A-CR-194175

MEASUREMENT OF HO_2 AND OTHER TRACE GASES IN THE STRATOSPHERE USING A HIGH RESOLUTION FAR-INFRARED SPECTROMETER AT 28 KM

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NASA GRANT NSG 5175

Semiannual Status Report No. 32

For the period 1 January 1993 to 30 June 1993

Principal Investigators

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Kelley V. Chance

August 1993

Prepared for

National Aeronautics and Space Administration

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The Smithsonian Astrophysical Observatory
is a member of the
Harvard-Smithsonian Center for Astrophsysics

The NASA Technical officer for this grant is Dr. William S. Heaps, Code 916, Atmospheric Experiments Branch, Goddard Space Flight Center, Greenbelt, Maryland 20771

(NASA-CR-194175) MEASUREMENT OF HO2 AND OTHER TRACE GASES IN THE STRATOSPHERE USING A HIGH RESOLUTION FAR-INFRARED SPECTROMETER AT 28 km Semiannual Report No. 32, 1 Jan. - 30 Jun. 1993 (Smithsonian Astrophysical Observatory) 26 p

N94-13816

Unclas

G3/46 0186017

Semiannual Report No. 32

NASA Grant NSG-5175

Measurement of HO_2 and Other Trace Gases in the Stratosphere Using a High Resolution Far-Infrared Spectrometer

1. Personnel Working Under this Grant During this Reporting Period

Dr. Wesley A. Traub (Principal Investigator)
Dr. Kelly V. Chance (Principal Investigator)
Dr. David G. Johnson (Co-Investigator)
Dr. Kenneth W. Jucks (Co-Investigator)
Dr. Steven C. Wofsy (Co-Investigator)
Dr. Changqin (Jim) Xue (Programmer-Analyst)

2. Status Summary

This report covers the time period 1 January 1993 to 30 June 1993. During this reporting period we had our third Upper Atmosphere Research Satellite (UARS) correlative balloon flight and submitted the results from this flight to the Central Data Handling Facility (CDHF). We made a number of improvements in our data processing software in preparation for a new analysis of our old balloon data sets. Finally, we continue to analyze the data obtained during the second Airborne Arctic Stratospheric Expedition (AASE II).

3. AASE II

We completed a detailed examination of our preliminary column density retrievals from the AASE II, and where possible we compared our results with simultaneous measurements made by other groups. Since column density retrievals depend on the choice of mixing ratio profile, we reanalyzed our data using a standard set of mixing ratio profiles supplied by G. Toon (private communication, 1992). Starting with the standard profiles, we determined an altitude scaling factor, or degree of subsidence, using our measurements of HF, and then shifted the standard profiles in altitude using the measured subsidence factor before retrieving columns. We completed a new analysis of HF, HCl, and O_3, and our results are in good agreement with other measurements. We also analyzed H_2O and HNO_3, molecules which were not included in our preliminary analysis, and again our results are in good agreement with other groups. Since the FIRS-2 measures these molecules in emission we provide the only column measurements of HF, HCl, H_2O and HNO_3 from the DC-8 during the times when the sun was too high or too low for absorption measurements.

Several trends become apparent when our measurements of subsidence are plotted as a function of potential vorticity. For the January, February, and March flights we observe that the subsidence increases as the potential vorticity increases, and the gradient of subsidence is the steepest at the vortex edge. Descent seems to have started before our January measurements, and the region of maximum subsidence shifts to regions of lower vorticity as the winter progresses. We are continuing to investigate the significance of these trends.

Our initial analysis of the AASE II data used a singular value decomposition routine to recover the column densities or mixing ratio profiles from measured equivalent widths. This method allowed us to perform a number of computational steps before the flight campaign, thus reducing the time required to produce preliminary results. However, it made it difficult to assess the effect of systematic errors on the retrieved columns. We have developed a second processing algorithm which provides improved error estimates, but at the cost of increased post-flight processing time. This algorithm also lacks the ability to produce mixing ratio profiles. Work is in progress to complete a third set of column estimates with the improved confidence limits, most of which has been submitted to the AASE II data archive.

4. UARS Correlative Measurements Program

We had one correlative balloon flight during this reporting period. The balloon was launched from Daggett, California on March 23, 1993 at 3:30 PM PST and reached the float altitude of 129,000 feet at 6:00 PM. The balloon was terminated over the Texas panhandle after seven hours at float. We recorded data both in California and at a downrange telemetry station in Santa Fe. This was the first field test of our downrange data recording and command system, and the system performed perfectly. We achieved one hour of overlap between stations, and the downrange station extended our active control of the instrument by four and a half hours. This was also our first nighttime correlative measurement. We retrieved profiles for $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, HDO, O_3, N_2O, HNO_3, HCl, HF, HOCl, HO_2, NO_2, OH, H_2O_2, temperature, and pressure for the March flight and submitted them to the UARS CDHF.

5. Analysis of Balloon Flight Data

We made a number of improvements in both the accuracy and computational speed of our data reduction software. In order to reduce phase errors in our spectra we added a small, non-linear correction term to our phase retrieval algroithm. This correction improved considerably the quality of the spectral region used for pressure retrievals by reducing the systematic phase error from 15° to less than 1°. We improved the accuracy of calculated line shapes for very strong lines by using a temperature interpolation function to correct for the effects of using finite homogeneous layers in our model atmosphere. Rather than use a single average temperature for each layer, we now use an effective temperature which is a function of the optical depth in the layer. By choosing a new set of spectral windows for fitting temperature we reduced our temperature fitting errors from about 0.8 K rms to 0.3 K rms. Finally, we reduced the computation time required for data reduction by a factor of four by increasing the efficiency of our software. This large increase in speed greatly enhances our ability to troubleshoot software modifications and to test for additional systematic errors.

6. Publications and Presentations

K. V. Chance, W. A. Traub, K. W. Jucks, and D. G. Johnson, Measurement and Analysis of the HO_x Family of Free Radicals in the Earth's Stratosphere, paper TF12, Ohio State University International Symposium on Molecular Spectroscopy, June 14–18, 1993.

APPENDIX A

Measurements and Analysis of the HO_x Family of Free Radicals in the Earth's Stratosphere

MEASUREMENT AND ANALYSIS OF THE HO_x FAMILY OF FREE RADICALS IN THE EARTH'S STRATOSPHERE, K. CHANCE, W. A. TRAUB, K. W. JUCKS, AND D. G. JOHNSON

Altitude profiles of the concentrations, and their diurnal variation, have been measured for stratospheric OH and HO_2, as well as H_2O_2 and a number of related atmospheric trace species. The measurements are made from far infrared thermal emission, using a Fourier transform spectrometer on a high altitude balloon platform.

Results of the measurements and analysis for OH, HO_2 and H_2O_2 using balloon-borne measurements from 36 km, obtained in the fall of 1989, are presented here. The underlying spectroscopy necessary for the identification and quantitative analysis of these species is discussed in detail.

Address of Chance, Traub, Jucks, and Johnson: Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138.

20 minutes required
Recommended for atmospheric applications of remote sensing

Measurement and Analysis of the HO_x Family of Free Radicals in the Earth's Stratosphere

I'm going to discuss our HO_x measurements in the context of far infrared atmospheric measurements in general. Far infrared measurements have turned out to be very successful for probing the chemistry of the earth's stratosphere, now that some of the more promising measurement techniques have been worked out. I want to introduce some of the spectroscopic issues involved in the measurements and give examples so that the laboratory spectroscopists here who may be finding themselves more oriented toward measurements in support of field studies get a feeling for what can really be involved.

A number of groups are currently engaged in making far infrared measurements in the stratosphere, including our own at the SAO, JPL, Stony Brook, a collaboration between an Italian group and NASA Langley, and several groups in Europe that are exploring some potential new techniques. Techniques employed to date include the use of Fourier transform spectroscopy (including our own measurements), Fabry-Perot instruments and, at longer wavelengths, heterodyne techniques. Work on new techniques is largely attempting to extend heterodyne techniques to shorter wavelengths. The bulk of the measurements have been made from balloons, like the launch of our instrument shown here, but also include ground-based heterodyne measurements of ClO and HO_2, airplane-based FTS measurements (ours), and the O_3 and ClO measurements made by the JPL MLS on the UARS satellite.

When I say FIR, I am generally speaking of the region from about 10-500 cm^{-1} (although both end points are certainly open to debate). We in particular have been very productive making FTS measurements in the region 80-200 cm^{-1} using a LHe cooled Ga:Ge photoconductor detector. A major reason why the FIR is such a productive region for stratospheric study is that this is the portion of the spectrum where light, polar molecules with hydrogenic rotational constants - diatomics and NSPTs - can be measured well from their rotational spectra. They have strong transitions and interference, while not negligible as we'll see, is not too bad, because the background spectrum, which is composed of the summed contributions of rotational transitions from every molecule that is present, has largely died away at frequencies below about 80 cm^{-1}. Above this point, the spectrum is dominated by those molecules with large rotational constants plus, because of its relatively large concentration, O_3. When we get to even higher frequencies, the spectrum due to the hydrogenic molecules fades out (it does this by about 200 cm^{-1}), and we begin to see low-lying vibrational bands from heavier species such as HNO_3, N_2O and CO_2. An additional advantage to making atmospheric measurements in the far infrared is that they can generally be made in emission, with the cold sky as a background, which means that they can be made looking in any direction in the sky and can be made at any time of day. Many of the species important in atmospheric chemistry have strong diurnal variation, and a major reason for measuring them is to follow this variation, so that emission techniques are ideal for the purpose. Use of emission also avoids the confusion arising from the mixing of temporal and altitude variation that can occur in occultation measurements.

Here is an example of measurements derived from one of our balloon flights. It shows altitude profiles of a number of species that have been measured simultaneously by pointing to various elevation angles on the earth's limb, mostly below the horizontal, with the telescope of our measurement apparatus, and taking spectra. The measurements here are at a solar zenith angle of 44 degrees. This measurement set includes virtually all species that have been measured in the far infrared, with the exceptions of ClO, which is measured at longer wavelengths than we generally use, and NO_2, which we are still learning how to analyze. Normally, for an atmospheric audience, I would save a slide like this for near the end, to show the results of our particular measurements, but for this audience I want to show it more as a survey slide and go on to concentrate on some of the spectroscopy underlying the measurements.

Here I show a portion of a limb-scan sequence of spectra from one of our stratospheric balloon flights: This illustrates that we measure lines with a large dynamic range in strengths (show saturated and unsaturated) down to a small fraction of a percent of full scale (i.e., normalized to a blackbody) at the kind of resolution that we use. This sort of signal to noise is useful not only for quantification of measured species, but can be critical for identification of interfering species, as we'll see in a bit. The spectral lines we measure in the atmosphere are characterized by their positions, intensities and widths. The line shapes are convolutions of Gaussian widths, from Doppler broadening, with Lorentzian widths, from pressure broadening. For this part of the spectrum, the Doppler and pressure broadening widths are the same at typically about 40 km, and are dominated by pressure broadening below that, that is, for most of the stratospheric region of interest. The resulting line shape is the Voigt shape; the Voigt shape is then distorted by the effect of Beer's law across the line width and, of course, the instrumental line shape changes the appearance even more. For FTS spectra in the far infrared, the measured spectra are usually unresolved except at the lowest levels in the atmosphere, and what we see is the instrument line shape. The line intensities are most often due to electric dipole transitions, although there are exceptions, including the rather prominent magnetic dipole rotational lines of O_2. For the pure rotational lines, which dominate below about 200 cm^{-1}, the intensities are usually determined by Stark effect measurements, which give strengths good to several percent in most cases. Lines in stratospheric spectra that are useful for measurements span the curve of growth from optically thin, or unsaturated, lines to lines that are fully saturated. Small (unsaturated) lines are lines whose area in the measured spectrum is proportional to the line intensity (show illustration); stronger (saturated) lines have measured areas that are (for Lorentzian lines) proportional the square root of the intensity times the line width.

