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IN SEARCH OF STRATOSPHERIC BROMINE OXIDE

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ABSTRACT

The Imaging Spectrometric Observatory (ISO) is capable of recording spectra in the wavelength range of 200-12000 Angstroms. Data from a recent Spacelab 1 ATLAS mission has imaged the terrestrial airglow at tangent ray heights of 90 and 150 km. These data contain information about trace atmospheric constituents such as bromine oxide (BrO), hydroxyl (OH), and chlorine dioxide (OClO). The abundances of these species are critical to stratospheric models of catalytic ozone destruction. Heretofore, very few observations have been made especially for BrO. We have developed software to purge unwanted solar features from the airglow spectra. The next step is a measure of the strength of the emission features for BrO. The final analysis will yield the scale height of this important compound.

ACKNOWLEDGEMENTS

My 10 week stay at the Marshall Space Flight Center has been very rewarding, both personally and professionally. The praises I sing and the laurels I give should be laid at the feet of many. First, I would like to thank Dr. Marsh Torr for including me in her group and for the time she has spent in helping me learn the ropes.

I am also very grateful to Hassan Dougani, a graduate student at UAH, for his friendship and for the long hours he has put in developing software and showing me how to use it.

Thanks to Barry Welsh for his patience when he taught me how to operate the spectrometer.

I appreciate the friendship of Alex Tejada, Richard Hoover, and the members of our lunch group for adding their personal touches.

Mr. Philip Butler deserves recognition for spending a week of his vacation developing a FORTRAN program to aid in screen management for the spectrometer analysis.

Finally, I want to thank Dr. Michael Freeman and Ms. E. Cothran for their untiring efforts in making the program a success.

I contributed, I learned, and I made good friends. Thank you all.

INTRODUCTION

The integrity of the terrestrial ozone layer has been a research topic of much concern and interest since the early 70's when it was demonstrated that industrial uses of halogenated compounds could lead to serious deliterious effects.(1)(2)

The critical nature of this shield against the near-ultraviolet is even more striking when you realize that the column abundance(3) of ozone is only 0.3 cm. Figure 1 shows the absorption characteristics of the atmosphere and the role played by ozone.

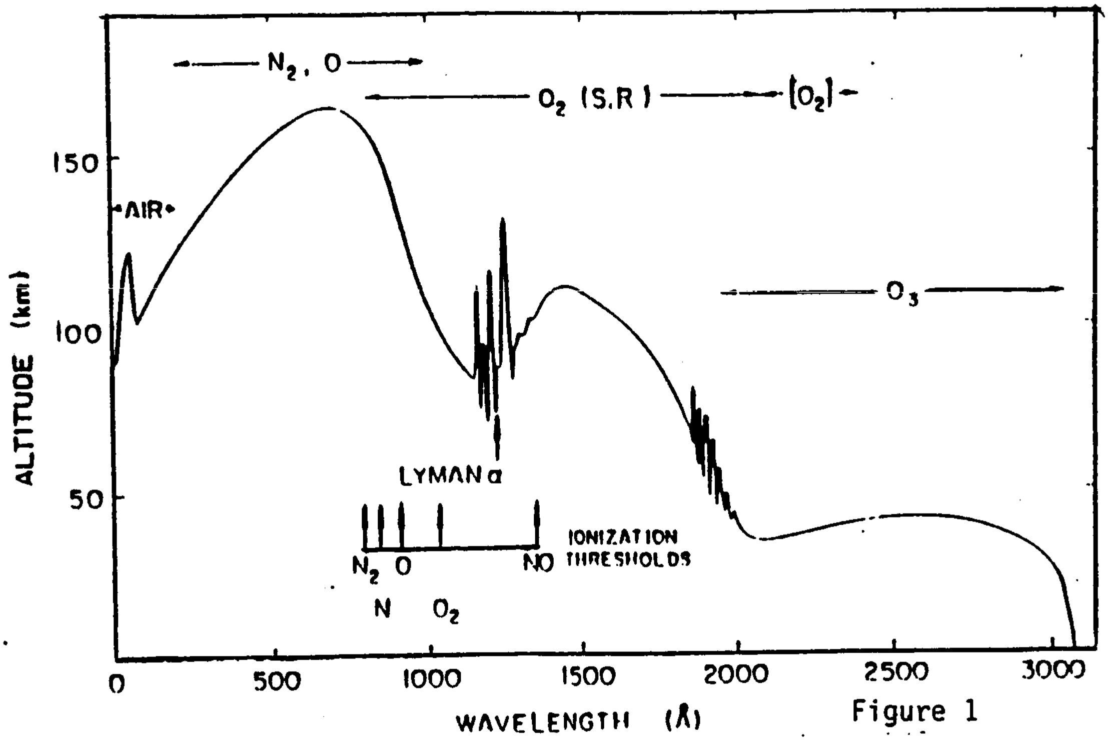


Figure 1

Ozone is the only atmospheric constituent with a significant absorption cross-section for the range of λ 2000-3000 Angstroms. This region is called the Hartley bands and continuum. It physically represents photodissociation of ozone, to wit:

$$O_3 + h\nu \rightarrow O + O_2 \;\ldots\ldots \quad (1)$$

Ozone is naturally replenished through the "reverse" of this reaction:

$$O + O_2 + M \rightarrow O_3 + M \quad .... \quad (ii)$$

where M is an unspecified third body.

Figure 2 shows the temperature profile of the atmosphere as well as the names for the major layers.

