Atmospheric Composition Measured by Solar Occultation Spectrometry

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Purpose of the MkIV balloon instrument:
•Evaluate technology improvements
•Validation of satellite instruments.
•Trend Detection.
•Validation of atmospheric models.

The JPL MkIV interferometer

Built at JPL in 1984, following the ATMOS optical design.

Mass=250kg, Size =1.4x0.7x0.8 m.

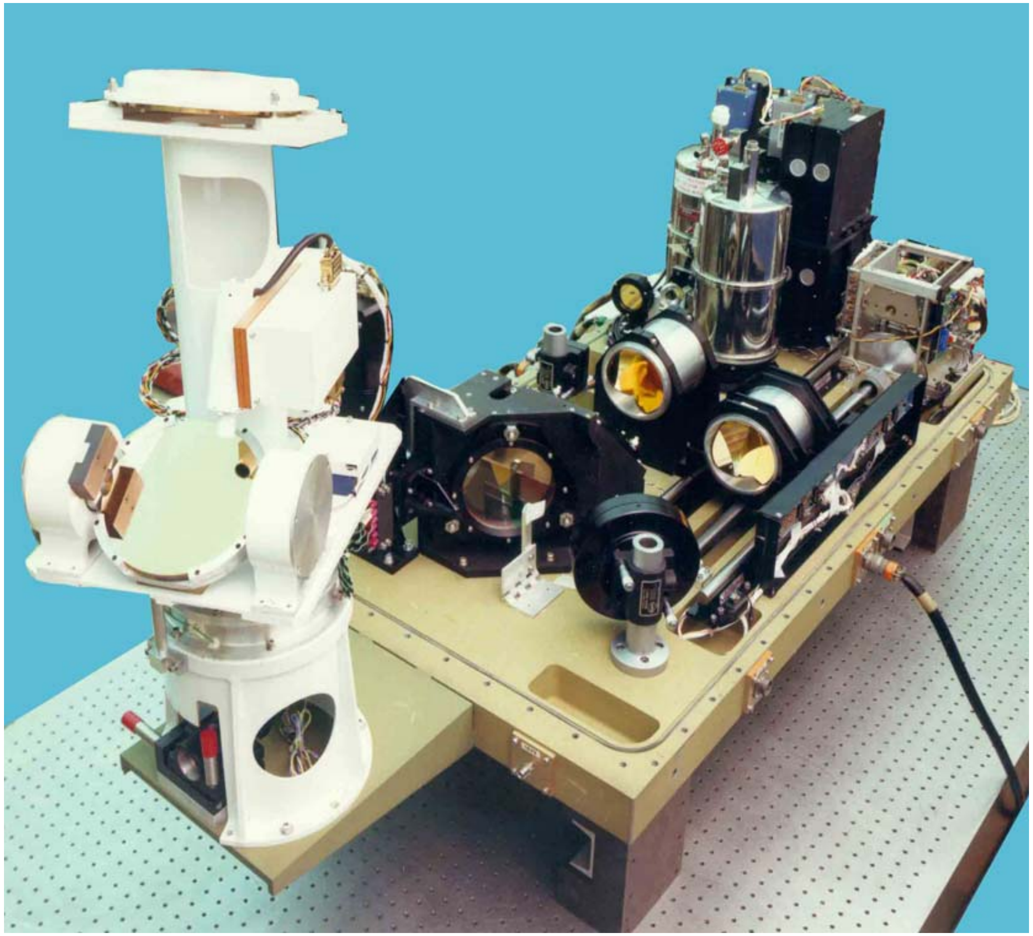
Parallel HgCdTe & InSb detectors simultaneously cover 650-5650 cm^{-1}

Double-passed optical configuration up to 120 cm OPD (0.008 cm^{-1} res)

Has performed 13 balloon flights,
3 aircraft campaigns, and 800+
days of ground-based observations.

KBr beamsplitter & compensator.