Why lines that look so modest can in fact be saturated is illustrated by this next figure: the cusp shape here is the characteristic shape of lines in the stratosphere - compare to FTS and FP instrument shapes. For techniques which fully resolve the line shapes - the heterodyne techniques - the width of the line at a particular intensity level is a direct measure of where in the atmosphere the emitting gas is located. Here is another example from a balloon spectrum that illustrates the cases of saturation. The actual lines here have widths much smaller than shown; what we see is almost all due to the instrumental resolution. In this spectrum, which shows seven different types of O_3 in one small portion of the spectrum, the weaker lines are almost unsaturated, while the stronger ones, although they don't look so impressive here, may almost be considered fully saturated. Thus, we generally need to have well-determined line positions, pressure broadening coefficients and intensities in order to properly analyze stratospheric spectra, with details depending on the particular molecule. (It doesn't pay to generalize, as each molecule is unique in what is necessary for its analysis, and must be considered in individual detail. I will also note parenthetically here that pressure broadening coefficients, when needed at all, must be determined by direct measurement; this includes their temperature dependences as well. Calculations have not been very successful in providing numbers that can reliably be used for quantitative measurements.) This slide shows, under typical stratospheric concentrations and viewing geometry, the strengths of the strongest lines of various species measured in the far infrared. I've drawn lines here to indicate at what point the lines can be considered unsaturated, with areas determined only by line intensities, and at what point they can be considered fully saturated, with areas determined by the square root of intensity times width. Obviously, for many atmospheric species, both intensity and width are important, as is the ability to model radiative transfer in the lines accurately.

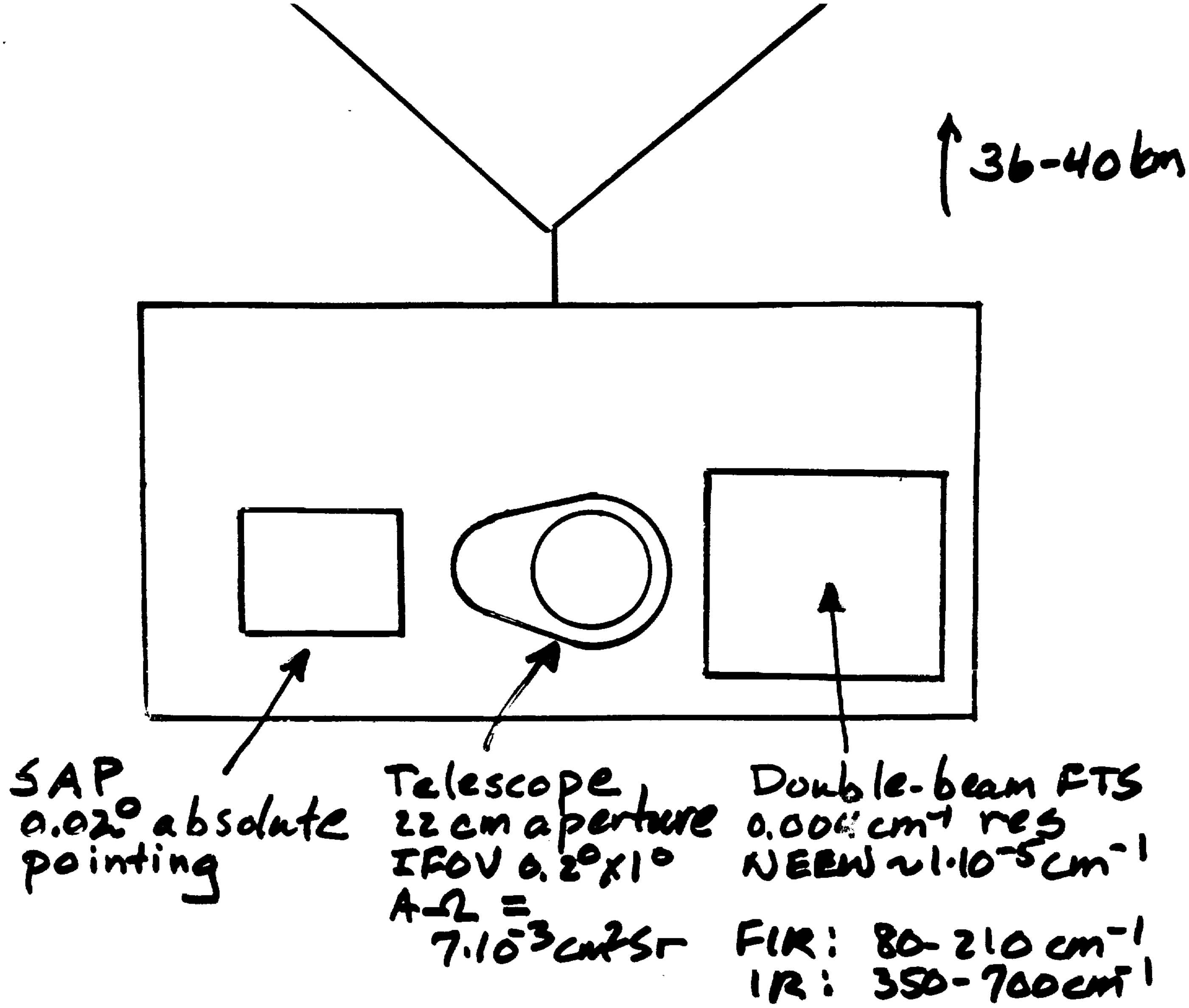
I'll show two atmospheric chemistry slides. This is from a WMO report. It shows the major chemical reactions in the three basic catalytic cycles involved in modulation and destruction of stratospheric ozone. Without going into the chemistry, I want to point out the large fraction of the ozone photochemistry that can be tested by making measurements in the far infrared. I also want to introduce the HOx catalytic cycle, because I want to focus on it as a rather instructive example to show what spectroscopic issues are involved in designing and carrying out measurements in this region, and in analyzing the results. The HOx catalytic cycle, whose main features are extracted here, is a natural cycle for modulation of the O_3 concentration. as opposed to the nitrogen and chlorine cycles which reflect man-made pollution more, but it is tightly coupled to them and is of primary importance for quantifying stratospheric chemistry - so much so that OH measurements are considered one of the Holy Grails for stratospheric measurements. I will make a common extension and speak of the

HOx family as including the radicals OH and HO_2 which actually do the catalysis of ozone destruction, water, which serves as a source and sink for the radical chemistry, and H_2O_2 which is a temporary reservoir for the radical species. The H_2O_2 concentration is very sensitive to the rates for HO_2 recombination and H_2O_2 photolysis, and it strongly modifies the effectiveness of the radicals in destroying ozone. These four species then form a tightly-coupled photochemical family. Among them they also exhibit most of the complexity involved in the quantitative spectroscopic analysis of far infrared atmospheric spectra. I will go on to discuss some of the specifics of the HOx species in more detail - particularly those of OH and H_2O_2; I'll mention HO_2 if there is time, and omit H_2O from detailed discussion other than noting that we see hundreds of H_2O lines including many hot band lines and lines from weaker isotopic species.

OH is quite prominent in stratospheric spectra; we see 13 emission lines quite easily (here is a figure showing some of them), and identification and interference checks are generally no problem at the FTS resolution used here. The intensities are well-determined from dipole moment measurements, and the positions have extremely well-measured, including the hyperfine structure. The chief difficulty in analyzing OH spectra is in getting the radiative transfer in the lines correct. They are quite saturated, they include hyperfine structure that is just at the level of the Doppler widths, and the concentration profile in the atmosphere is such that the normally stable onion-peeling type of retrieval scheme is just about pushed to its limits. Thus, the chief laboratory activity we have been engaged in to support the stratospheric measurements is laboratory determination of the pressure broadening coefficients. This has been done in collaboration with several other groups and carried out at NIST in Boulder, CO. Here is an example of determination of pressure broadening for one of the prominent atmospheric lines using fully line-resolved spectroscopy by the TuFIR method of laser mixing. Extension of pressure broadening studies to all of the lines that are prominent in the stratospheric spectrum is the major remaining spectroscopic need for OH.

H_2O_2 presents an almost totally different spectroscopic picture in the stratosphere. Here the lines are quite weak, due largely to the greater partition function compared to OH. Pressure broadening coefficients are not necessary because the measured features (Q branches in the torsional-rotational spectrum) correspond very well to the optically thin, or unsaturated, limit. The strengths are well determined from dipole moment measurements of transitions in the same torsional band. Determination of the exact contribution of H_2O_2 to the stratospheric spectrum is complicated by the fact that it is not single lines that are measured, but very compact Q branches of the rotational torsional spectrum, in particular the $^{R}Q_5$ branch at 112 cm^{-1}, shown here. H_2O_2 is the most nearly symmetric prolate top that I know of; even in microwave spectra it has not been necessary to include any asymmetry in the fitting to the Hamiltonian, and yet it is perpendicular transitions (actually c- type) that we are measuring here. One reason why these Q branches are so highly condensed is that centrifugal distortion is almost exactly offset by the effect of slightly different rotational constants in the upper and lower torsional states. There is another set of Q branches, where the effects are additive, and which are quite smeared out and not useful for atmospheric measurements. The top panel shows the atmospheric measurement, along with a least-squares fit to the spectrum. The bottom panel shows a decomposition of the fitted spectrum into its constituents. The spectroscopic challenge with H_2O_2 has been to get the line positions accurately enough to measure Q branches such as this, including the temperature dependence, to fit the atmospheric spectra properly and avoid problems of interference by other species. The study that finally accomplished this was an FTS study in Europe, including some of the colleagues here. You can see from this figure why it is sometimes necessary to know the spectral database in such detail and to be able to measure with such high resolution and S/N. There is one remaining unassigned line in this spectrum - most likely a hot band line of O_3 - while line rest of the spectrum is fitted down to the noise level, which is about 1/600 in this case. This measurement, incidentally has a noise level corresponding to a stratospheric concentration of 17 parts-per-trillion.

In conclusion, I think that these cases are fairly illustrative of the sorts of challenges one is faced with in planning, executing, and analyzing spectroscopic measurements in the atmosphere, and I hope that you have found them interesting and, perhaps, useful.