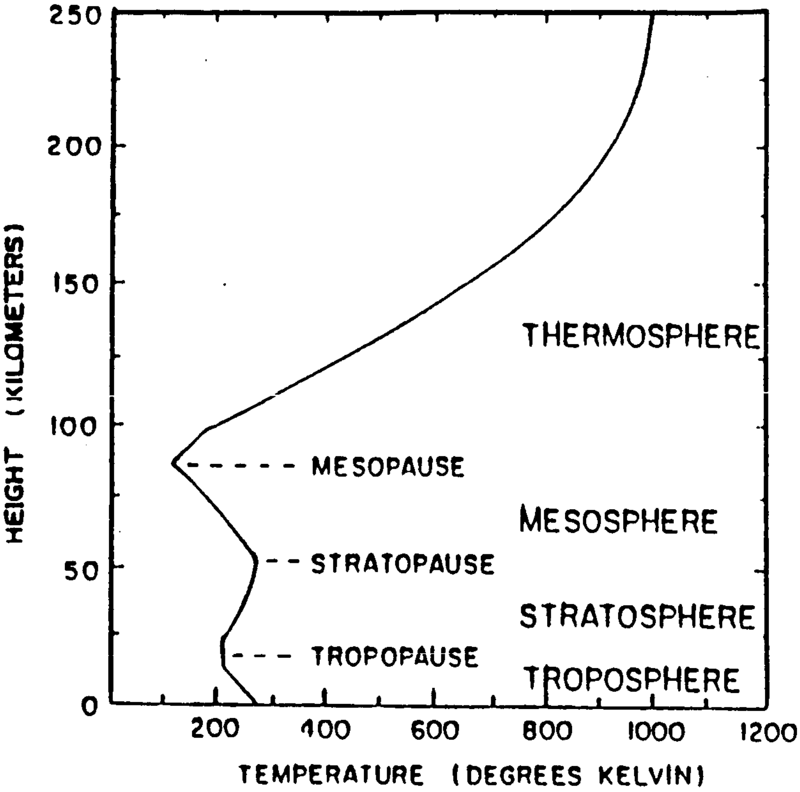


Figure 2

The troposphere has a ceiling at 18 km near the equator and roughly half that near the poles. The stratosphere extends from there up to about 50 km where it meets the mesosphere. The maximum concentration of ozone occurs at about 50 km. This fact, along with the absorption of energy shown in eq (i), results in heating at the stratopause and the observed temperature reversal through the stratosphere.

BACKGROUND

For a very long time there has been a balance or ozone production and destruction. The former principally through eq (ii) and the latter through photodissociation and chemical reactions with minor species.

One of the primary sinks for O_3 is a group of molecules termed the halomethanes. These are compounds where one or more of the hydrogens in methane (CH_4) is replaced with a halogen such as chlorine, bromine, or fluorine. Three examples of halogenated compounds found in the atmosphere are methyl bromide (CH_3Br), and the chlorofluoromethanes, Freon-11 (CF_2Cl_2) and Freon-12 ($CFCl_3$).

Although many such molecules do occur in nature, e.g. methyl bromide is a result of marine biology, the tipping of the scales occurred with the onset of industrial production of these compounds.

Methyl bromide is used as an agricultural fumigant, as a gasoline additive, and in fire extinguishers. The freons, of course, are used in cooling systems and as inert carriers in aerosol spray cans.

These compounds are very inert. It is difficult to get them to chemically react with anything. This is the reason that they are attractive to industrial users. They are also insoluble in water, so the ocean is not a sink for these contaminants. This inert property results in their collecting in the troposphere for extended periods of time until they are transported up to the stratosphere.

In the stratosphere, they are photolysed by the ultraviolet into atomic Cl, Br, etc. Some researchers(4) have shown that when adhered to the surface of dust or grains these halomethanes can be photodissociated by the more abundant visible wavelengths due to quantum mechanical surface chemistry effects.

A free chlorine or bromine atom has an average lifetime for chemical reaction in the stratosphere of approximately 0.05 seconds. It reacts principally with an ozone molecule as

$$Cl + O_3 \rightarrow ClO + O_2$$
$$Br + O_3 \rightarrow BrO + O_2 \qquad ....(iii)$$

On the face of it, the situation is not critical; one bromine destroys one ozone. Unfortunately, that is not the whole story. The BrO (and similarly for ClO) is then dissociated through one of many possible paths back into Br. Two of the important reactions are:

$$BrO + O \rightarrow Br + O_2 \text{ or}$$
$$BrO + BrO \rightarrow 2\ Br + O_2 \qquad ....(iv)$$

The bromine atom is thus free to react with another ozone. It typically goes through approximately 1000 cycles before being trapped as HBr and rained out as acid rain.

It is important to keep in mind that perforce I am simplifying the reactions involved--while keeping the principle ideas. Modern stratospheric computer codes contain hundreds of reactions that are both strongly interdependent and usually very stiff. This makes definitive answers hard to find.

As an example of the complexity, the following set of equations show some of the possible reactions involved in freeing Br from BrO.

$$BrO + h\nu \rightarrow Br + O$$
$$BrO + BrO \rightarrow 2\ Br + O_2$$
$$BrO + BrO \rightarrow Br_2 + O_2$$
$$BrO + O \rightarrow Br + O_2$$
$$BrO + O_3 \rightarrow Br + 2O_2 \qquad ....(v)$$
$$BrO + OH \rightarrow HBr + O_2$$
$$BrO + NO \rightarrow Br + NO_2$$
$$BrO + NO_2 + M \rightarrow BrONO_2 + M$$
$$BrO + HO_2 \rightarrow HOBr + O_2$$

The models are so untenable that it is usually the custom to group different equations into families or "chemistries". Then the assumption is made that the reaction rates are fast enough that the family is always in equilibrium. In the last few years this has been shown to be a false assumption. For example, considering the bromine and chlorine catalytic cycles separately a certain degradation of the ozone abundance would be calculated for each. The amount depends on how fast bromine (or Cl) is freed (see eqs (v)) to participate in the ozone cycle.