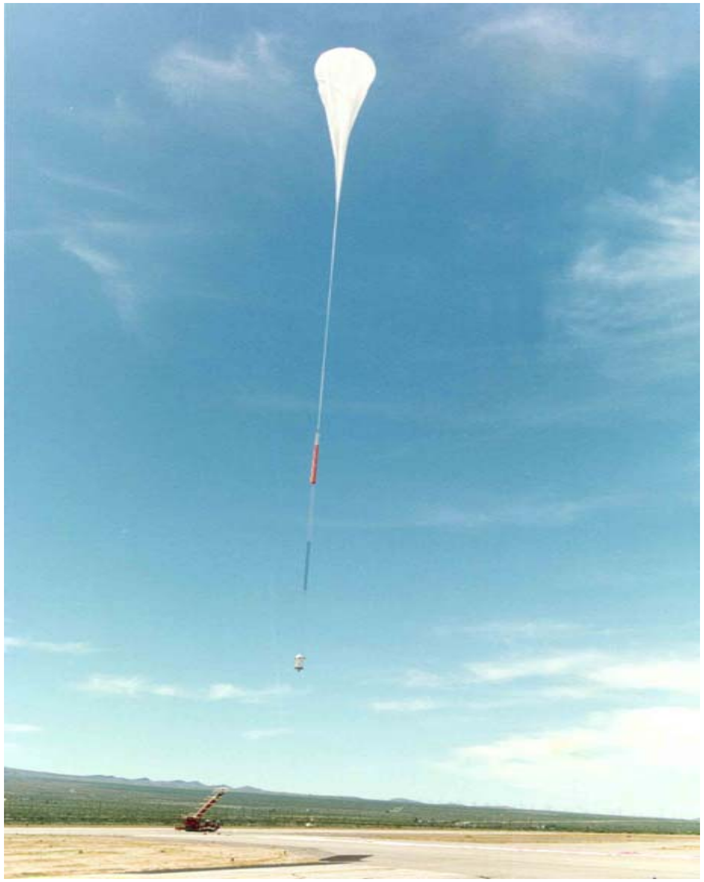
Moving cube-corner retro-reflector driven by leadscrew at 0.633 cm/s.



MkIV Balloon Flight History

Date	Tangent Latitude (degrees)	Tangent Longitude (degrees)	Minimum Altitude (km)	Balloon Altitude (km)	Launch Site	Event
05-Oct-89	34.6	-105.7	13	37	New Mexico	Sunset
27-Sep-90	34.2	-106.0	10	36	New Mexico	Sunset
05-May-91	37.5	-111.8	15	37	New Mexico	Sunset
06-May-91	36.5	-103.0	15	32		Sunrise
14-Sep-92	35.2	-110.2	23	38	New Mexico	Sunset
15-Sep-92	35.3	-103.9	22	40		Sunrise
3-Apr-93	34.8	-115.5	17	37	California	Sunset
25-Sep-93	34.0	-109.4	4	37	New Mexico	Sunset
26-Sep-93	33.2	-100.4	11	38		Sunrise
22-May-94	36.6	-109.7	15	36	New Mexico	Sunset
23-May-94	36.3	-100.8	11	37		Sunrise
24-Jul-96	56.8	-101.0	11	24	Manitoba	Ascent
28-Sep-96	32.7	-113.0	6	38	New Mexico	Sunset
08-May-97	68.0	-147.0	8	37	Alaska	Sunrise
08-Jul-97	67.0	-148.0	8	32	Alaska	Ascent
09-Jul-97	65.0	-150.0	9	32	Alaska	Descent
03-Dec-99	64.0	19.0	6	34	Sweden	Sunset
15-Mar-00	69.0	27.0	12	30	Sweden	Sunrise

Balloon Launch of the JPL MkIV Interferometer



Advantages of High Resolution Solar Occultation Technique

Broad Spectral coverage (typically 650-5650 cm^{-1}):

Allows determination of aerosol composition and size distribution.