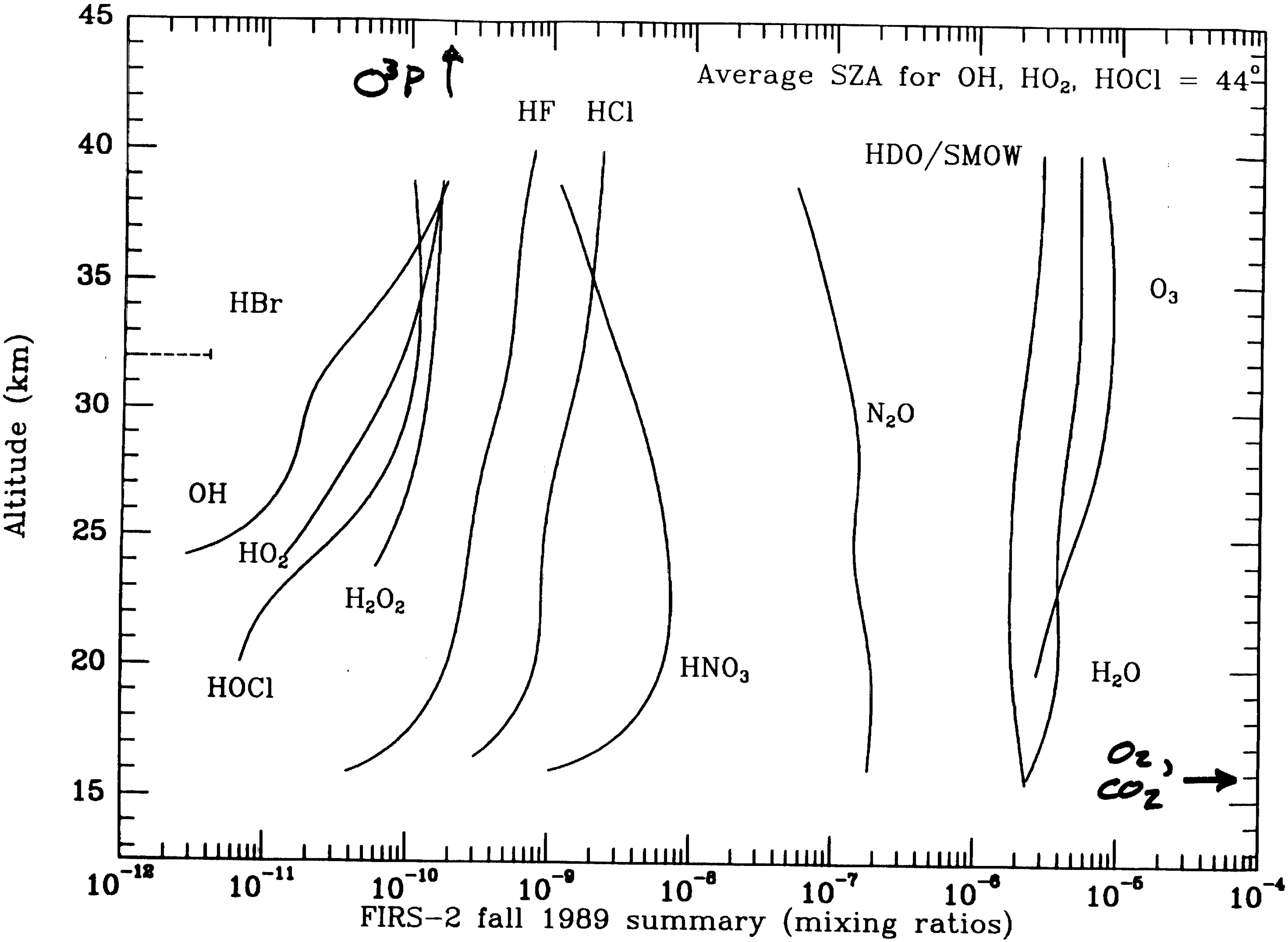
FIR

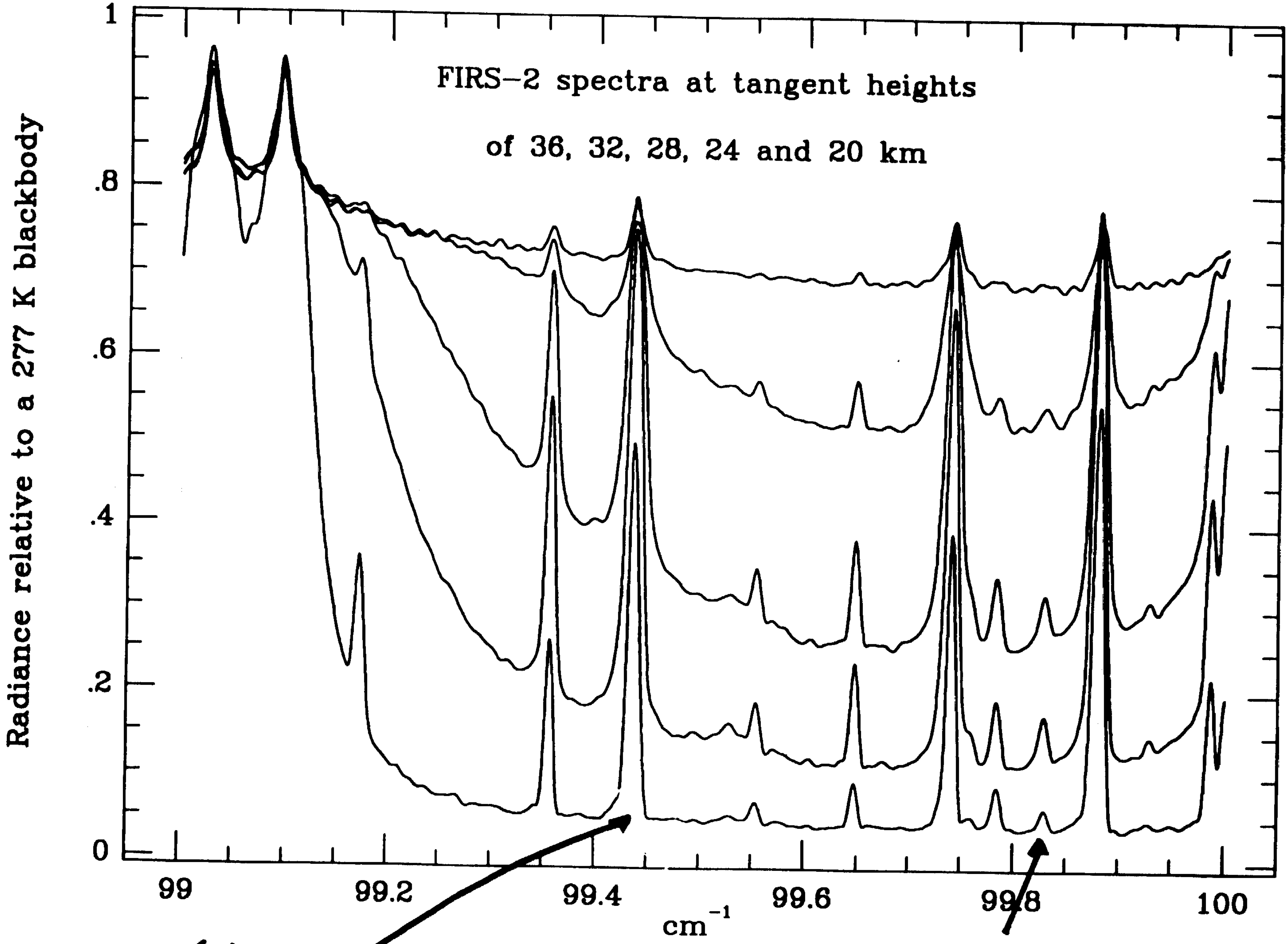
O, O_2, O_3
H_2O, OH, HO_2, H_2O_2
HCl, HF, $HOCl$, (ClO), (HBr)
NO_2