However, because the two chemistries have been studied separately, a very important reaction between the two families is overlooked, viz:

$$\begin{aligned} BrO + ClO &\rightarrow Br + Cl + O_2 \\ \text{or} \quad &\rightarrow Br + OClO \end{aligned} \qquad \text{.......(vi)}$$

This is an exothermic reaction that is very important to the catalytic cycles of both Br and Cl. The presence of bromine then, not only results in the destruction of ozone directly, but it also helps the catalytic cycle of chlorine. How important is bromine to the catalytic cycles? Consider that the concentration of chlorine is approximately 2 parts per billion by volume (ppbv). Figure 3 shows that as little as 20 parts per <u>trillion</u> by volume (20 pptv) of bromine can reduce the ozone layer by 2.5 %.

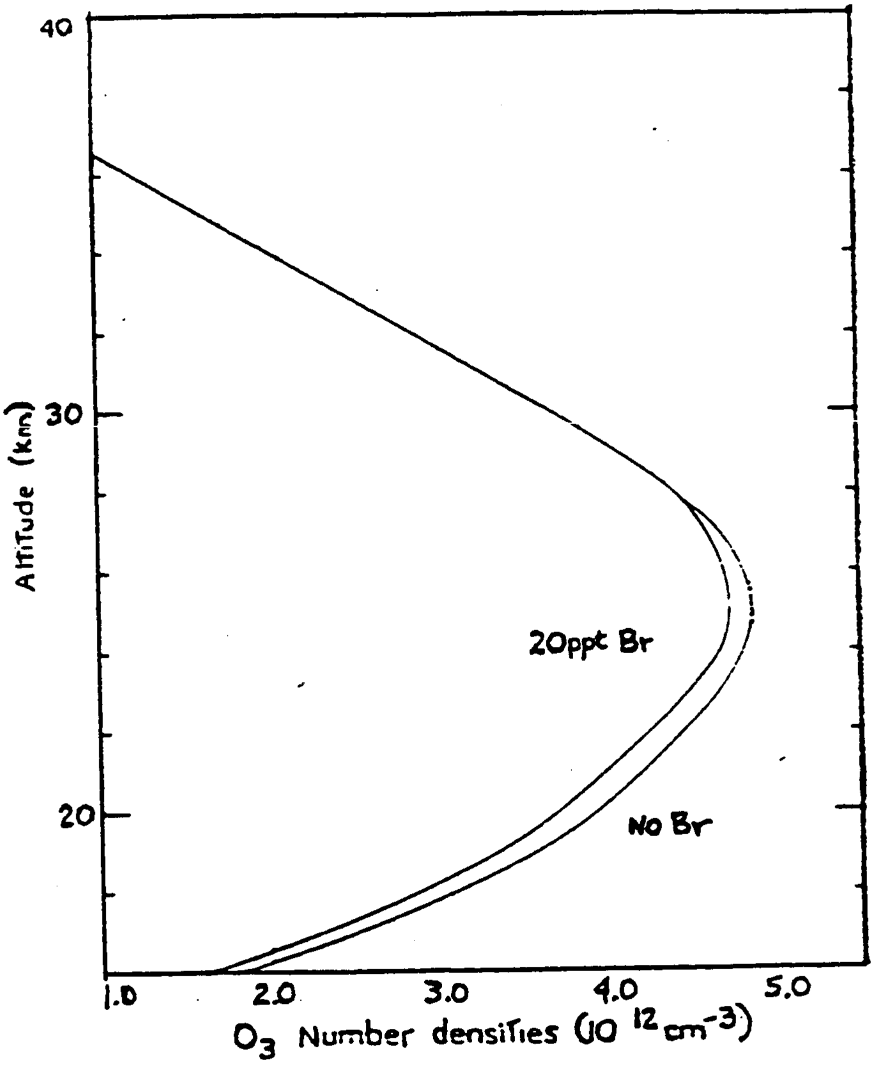

40
30
20
Altitude (km)
20ppt Br
No Br
1.0
2.0
3.0
4.0
5.0
O_3 Number densities (10^{12} cm^{-3})

Figure 3

OBJECTIVES

In the troposphere, bromine is found as CH_3Br. In the stratosphere, it occurs principally as BrO. Figure 4 shows model calculation of stratospheric concentrations.

