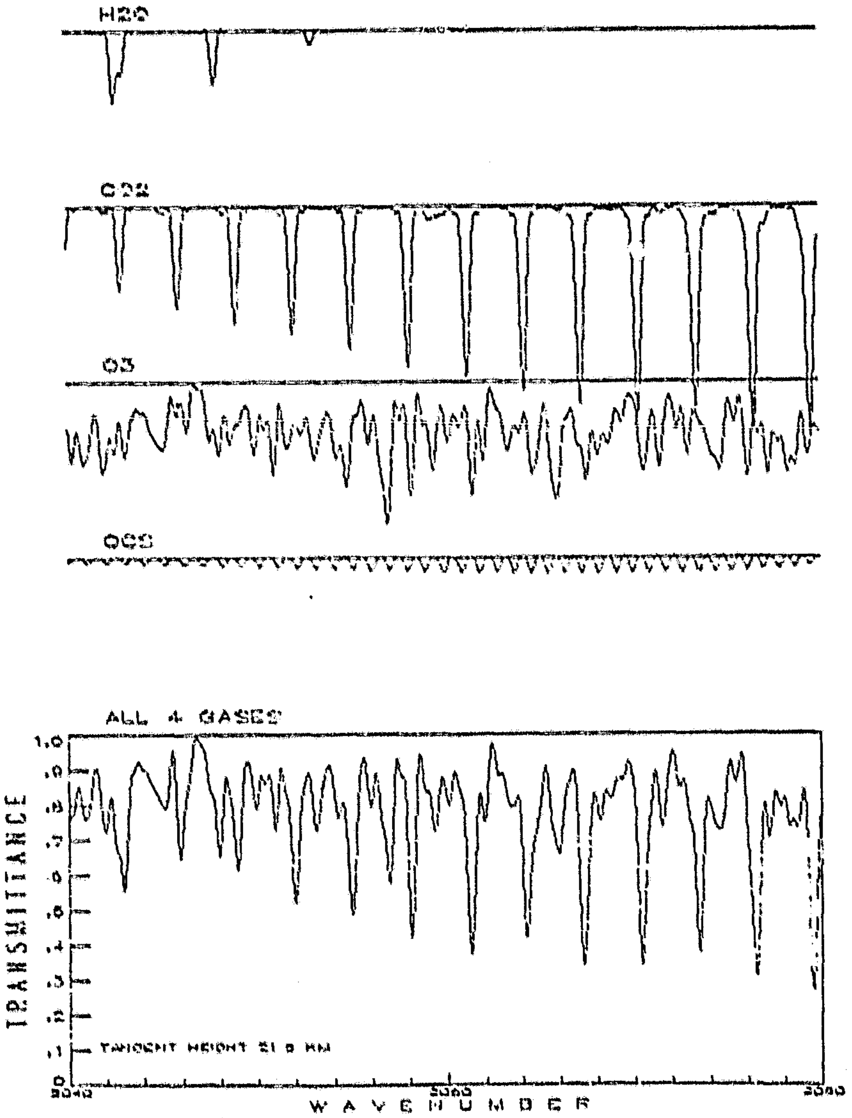

Figure A-4: Simulation of Mark I balloon-flight spectrum. The calculations are based on spectroscopic parameters from the AFGL compilations (see Figure 3-2) and a multi-layer atmospheric model with H_2O, and CO_2 and O_3 profiles retrieved from this same set of Mark I spectra. The OCS profile was adopted from photochemical model results (Crutzen, private communication, 1979). The simulated signals for the individual gases are represented by the four upper curves, while the lowest plot shows the spectrum due to simultaneous absorption by all the gases.