IR

HNO_3, N_2O
CO_2
H_2O

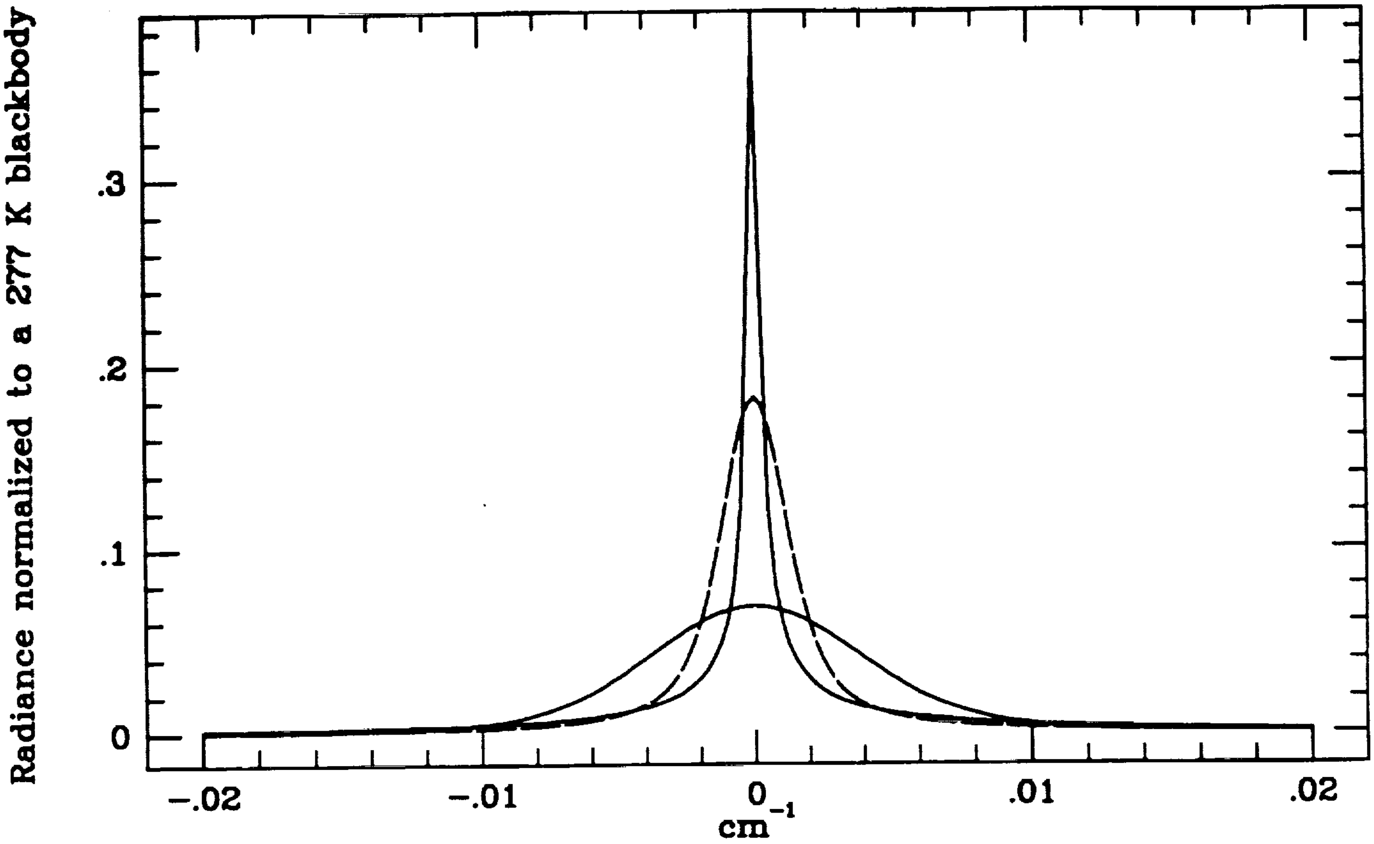
Emission ⇒ Full diurnal coverage

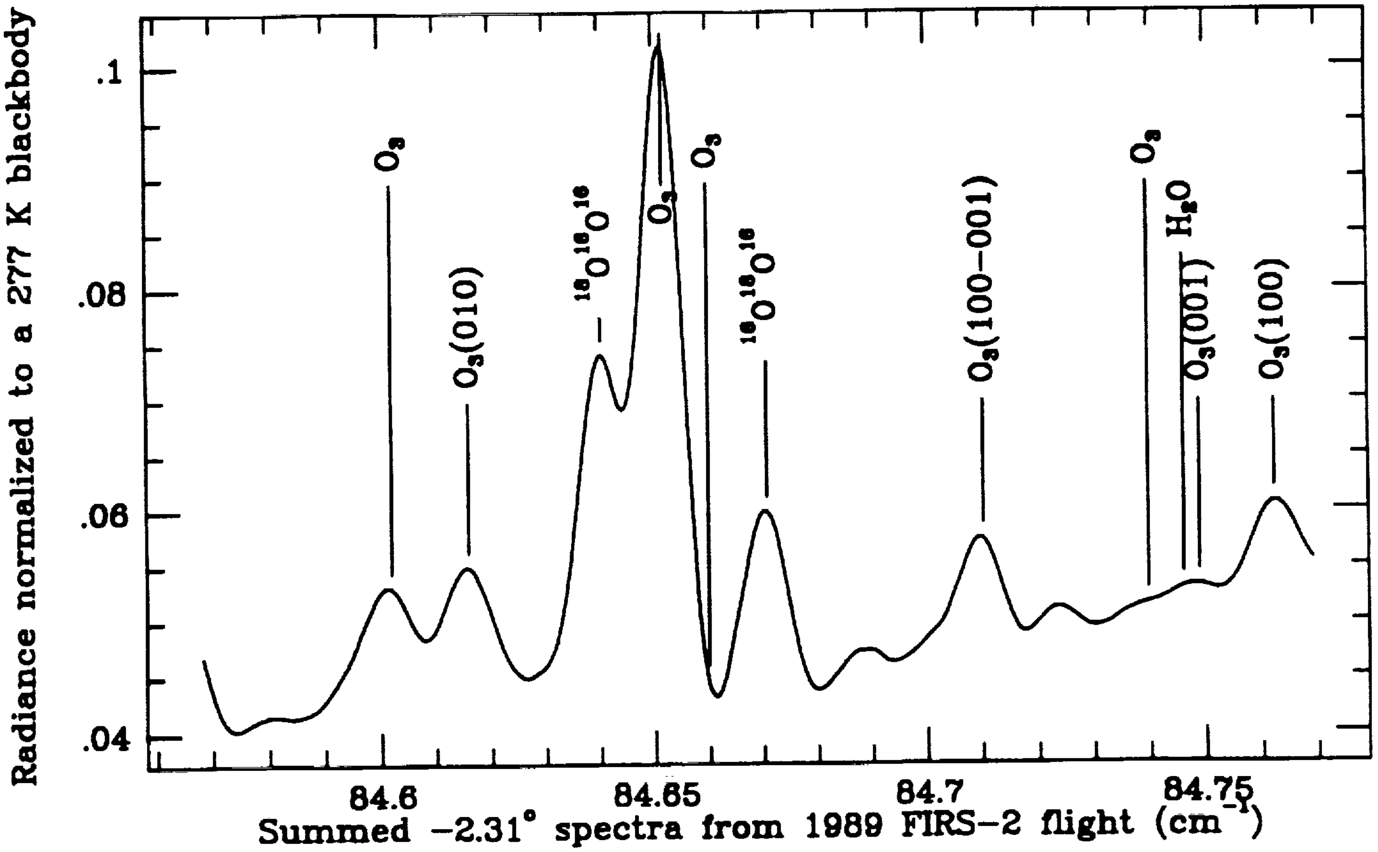

Average SZA for OH, HO$_2$, HOCl = 44°
O^3P ↑
HF
HCl
HDO/SMOW
HBr
O_3
N_2O
OH
HO_2
H_2O_2
HOCl
HNO_3
H_2O
O_2, CO_2 →
Altitude (km)
45
40
35
30
25
20
15
10^{-12}
10^{-11}
10^{-10}
10^{-9}
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
FIRS-2 fall 1989 summary (mixing ratios)

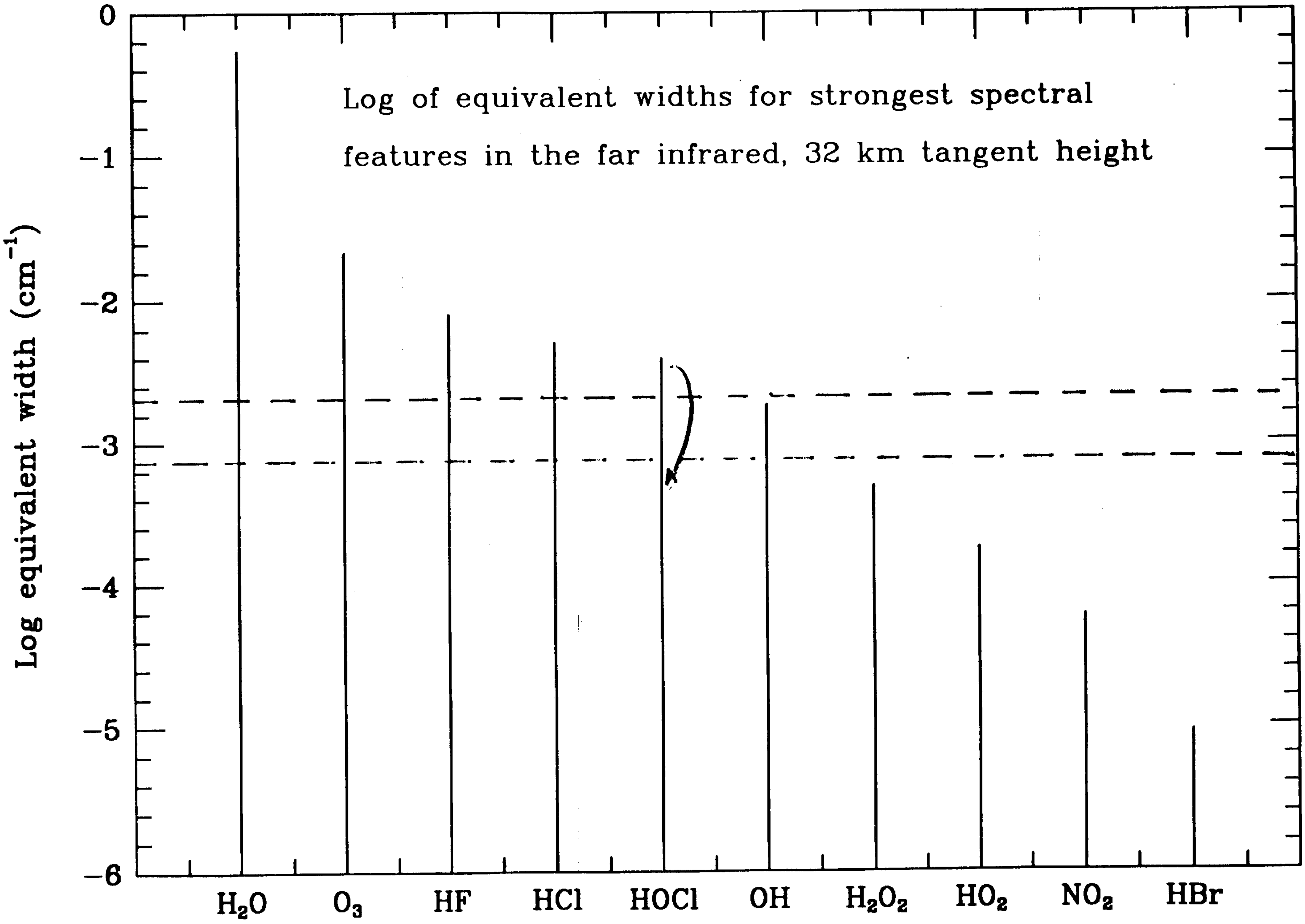


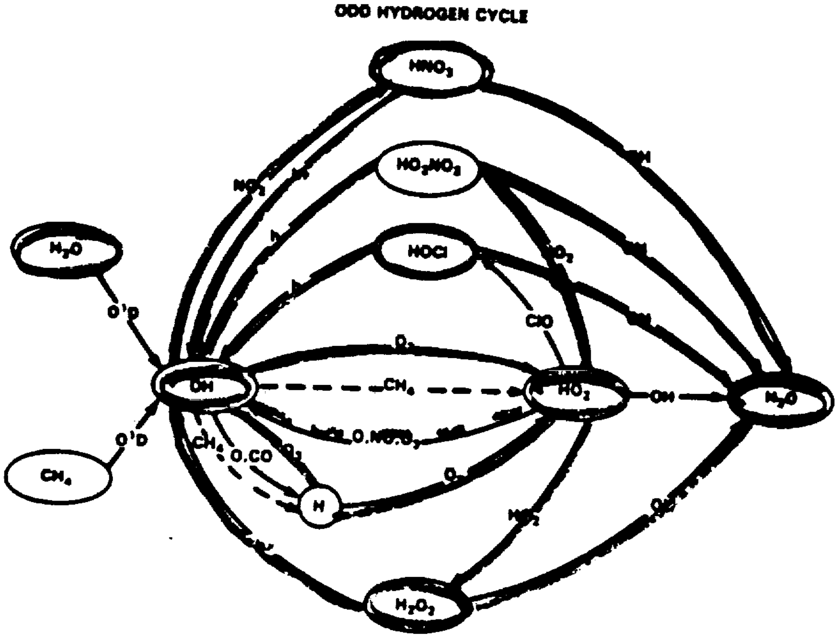
Saturated
$EW \simeq 2\sqrt{s \cdot b \cdot X}$

Unsaturated
$EW \simeq s \cdot X$

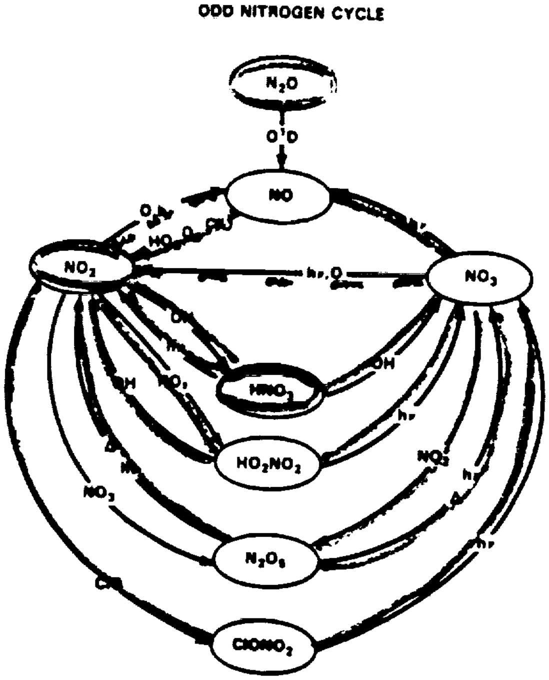

Radiance normalized to a 277 K blackbody
.3
.2
.1
0
-.02
-.01
0
.01
.02
cm^{-1}


Radiance normalized to a 277 K blackbody
.1
.08
.06
.04
O_3
$O_3(010)$
$^{18}O^{16}O^{16}$
O_3
O_3
$^{16}O^{18}O^{16}$
$O_3(100-001)$
O_3
H_2O
$O_3(001)$
$O_3(100)$
84.6
84.65
84.7
84.75
Summed -2.31° spectra from 1989 FIRS-2 flight (cm^{-1})

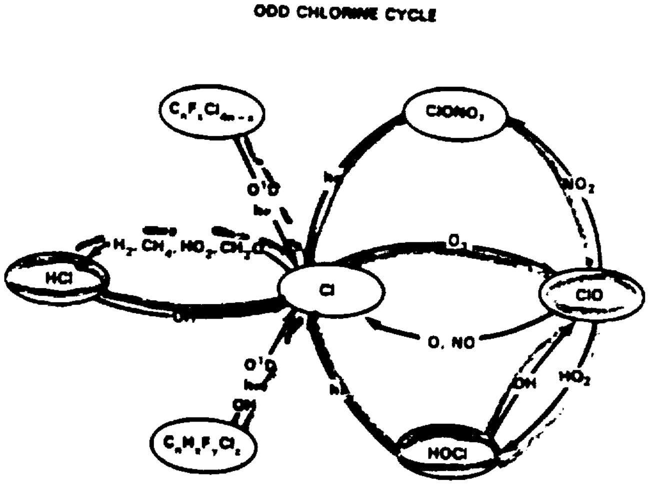

Log of equivalent widths for strongest spectral
features in the far infrared, 32 km tangent height
Log equivalent width (cm^{-1})
0
−1
−2
−3
−4
−5
−6
H_2O
O_3
HF
HCl
HOCl
OH
H_2O_2
HO_2
NO_2
HBr



Schematic of the Odd-Hydrogen Cycle.