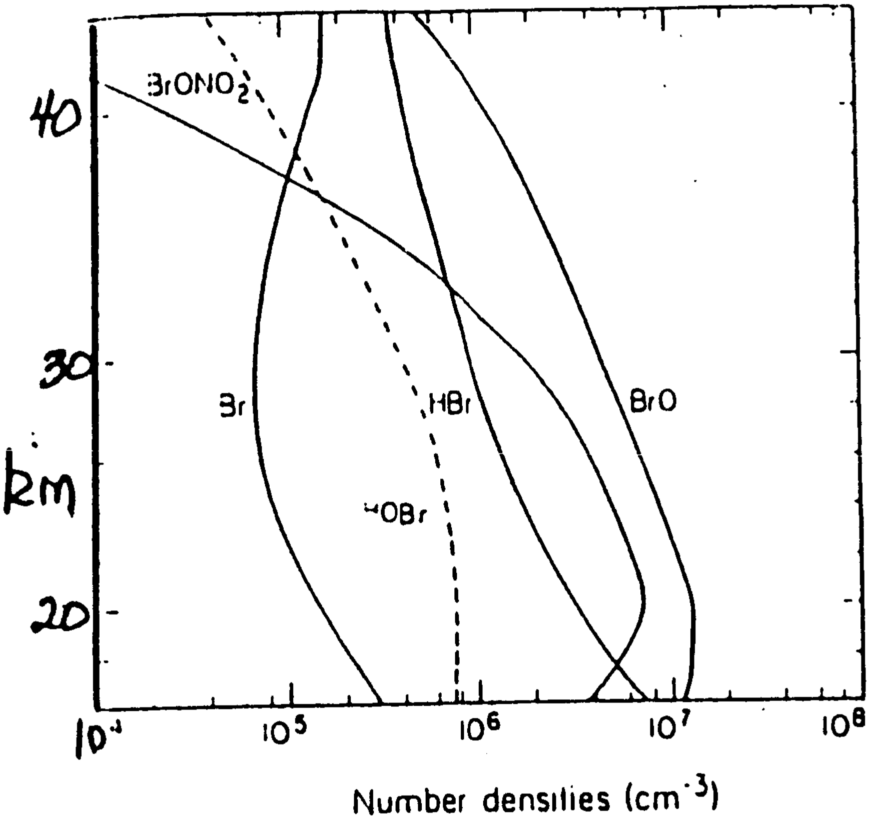


Figure 4

One problem with the stratospheric codes is the lack of data for the abundances of minor species such as OH, BrO, and OClO. Dr. Marsha Torr has designed and built an imaging spectrometer that simultaneously measures spectra from 200 to 12,000 Angstroms. In one form or another this instrument has flown on the space shuttle (ATLAS mission Spacelab 1), as a balloon payload from Palestine, TX, and a scaled-down version could be available for future planetary studies.

Figure 5 shows a diagram of the Imaging Spectrometric Observatory (ISO) instrument that flew on the shuttle.

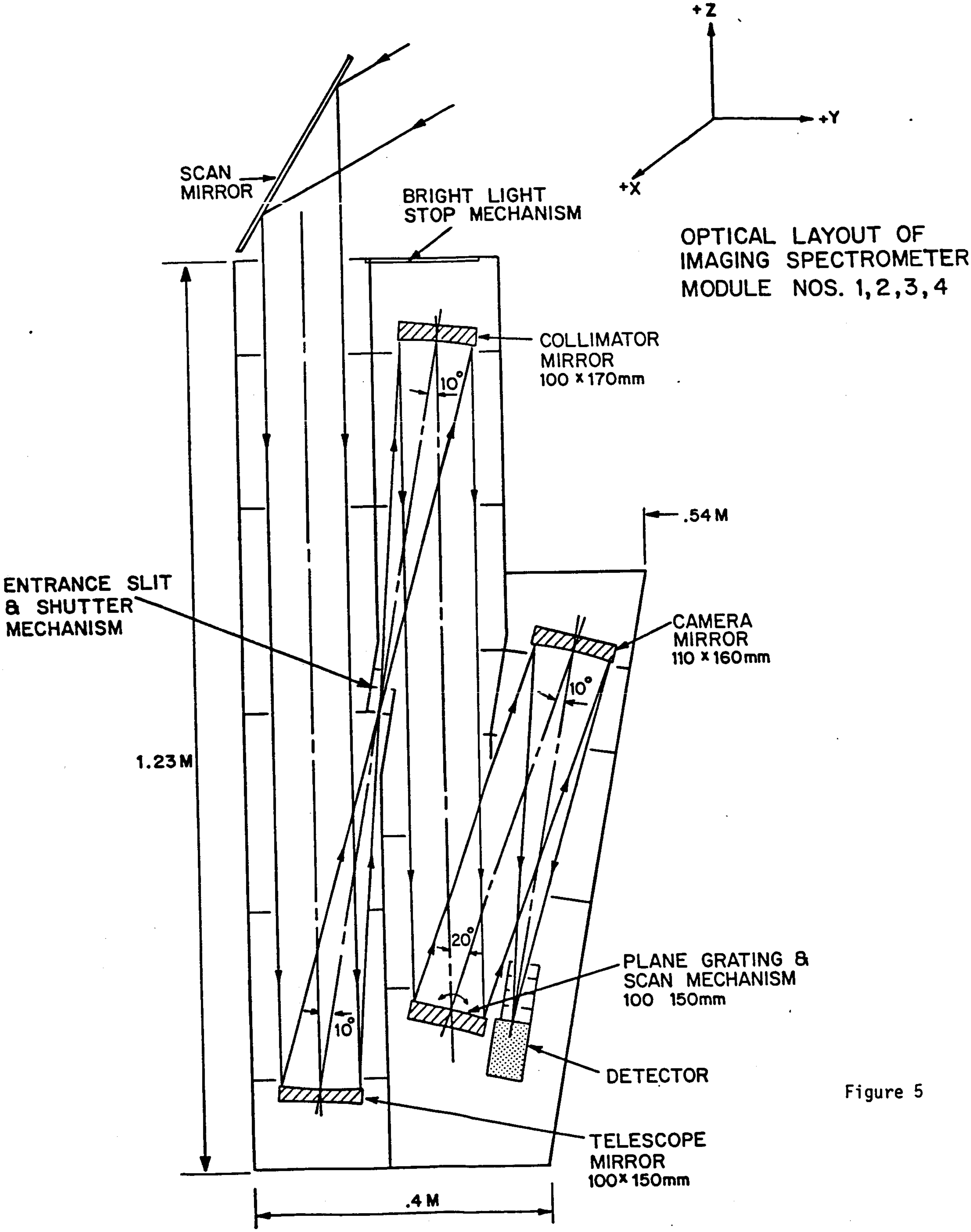
The objective this summer has been to analyze the ATLAS mission data to determine the concentration of BrO through the strengths of its emission bands. Furthermore, since the geometry of the spectrometer allows a degree of altitude separation, the possibility exist to determine the scale height of bromine oxide.