20 cm^{-1}. We also have an operational version of the AFGL FASCOD1B program (Clough et al., 1981) which can be used to simulate broad regions of Mark I, Mark II, and ATMOS spectra. A third line-by-line model, running on the Cyber 203 computer at LaRC, has been used by investigators on several other remote sensing projects in our group and appears to offer some advantages in speed and efficiency. An alternative spectral simulation technique, based on the Fourier transform method of Dr. Mankin at NCAR, has been successfully used in LIMS (Limb Infrared Monitor of the Stratosphere) data analysis at Langley Research Center. These alternative simulation programs will be tested and evaluated for use in analysis of ATMOS spectra.

A-3 Pressure and Temperature Sensing Using CO_2 Lines

In a single limb-viewing experiment from a balloon platform, the tangent height is usually determined from the instrument pointing information, and pressure and temperature data needed for retrieval of gas concentrations are obtained from separate balloon or rocketsonde observations or are adopted from climatological data. However, for a satellite experiment which has wide spatial and temporal coverage and yields a large volume of data, climatological pressure and temperature data may be incomplete and correlative rocketsonde measurements nonexistent, particularly over the oceans. Thus, it is desirable to get temperature and pressure profiles directly from the measured spectral data. In addition to reducing dependence on climatological data or correlative measurements, the use of pressure and temperature profiles retrieved from the experimental spectroscopic data leads to reduced errors in the mass paths and gas mixing ratios determined from the same experiment.

We have developed a technique for retrieval of pressure profiles from radiometric measurements (Park et al., 1979) and an equivalent-width technique for simultaneous retrieval of pressure and temperature profiles using a pair of CO_2 absorption lines having different lower-state energies, but appearing in the same spectrum (Park et al., 1980a, b; Park 1982). Tests using both simulated and measured CO_2 absorption data (from the 1976 Mark I spectra) show that the simultaneous retrieval method can be used to infer upper atmospheric pressure and temperature profiles with small RMS errors (fig. A-5), provided that CO_2 absorption line parameters are known very accurately. Recently, the effects of interferogram smearing and continuous absorption were included in a reanalysis of Mark I data (Park, 1982).

As has already been mentioned in the earlier discussion of the equivalent width method of gas concentration retrievals, uncertain knowledge of the level of background absorption in the spectrum can result in significant pressure and temperature errors. Techniques to improve the accuracy of equivalent width or integrated absorption values determined from measured spectra are now being studied, particularly in the 4.3-μm temperature sensing region where continuous absorption by N_2 and CO_2 is important in the lower stratosphere. We also intend to incorporate the nonlinear least-squares technique in the pressure-temperature retrieval scheme.

A-4 Compilation of Spectroscopic Parameters

Accurate knowledge of spectroscopic line parameters is an essential prerequisite for the simulation of atmospheric spectra and the retrieval of pressure, temperature, and gas concentration profiles. For the past