Schematic of the Odd-Nitrogen Cycle.



Schematic of the Odd-Chlorine Cycle.

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May, 1986
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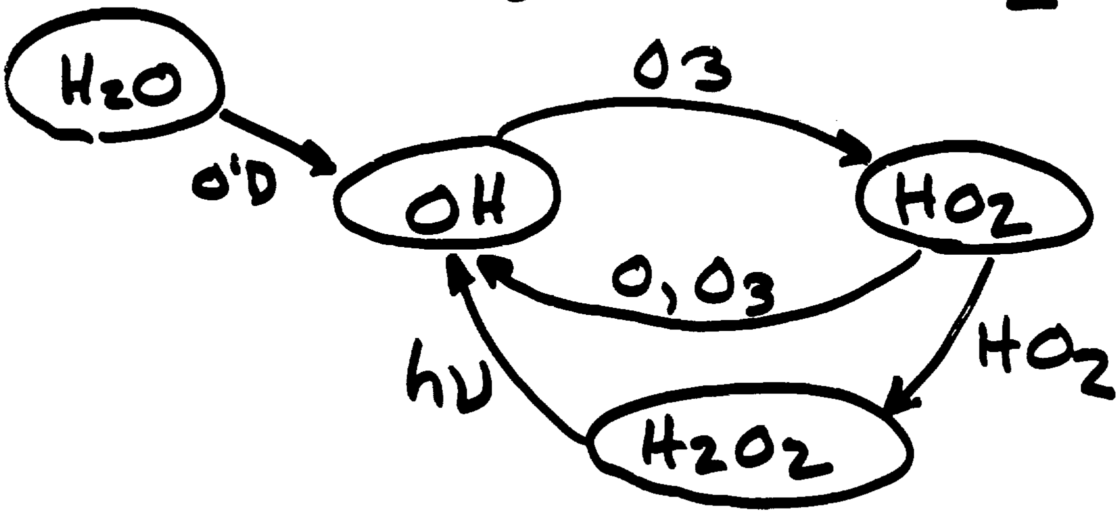
$$O_3 + h\nu (\lambda \leq 310\,nm) \rightarrow O_2(^1\Delta_g) + O(^1D)$$

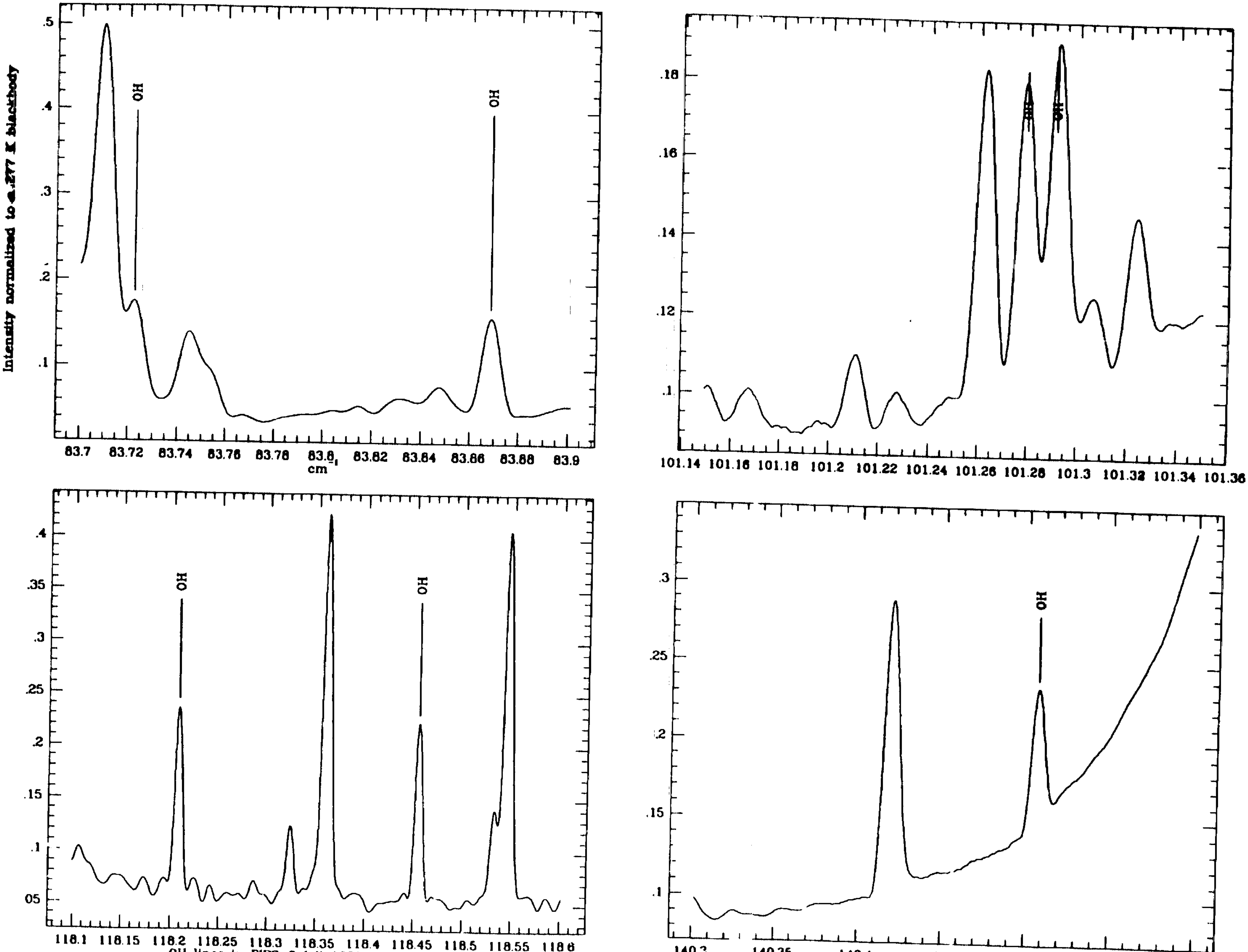
$$O(^1D) + H_2O\,(\text{or } CH_4) \rightarrow 2OH \quad (\text{or} \cdots)$$

$$\begin{array}{ll} & OH + O_3 \rightarrow HO_2 + O_2 \\ & \underline{HO_2 + O \rightarrow OH + O_2} \\ \text{net:} & O_3 + O \rightarrow 2O_2 \end{array}$$



$$O_3 \underset{M}{\overset{h\nu}{\rightleftharpoons}} O + O_2$$

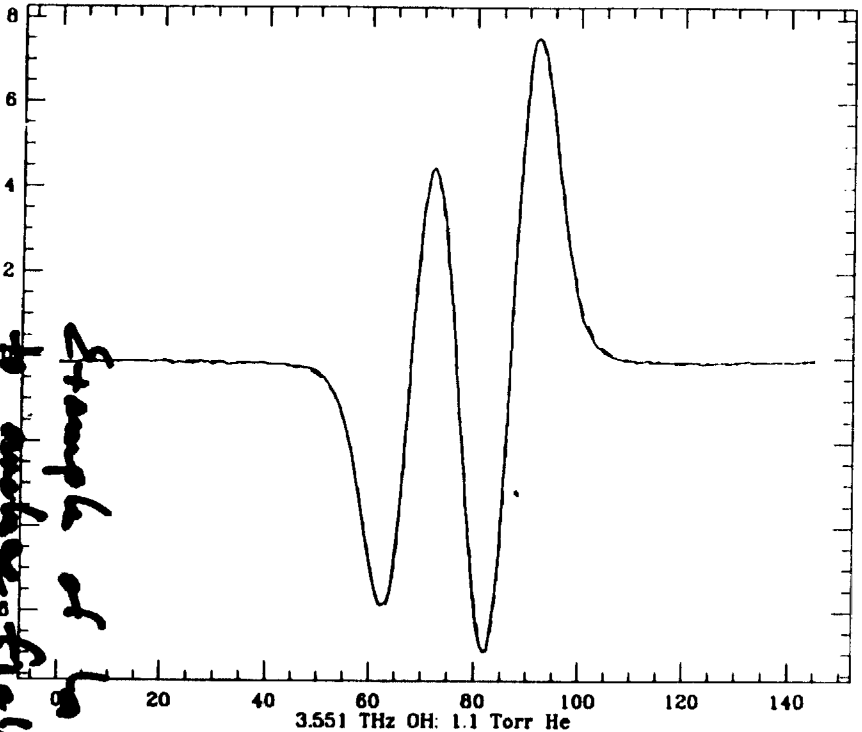
OH meas. is one of most important and difficult problems in remote sensing