THE DATA

Figure 6 presents the ISO airglow spectrum measured at a tangent ray height of 150 km. Some obvious features are the H and K calcium solar absorption lines at 3933 Angstroms and 3956 Angstroms. At 3914 Angstroms there is the strong terrestrial emission due to $N_2{}^{+}1N$. There is also a strong emission feature at 3570 Angstroms due to $N_2 2P$ and $N_2{}^{+}1N$. In order to better see which features are terrestrial in nature it is necessary to divide this spectrum by a similar solar spectrum. This will presumably remove such features as the two calcium absorption lines and other features indigenous to the sun. Figure 7 shows a solar spectrum taken at the National Solar Observatory (Kitt Peak).

Since the scales and resolution of the two spectra are different (FWHM = 7.5 Angstroms and 0.05 Angstroms respectively), the solar spectrum must first be smoothed or convolved with the instrumental profile and then scaled so that dividing one into the other will effectively remove the common (solar) features.

A gaussian distribution with a full width at half maximum (FWHM) of 8 Angstroms was first used as an approximation for the instrument profile. Figure 8 is an expanded plot of the H and K lines for the smoothed solar spectrum and the ISO data. This figure shows how well the convolution and scaling work. It also showed the need to slip one spectrum approximately three pixels to have it match up feature-for-feature with the other.



OPTICAL LAYOUT OF IMAGING SPECTROMETER MODULE NOS. 1,2,3,4

Figure 5

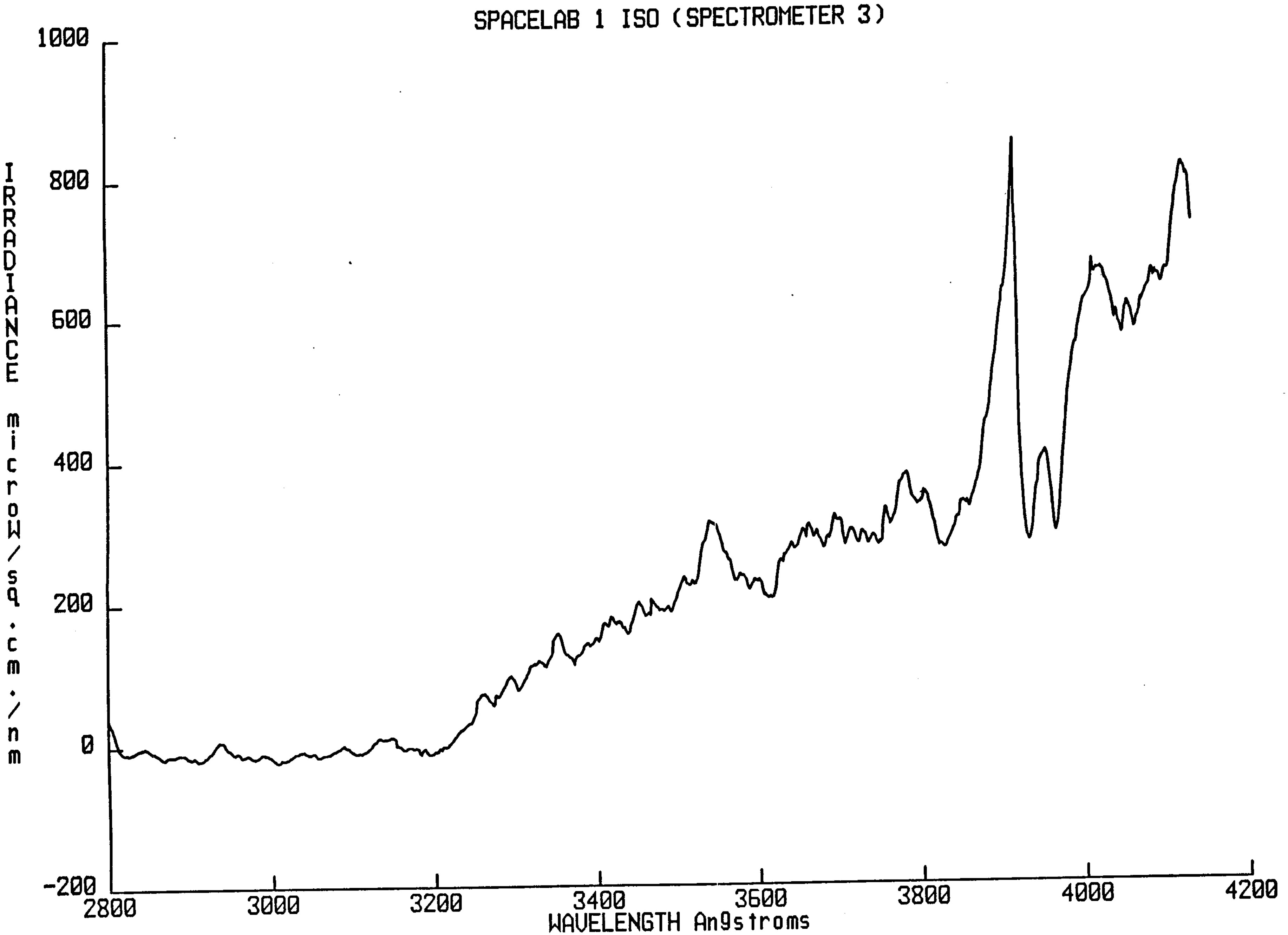

SPACELAB 1 ISO (SPECTROMETER 3)
IRRADIANCE microW/sq.cm./nm
1000
800
600
400
200
0
-200
2800
3000
3200
3400
3600
3800
4000
4200
WAVELENGTH Angstroms