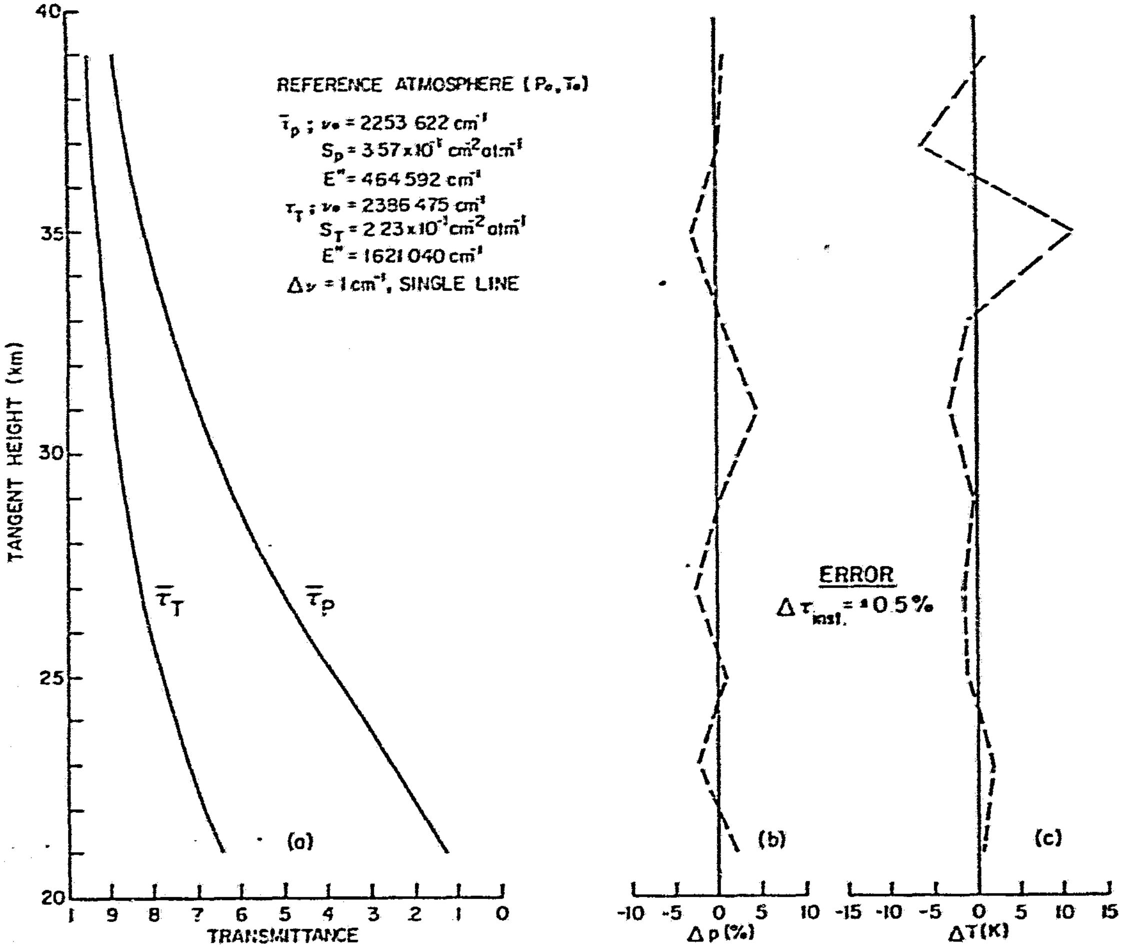

Figure A-5: Simultaneous inversion of pressure and temperature using simulated data for absorption by two single CO_2 lines near 4.3 μm in a realistic atmosphere: (a) mean transmittances for 1 cm^{-1} intervals centered at ν_0, $\bar{\tau}_p$ (for pressure sensing) and $\bar{\tau}_T$ (for temperature sensing): (b) error (Δp in percent) in retrieved pressures: (c) error (ΔT in K) in retrieved temperatures.

several years, an active effort has been made at Langley to maintain an up-to-date compilation of line parameters in support of ATMOS, HALOE, LIMS, ALS, LHS, and other remote sensing experiments. Absorption line parameters for a number of trace gases which are of interest in upper atmospheric studies but not listed in the earlier AFGL compilations (McClatchey et al., 1973; Rothman and McClatchey, 1976; Rothman, 1978; Rothman et al., 1978) have been compiled from a number of sources and used by us in line-by-line simulations of the JPL Mark I spectra and in the development and testing of algorithms for retrieval of pressure, temperature, and mixing ratio profiles (Smith et al., 1980b). We, along with members of the diode laser spectroscopy group, have had considerable interaction with other groups (Goldman and Hoell, 1980) and with Dr. L. Rothman regarding the most recent update of the AFGL compilations (Rothman, 1981; Rothman et al., 1981). Line parameters for the quadrupole lines of the fundamental band of N_2 and for the two strongest C_2H_2 bands in the 3-μm region were communicated to L. Rothman for inclusion in the next update to the AFGL line parameter compilation. Parameters for solar carbon monoxide lines from the fundamental and first-overtone sequences have been calculated, and the results of this work were communicated to the JPL ATMOS team. Methods for simulating the solar carbon monoxide lines have been developed based on the Minnaert semi-empirical formula of radiative transfer (Minnaert 1935).

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