30+ different gases measured simultaneously in the same airmass, providing tight constraints on models.

A range of different strength bands are available for retrieval (strong for high altitude; weak for low).

High Signal-to-Noise Ratio and Resolving Power:

Able to measure weak absorptions of traces gases that lie close to much stronger lines.

Broad absorptions due to aerosol easily distinguished from narrow gaseous absorptions.

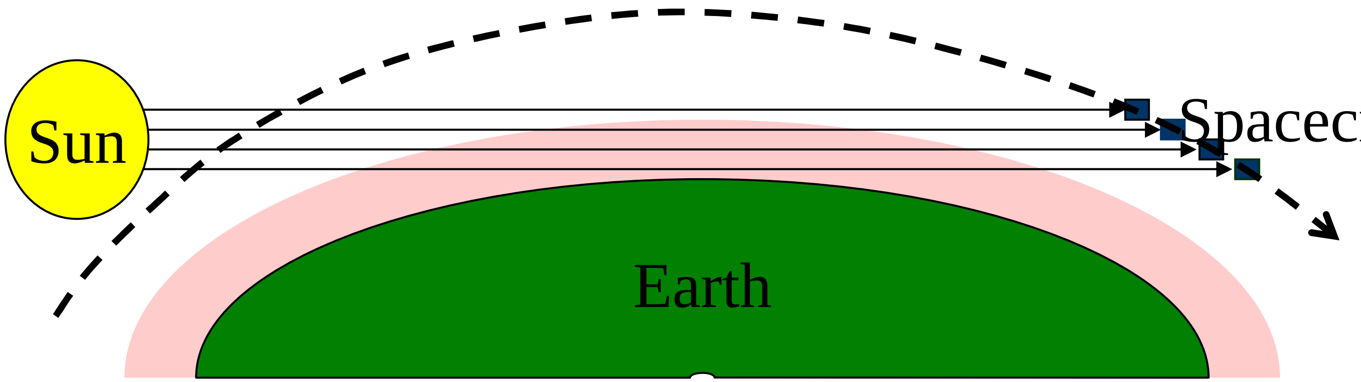
High Radiometric Calibration Accuracy:

Radiation thermally emitted by the instrument or atmosphere is negligible compared to Sun.

Ratioing limb spectra against exo-atmospheric spectrum removes solar & instrumental features.

Unambiguous photon path history:

All measured photons come from Sun and traverse the full limb path.