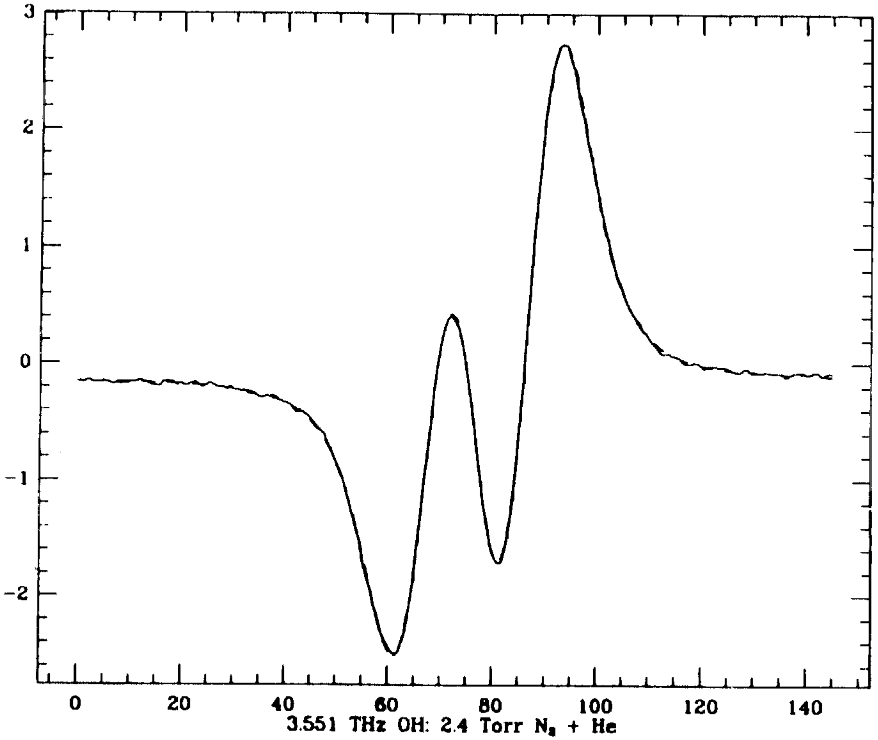


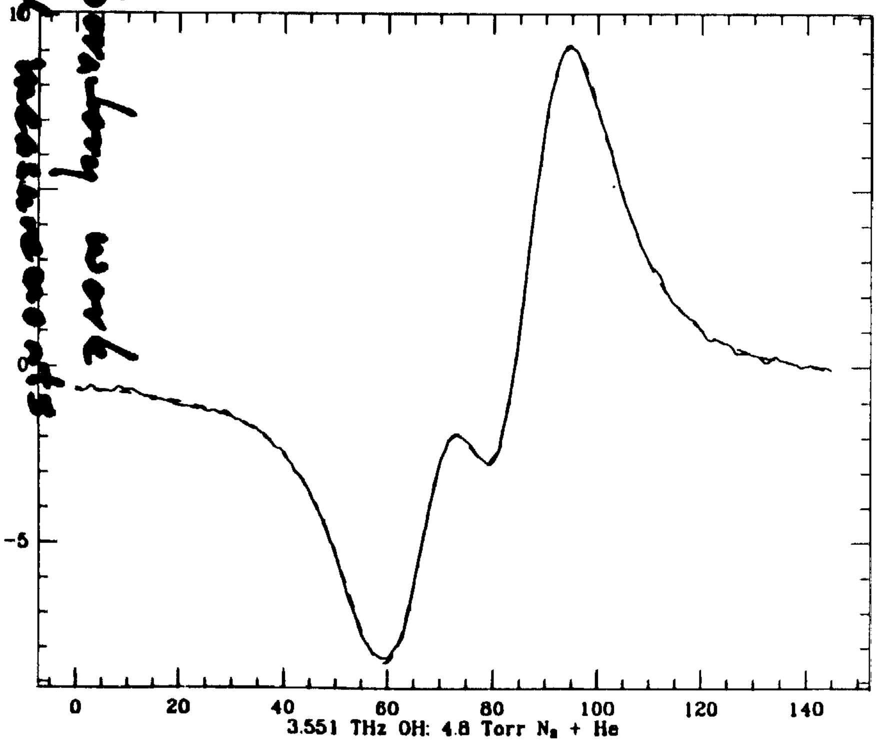
OH lines in FIRS-2 fall 1989 flight spectra

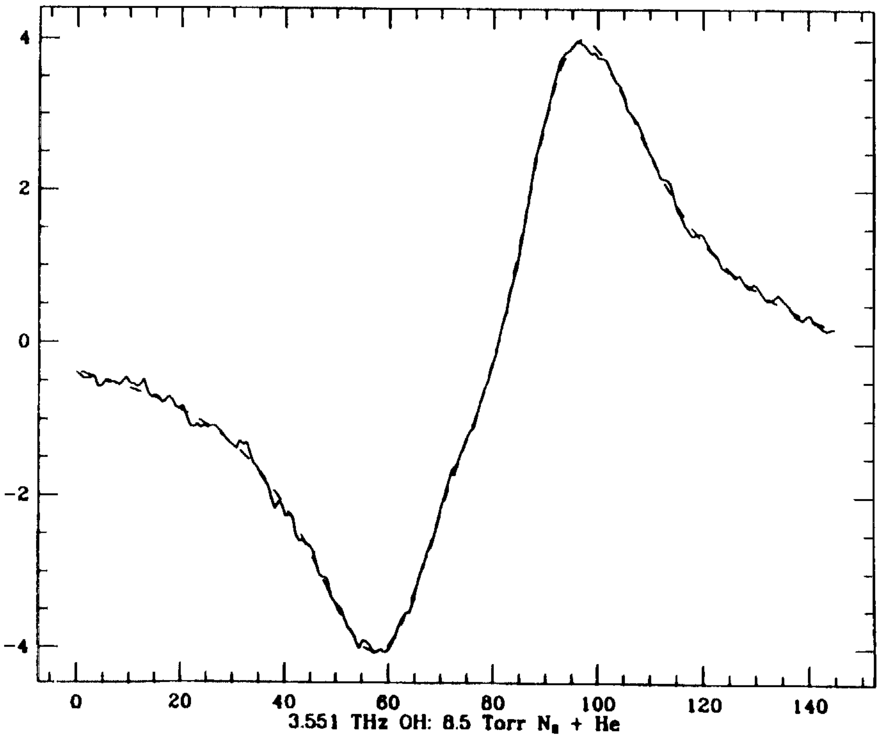
-2.31°, 31.5 km tangent K. Chance April 3, 1990

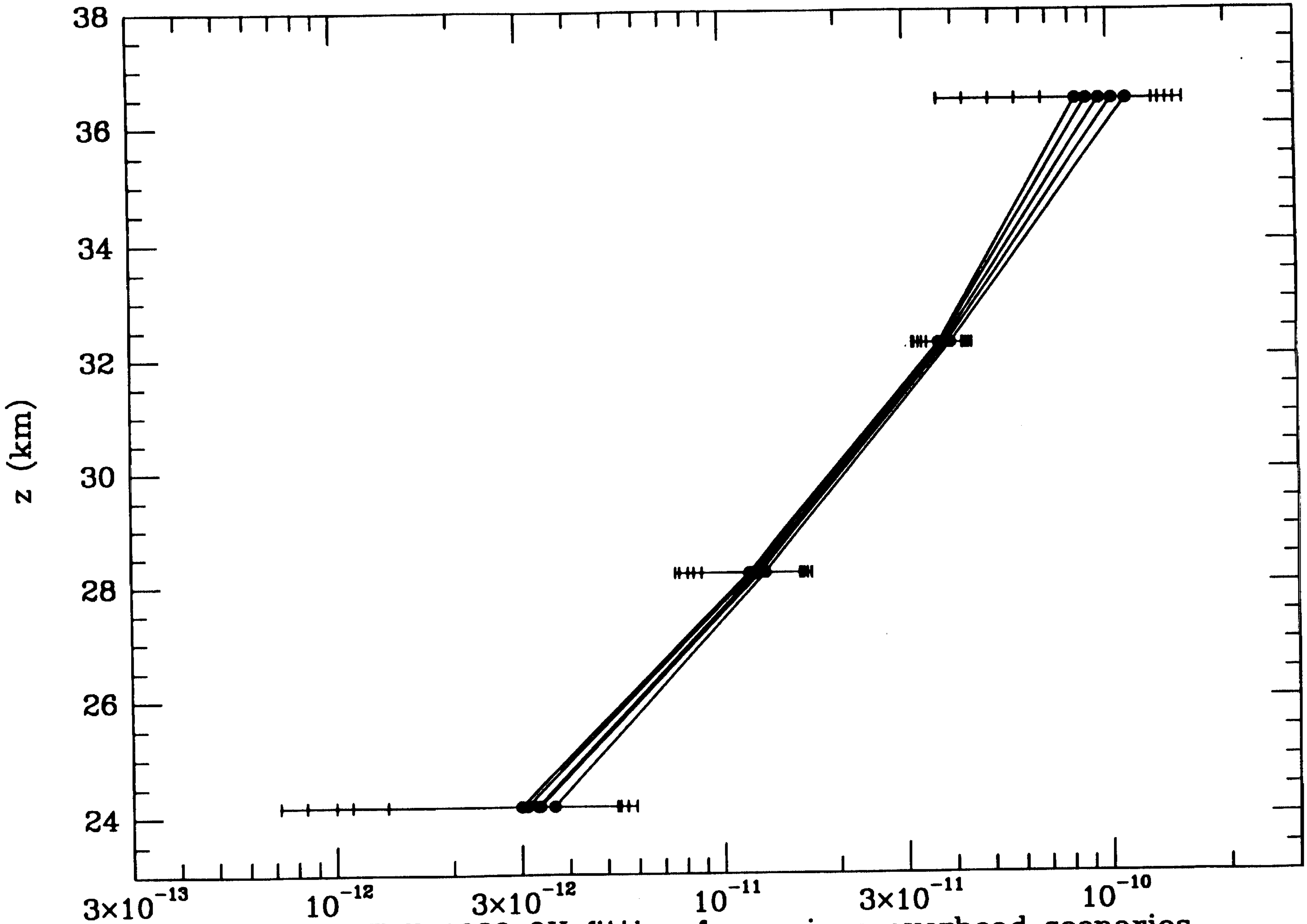
Example of laboratory work
to analyze field measurements