Figure 6

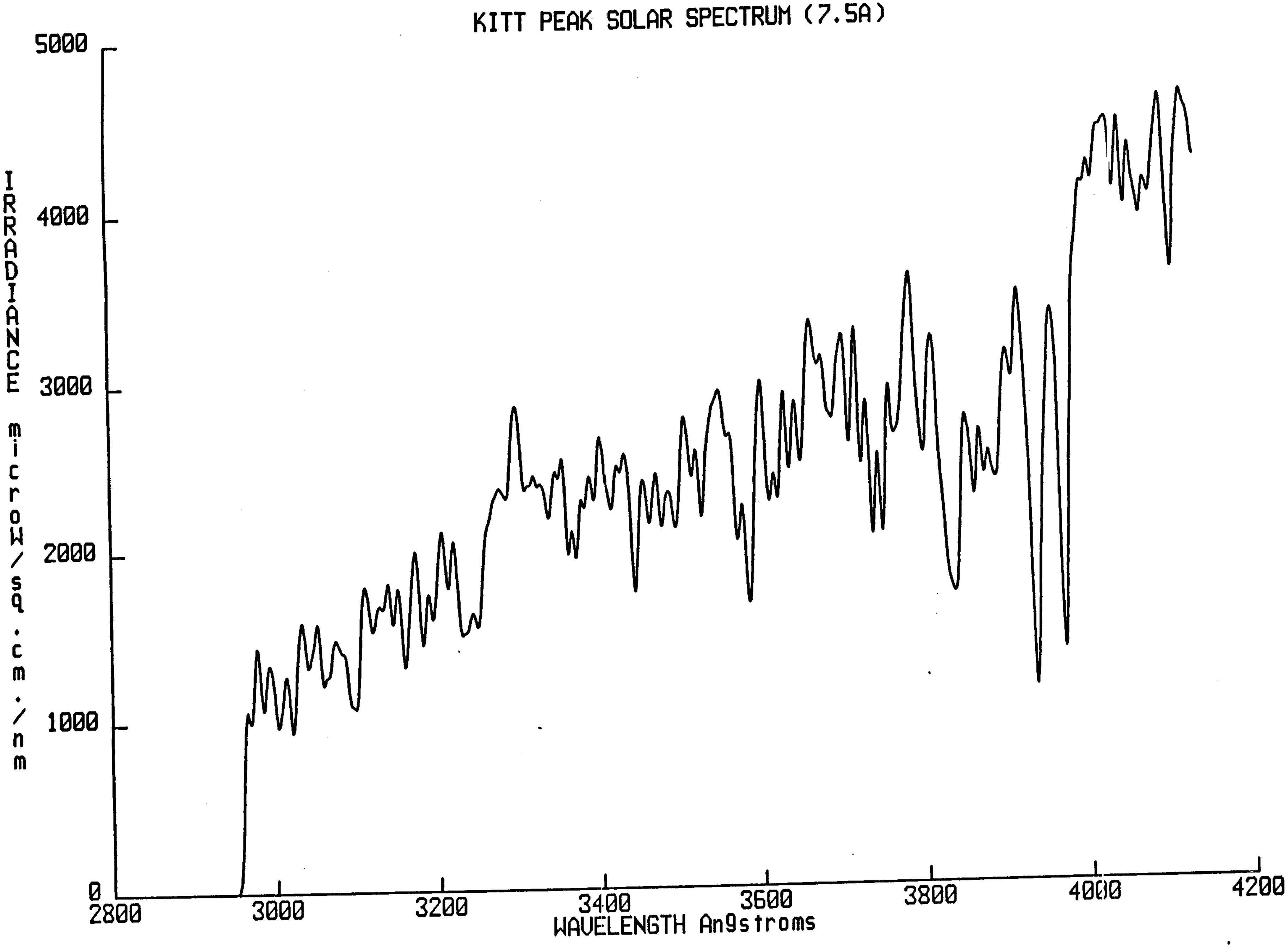

KITT PEAK SOLAR SPECTRUM (7.5A)
IRRADIANCE microW/sq.cm./nm
5000
4000
3000
2000
1000
0
2800
3000
3200
3400
3600
3800
4000
4200
WAVELENGTH Angstroms