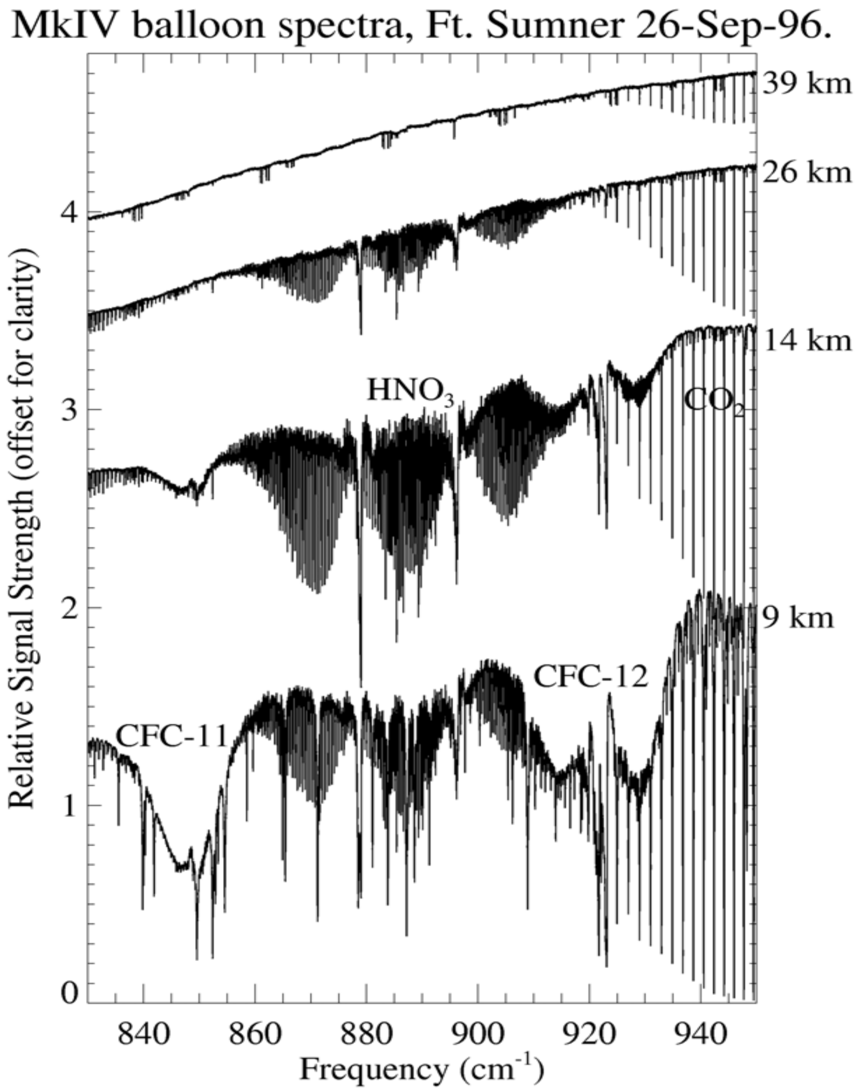
Examples of MkIV Limb spectra

Figure shows a series of MkIV balloon Spectra at different tangent altitudes.

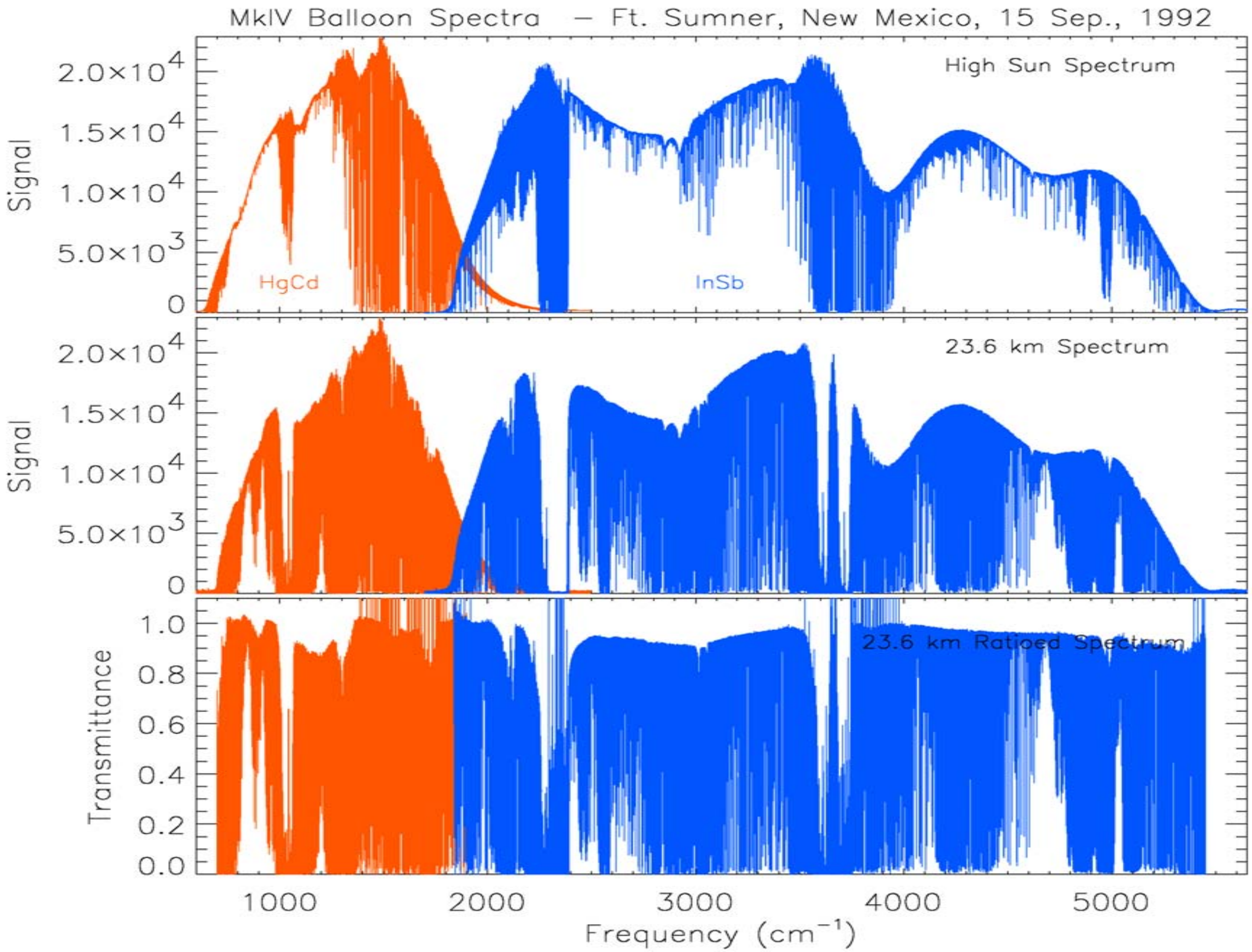
Solar and instrumental features (e.g. OH lines do not vary with altitude.