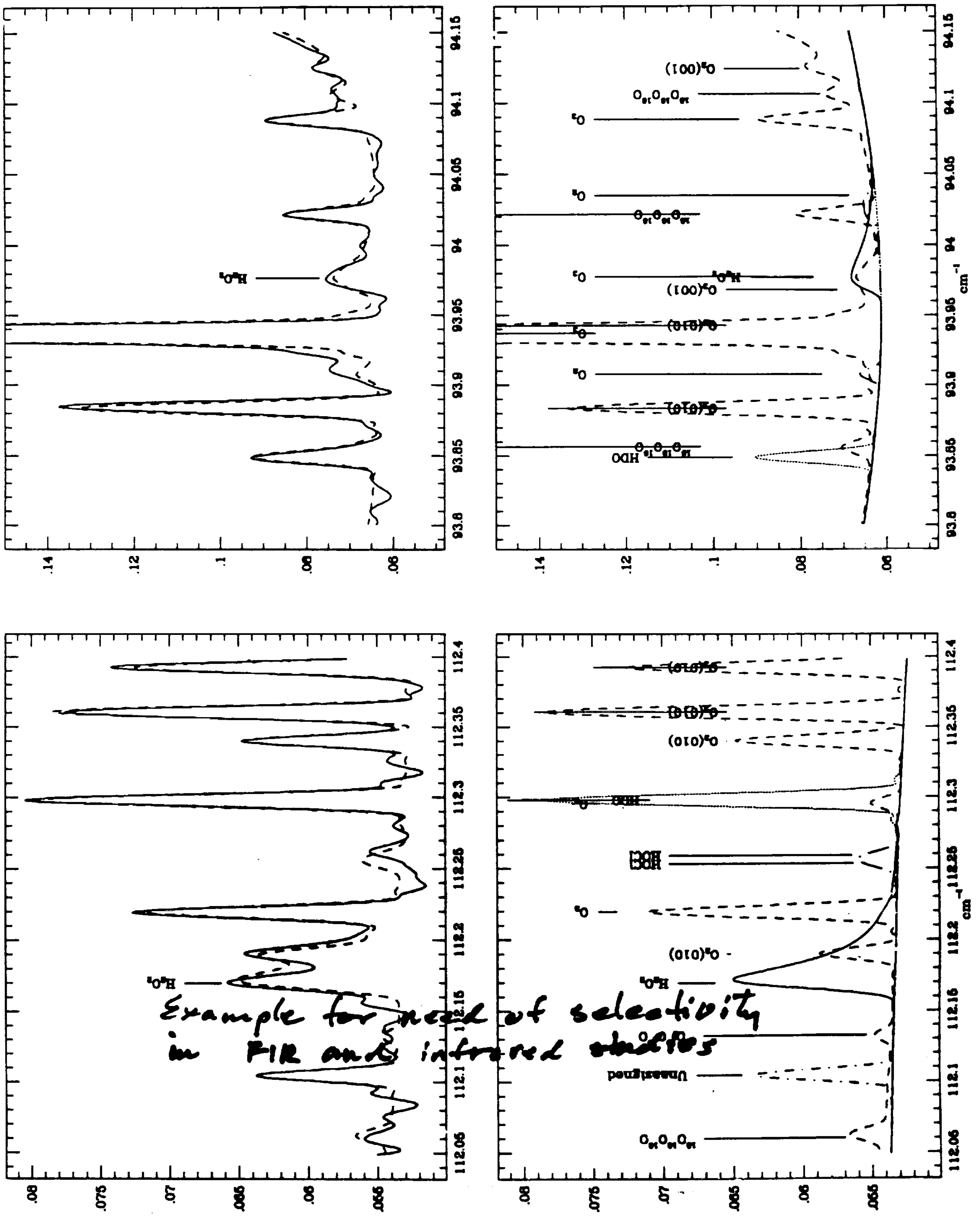




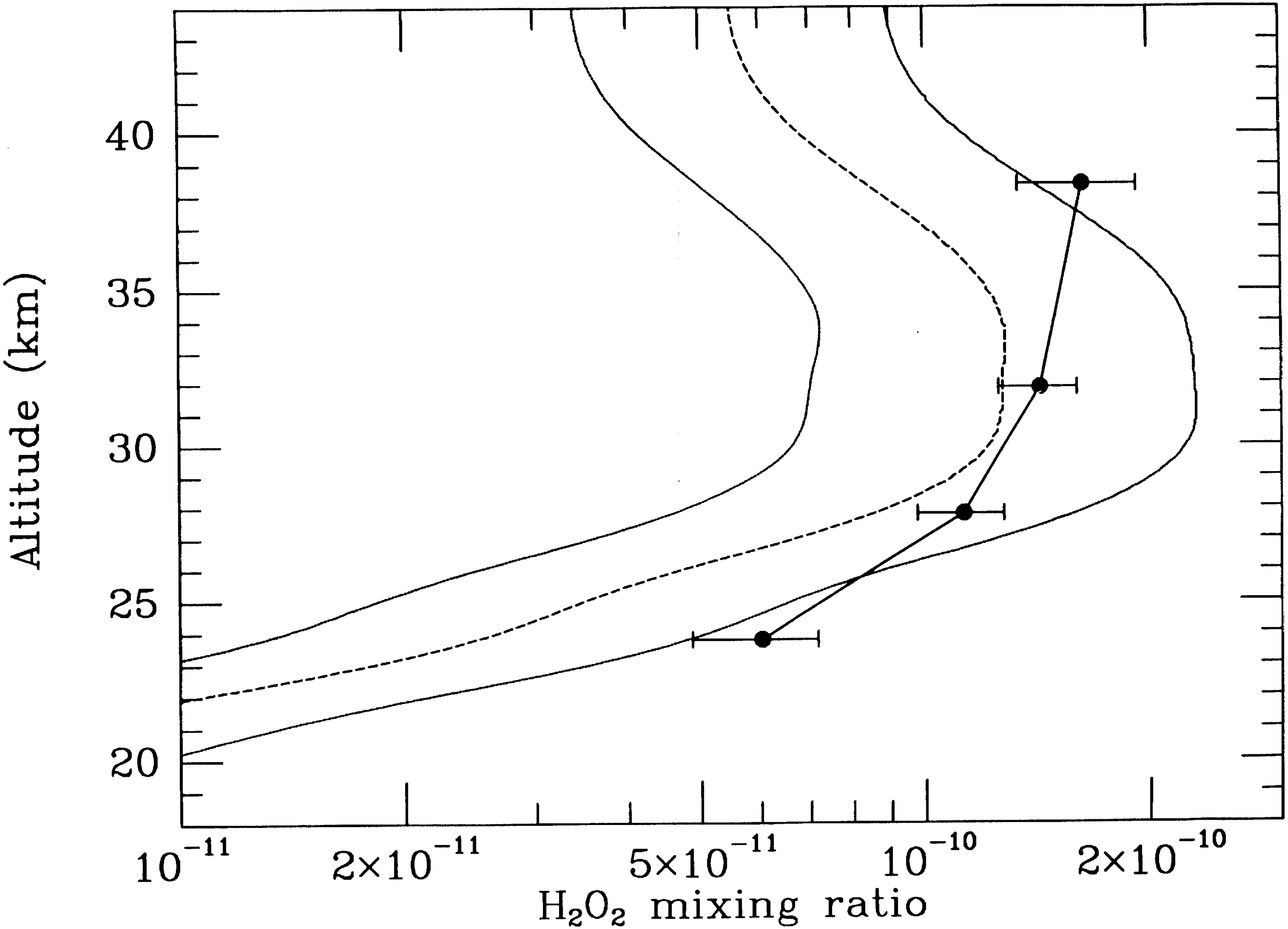


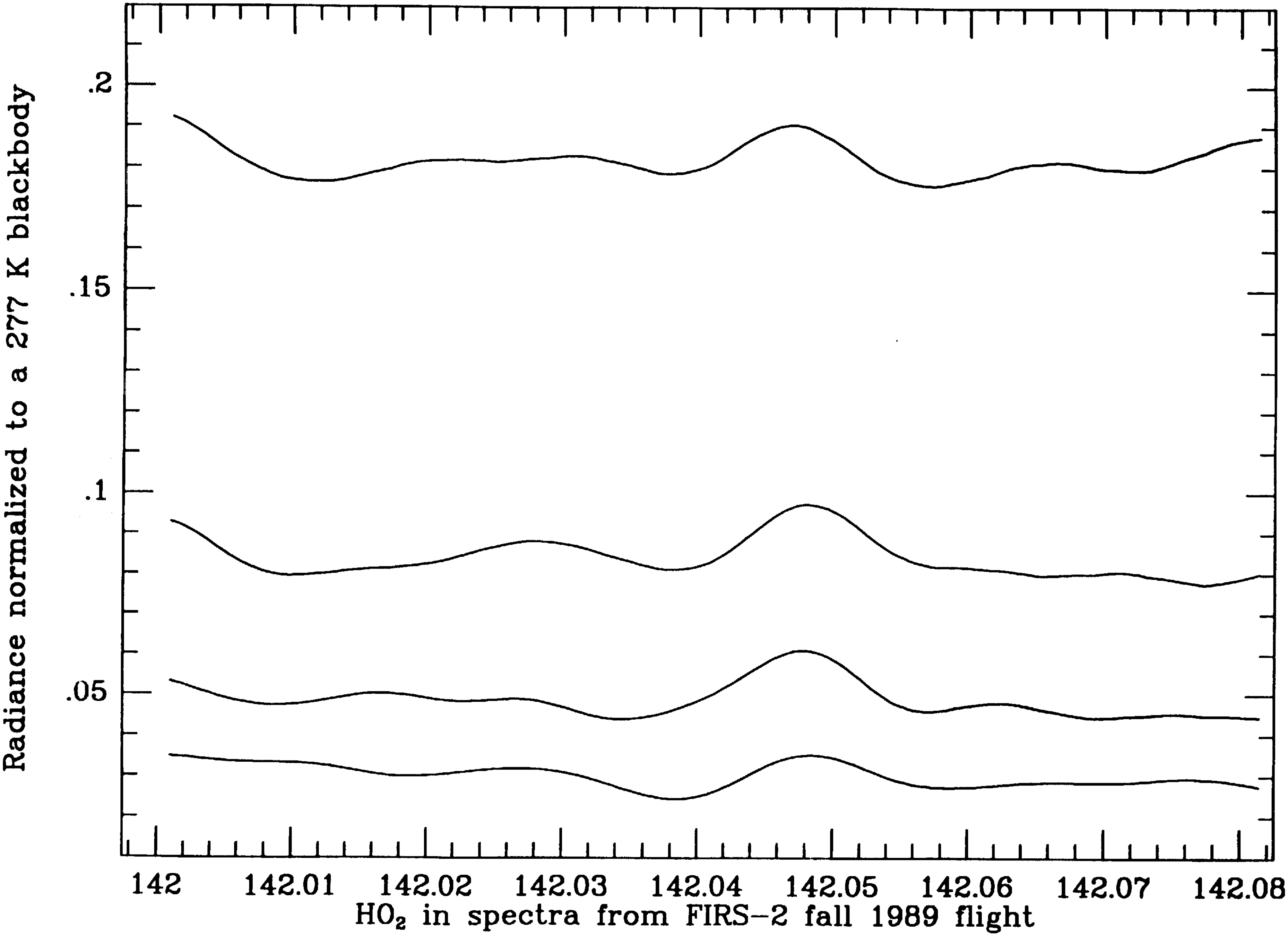


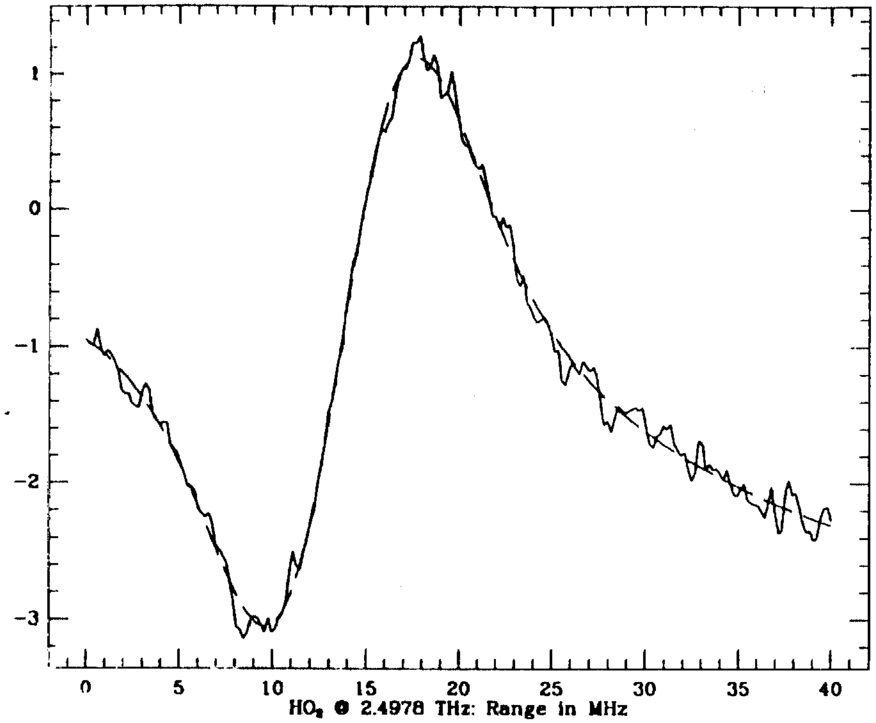
FIRS–2 Fall 1989 OH fitting for various overhead scenarios