Figure 7

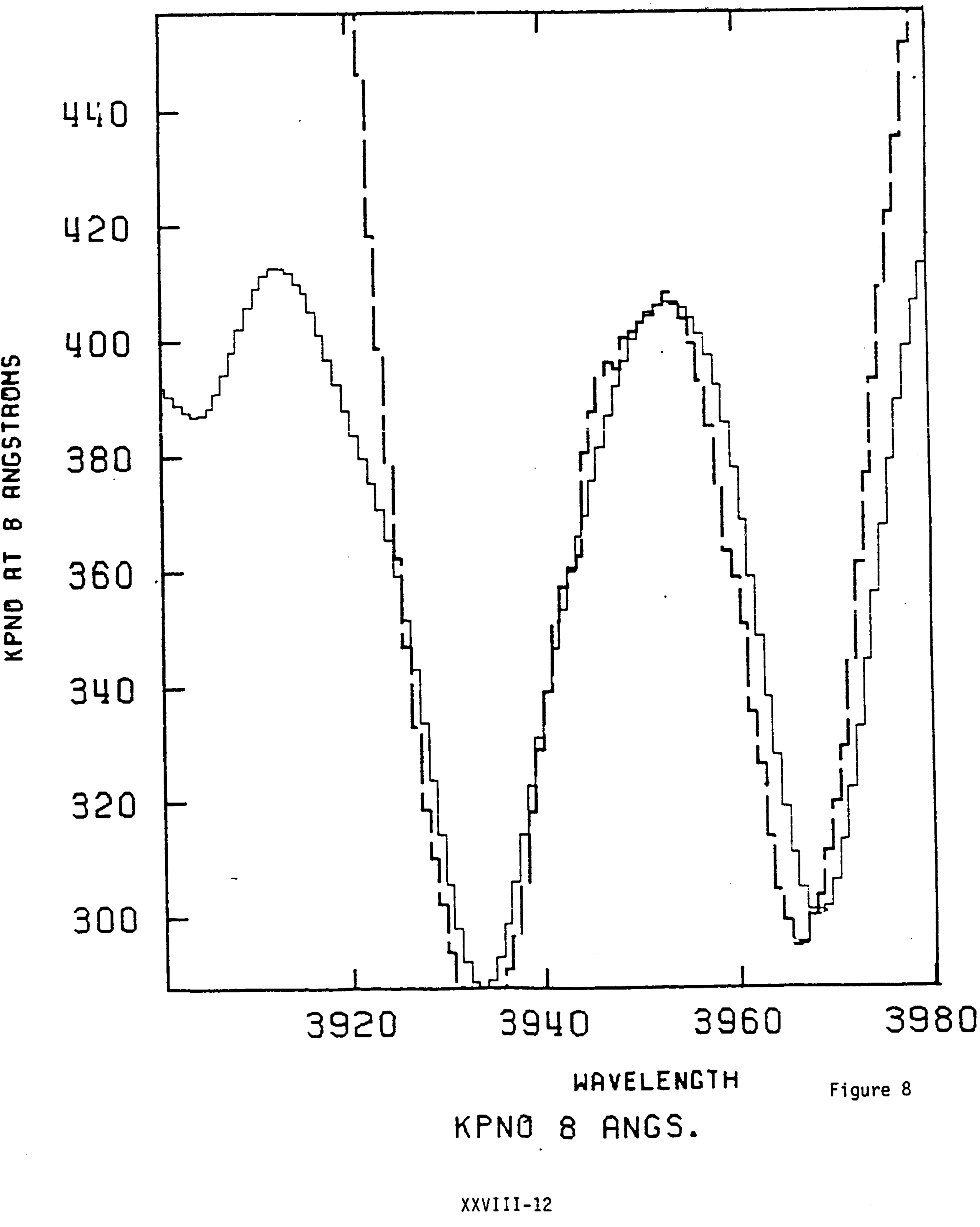


Figure 8

KPNO 8 ANGS.

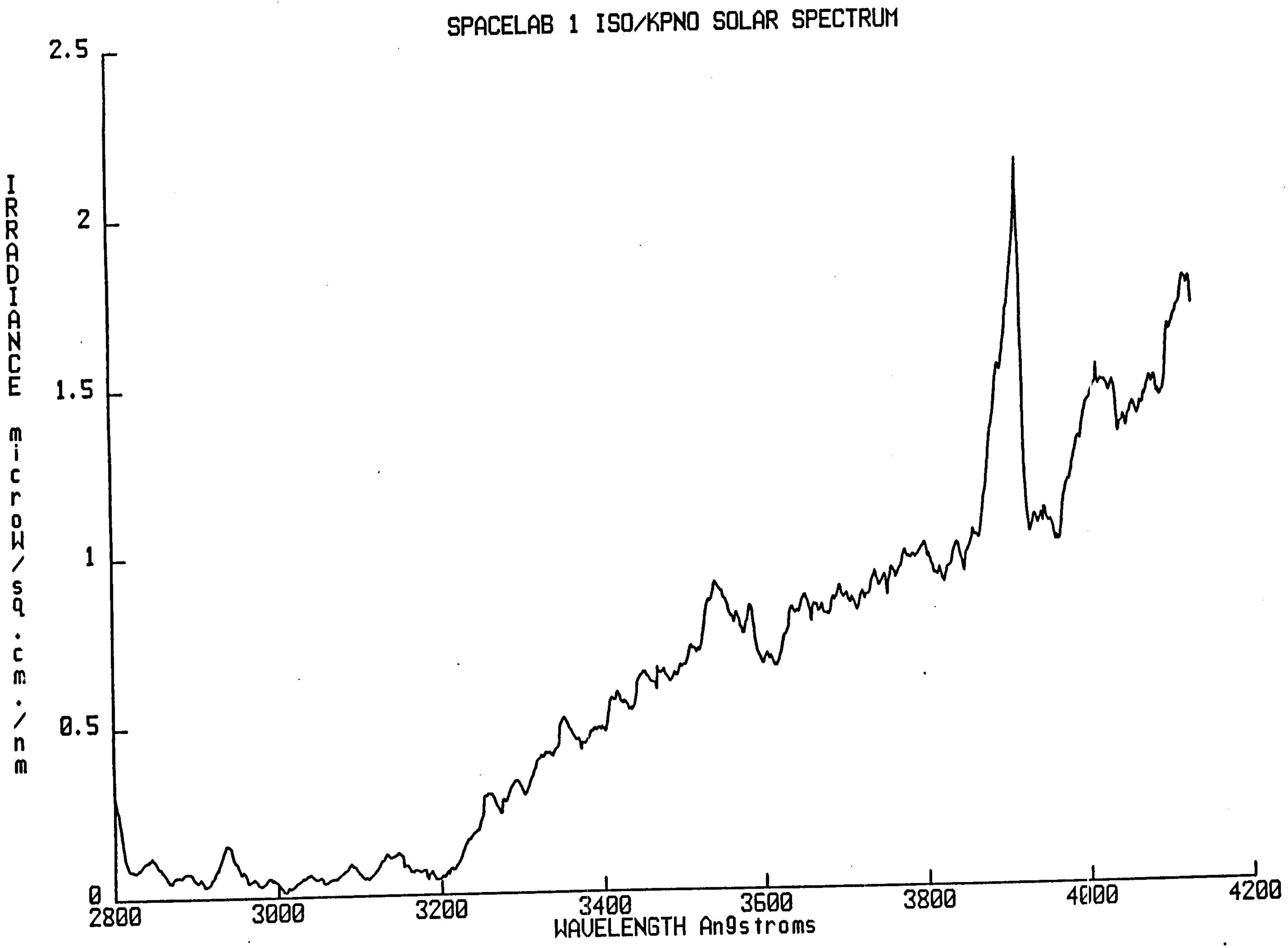

SPACELAB 1 ISO/KPNO SOLAR SPECTRUM
IRRADIANCE microW/sq.cm./nm
2.5
2
1.5
1
0.5
0
2800
3000
3200
3400
3600
3800
4000
4200
WAVELENGTH Angstroms