Absorptions from stratospheric gases e.g. HNO_3 peak in strength at ~15 km.

Absorption from tropospheric gases (e.g. CFC-11 & CFC-12 become strongest at the lower altitudes.



Solar occultation spectra: High-sun, Limb, and Ratio



Solar Occultation Spectra for Spectroscopy Validation

The broad spectral coverage of FTIR solar occultation spectra, together with their high SNR and resolving power, make them very useful for assessing the adequacy of the spectroscopic databases.

•Look for significant omissions in the current linelist (e.g. missing gases, isotopologues, hot-bands)

•Investigate adequacy of physics (e.g. far-wing line shapes, line-mixing)

•Assess relative strengths of bands in different spectral regions (laboratory spectrometers tend to have narrower spectral coverage)

•Assess pressure-dependent parameters (widths, shifts)

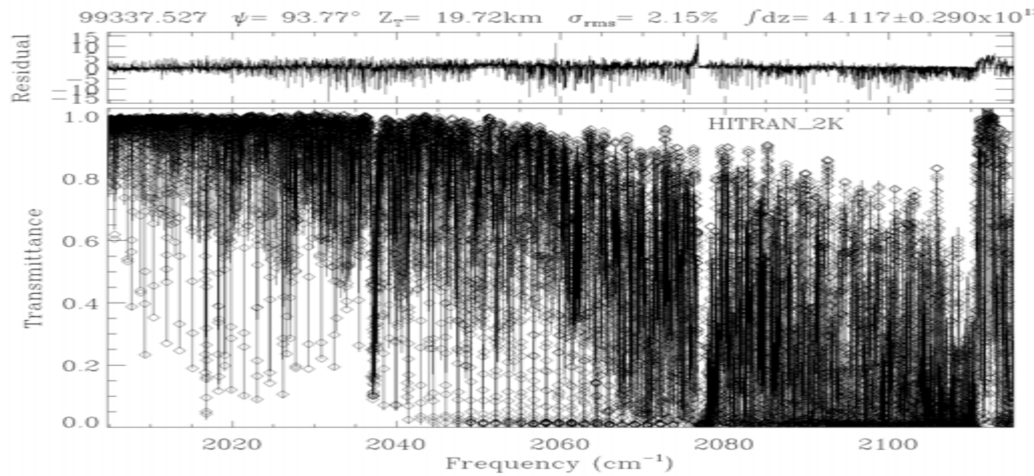
•Check parameters of gases for which laboratory measurements are very difficult (e.g. O_2, N_2, low-temperature H_2O,)