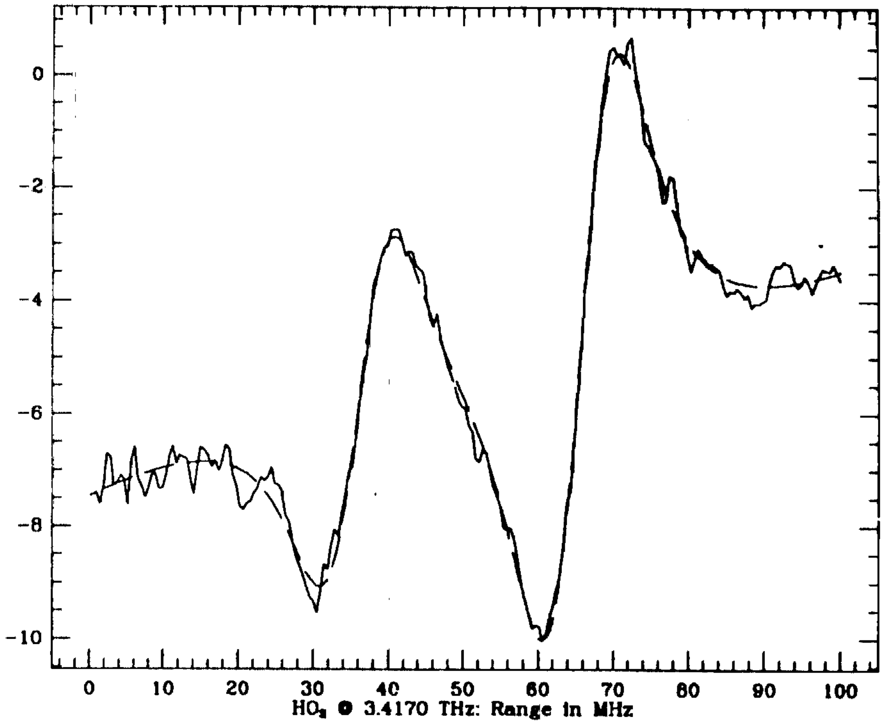


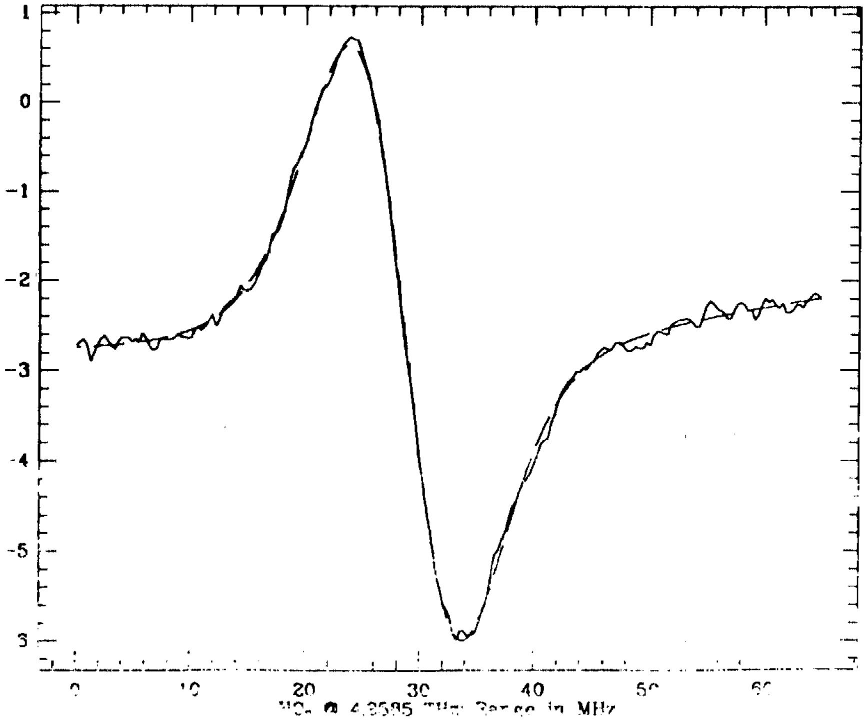
Example for need of selectivity in FIR and infrared studies

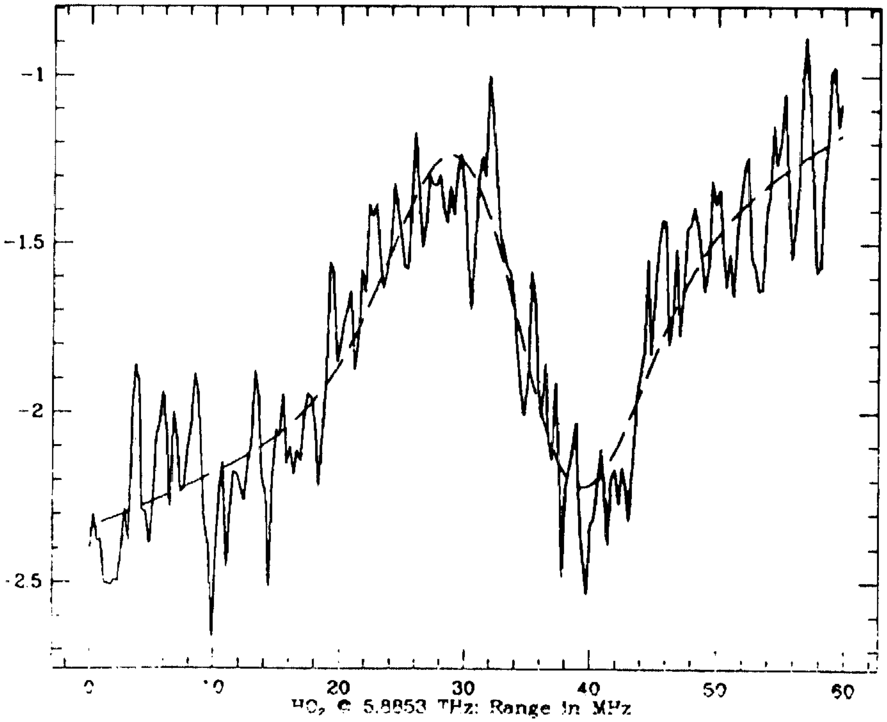

Altitude (km)
40
35
30
25
20
10^{-11}
2×10^{-11}
5×10^{-11}
10^{-10}
2×10^{-10}
H_2O_2 mixing ratio

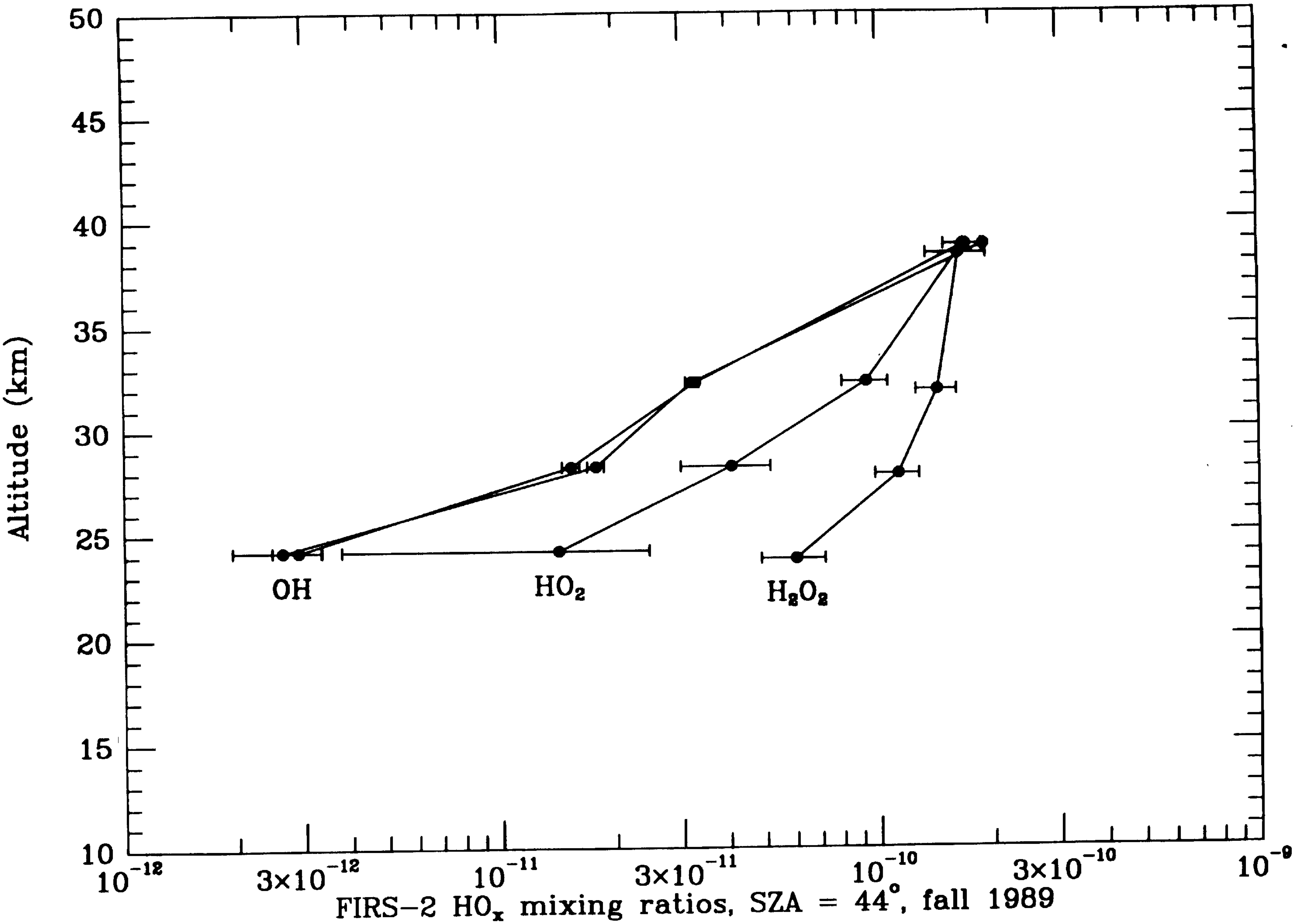

Radiance normalized to a 277 K blackbody
.2
.15
.1
.05
142
142.01
142.02
142.03
142.04
142.05
142.06
142.07
142.08
HO_2 in spectra from FIRS-2 fall 1989 flight


1
0
-1
-2
-3
0
5
10
15
20
25
30
35
40
HO$_2$ @ 2.4978 THz: Range in MHz


0
-2
-4
-6
-8
-10
0
10
20
30
40
50
60
70
80
90
100
HO$_2$ @ 3.4170 THz: Range in MHz


1
0
-1
-2
-3
-4
-5
0
10
20
30
40
60
HO$_2$ @ 4.3595 THz: Range in MHz


-1
-1.5
-2
-2.5
0
10
20
30
40
50
60
HO$_2$ @ 5.8853 THz: Range in MHz


Altitude (km)
50
45
40
35
30
25
20
15
10
OH
HO_2
H_2O_2
10^{-12}
3×10^{-12}
10^{-11}
3×10^{-11}
10^{-10}
3×10^{-10}
10^{-9}
FIRS-2 HO_x mixing ratios, SZA = 44°, fall 1989