Figure 9

Figure 9 is the spectrometer data after division by the solar spectrum. The H and K lines are effectively removed. It is obvious that the spectrometer data (fig 6) shows a greater difference between the intensity at 3000 Angstroms and that at 4000 Angstroms than does the KPNO solar spectrum (fig 7). This can be understood when you realize that the ISO spectrometer is pointed tangent to the ozone layer while the solar spectrum was taken normal to the layer. The ISO configuration line of sight has a larger optical path length through the ozone than does that of the KPNO. The increased ozone absorption distorts the divided spectrum (Figure 9). We are currently studying ways to remove this effect.

CONCLUSIONS AND RESULTS

Since the amount of ATLAS data is voluminous, final results and conclusions are not yet available. However, during the course of the summer, there have been many small accomplishments that together will ultimately contribute to the final report. It is appropriate to record some of these here.

Solar Spectrum

Ideally, we would like to divide the ISO spectrum by a solar spectrum that is free of terrestrial features. This means that the spectrum must be taken from a platform above the earth's atmosphere. After a thorough literature search and phone calls to many well-known researchers in the field, we found three sources of solar spectra. Actually, only two fit the bill of being high-altitude spectra. The third was the ground-based spectrum from the National Solar observatory (KPNO). It had the benefits of being immediately available and of very high resolution.

The other two spectra are from the space shuttle and rocket-borne measurements. The investigators responsible for the data reduction and ultimate dissemination are Jim Mentall and G. Bruckner. They both said that their data were not yet available, but we would be on their mailing list for future delivery. We decided to use the KPNO data in order to proceed with software development. The new solar data will be substituted when it arrives.

KPNO Data

The KPNO solar spectrum is the same as that described in Solar Flux Atlas from 296 to 1300 nm by Kurucz , Furenlid, Brault, and Festerman. The tape is marked KURUCZ TAPE 1 in the Atomic Physics Branch. There are basically two sets of data on the tape, both covering the complete spectral range above. The first is at a resolution of 0.5 pm from 296 to 800 nm and 1.0 pm from 800 to 1300 nm. The second spectrum is the first degraded by a factor of 10. The resolutions are therefore 5 pm and 10 pm respectively. The resolution of the latter is much better than the 800 pm resolution of the ISO instrument and its size is one-tenth the size of the first. Consequently, it was deemed appropriate and stored on the VAX disk for use. It can be read on DISKO:[LESTRADE.SOLAR]KPNO.DAT.

Software

There are two principal programs developed for data reduction. The first (GENSOLAR.EXE) convolves the Kitt Peak spectrum with a gaussian function to generate a solar spectrum suitable for division into an ISO spectrum. The second (DIVSOLAR.EXE) does the actual division. They also reside in the VAX area DISKO:[LESTRADE.SOLAR]. Executing the programs is quite straightforward. GENSOLAR asks for the input solar file (KPNO.DAT) and the output convolved spectrum. I used an extension of ".SMO" for the latter. You have the choice of having the output spectrum at user-supplied wavelengths or at those matching the ISO spectrum file. A sample ISO file might have the name "ARRAYOUT.REQ".

Mr. Phil Butler had more experience than most with the VAX screen management processes. He spent a week working to develop a friendly user-interface for these programs. Due to a lack of time, the interface was not implemented. However, it will be in the near future.

Future Plans

My immediate plans are twofold. First, I will develop the software to run on the Zenith microcomputer. This will enable me to do further processing while at Mississippi State. With a micro, it will be possible to make the data smoothing and division a more interactive process. For example, the ISO spectrum could be displayed on the screen and a certain portion selected for magnification. Then the solar spectrum could be superimposed and scaled-real time, and finally divided to reveal important features.

Second, I have been assigned the 90-kilometer ISO data for analysis. The first steps will involve getting these data off the appropriate tapes, compressing them, and transferring them to the VAX. I would like to accomplish this remotely using telecommunications. The one dark cloud is the absurd security measures taken to protect the VAX from hackers. The "call-back" system installed effectively keeps everybody out. Even researchers calling in to the VAX from within the same building have given up in frustration. Efforts are continuing.

Ultimately, we plan to derive abundances of bromine oxide. My past experience with radiative transfer and level of line formation(5) should help with this goal. With the industrial usage of bromine increasing at a rate of 7% per year, this is an important goal.

REFERENCES

1. The definitive review on the catelytic destruction of ozone is: Nicolet, M., "Stratospheric ozone: an introduction to its study.", Rev. Geophys. and Space Phys. , 13, 593-636, (1975)

2. For a well-balanced discussion see: Chamberlain, J. W., Theory of Planetary Atmospheres: An introduction to their physics and chemistry. Chap. 1 and 3. (1978)

3. Consider a vertical column of atmosphere with a basal cross-section of 1 cm^2. If the total amount of ozone in that column were compressed to STP, the vertical height would be 0.3 cm. This is column abundance.

4. Yung, Y. L., J. P. Pinto, R. T. Watson, and S. P. Sander, "Atmospheric Bromine and Ozone Perturbations in the Lower Stratosphere", J. Atmos. Sci., 37, 339-353, (1980).