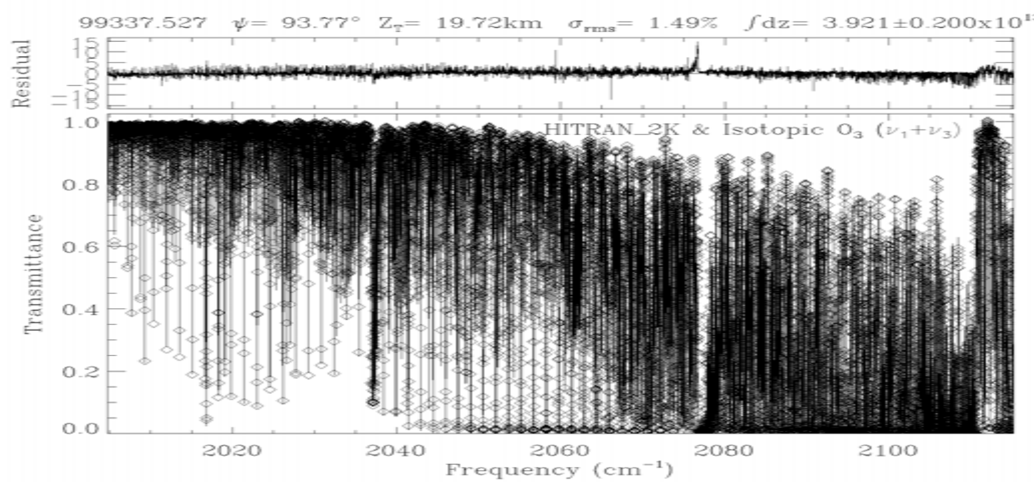
Balloon measurements of $^{34}S/^{32}S$ isotopic fractionation in OCS

Spectra in the 2000-2100 cm^{-1} region have been used to retrieve vertical profiles of $OC^{32}S$ and $OC^{34}S$.
There are strong absorption lines in the 2000-2100 cm^{-1} spectral region due to H_2O, CO_2, O_3, CO, and OCS.

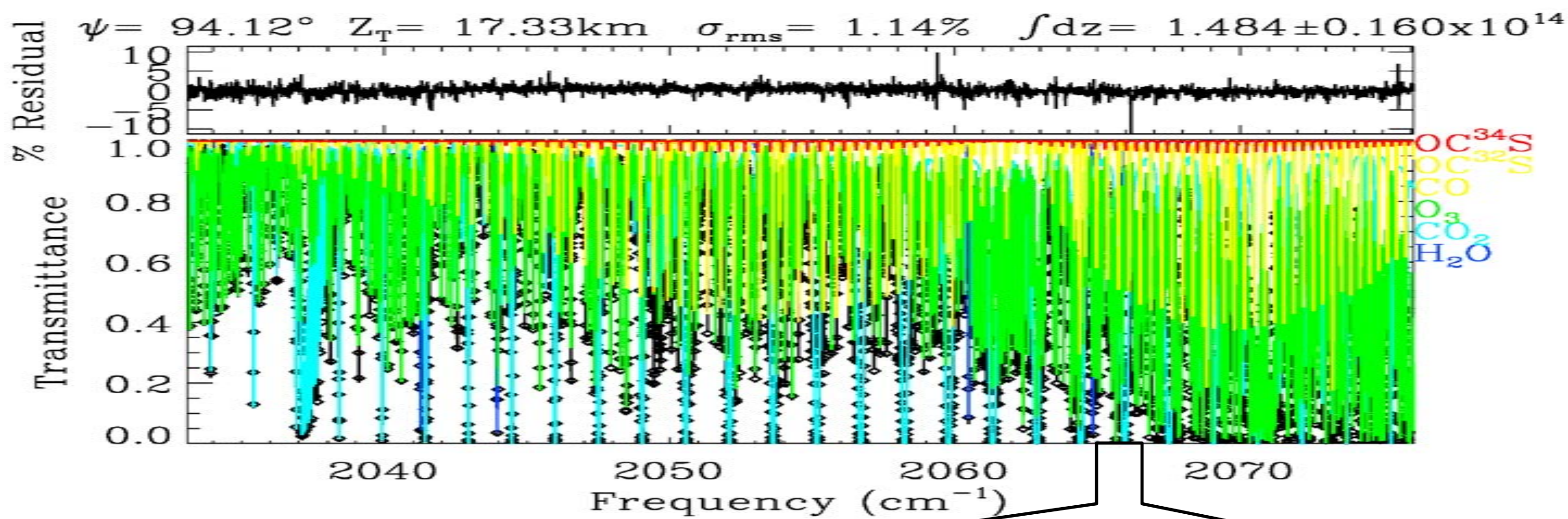
Upper Panel: The spectral residuals are poor using just the HITRAN linelist.

Lower Panel: Adding the missing v_1+v_3 bands of the 668 and 686 isotopomers of O_3 centered at 2092 and 2051 cm^{-1} (provided by Alain Barbe) improves the fits.



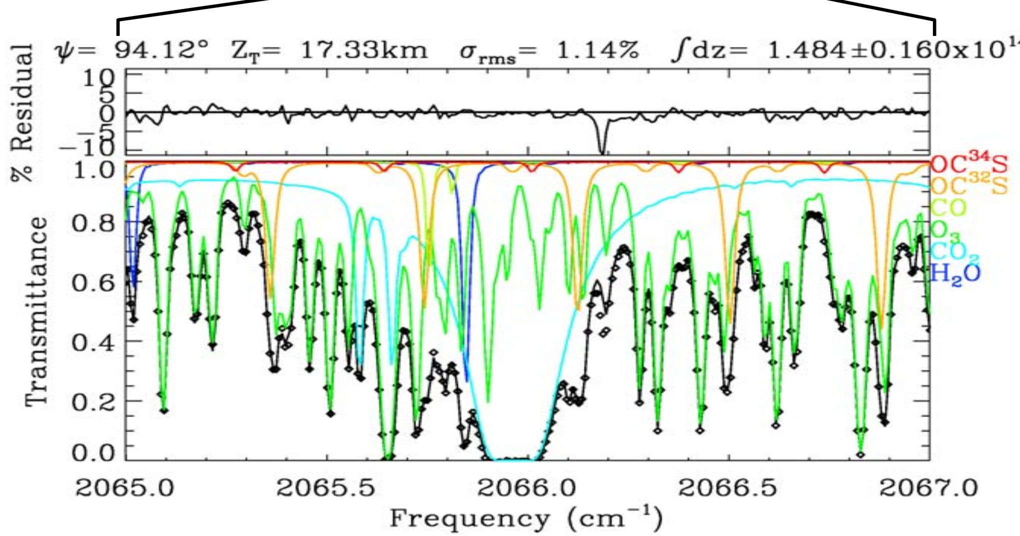


Balloon measurements of $^{34}S/^{32}S$ isotopic fractionation in OCS



Upper Panel: Example of a fit to a MkIV limb spectrum in the 2030-2080 cm^{-1} region used to measure OCS. The spectrum can be fitted well (~1% rms) allowing the $OC^{34}S$ lines of 3-4% depth to be easily detected.

Lower Panel: Blow-up of the 2065-2067 cm^{-1} region.

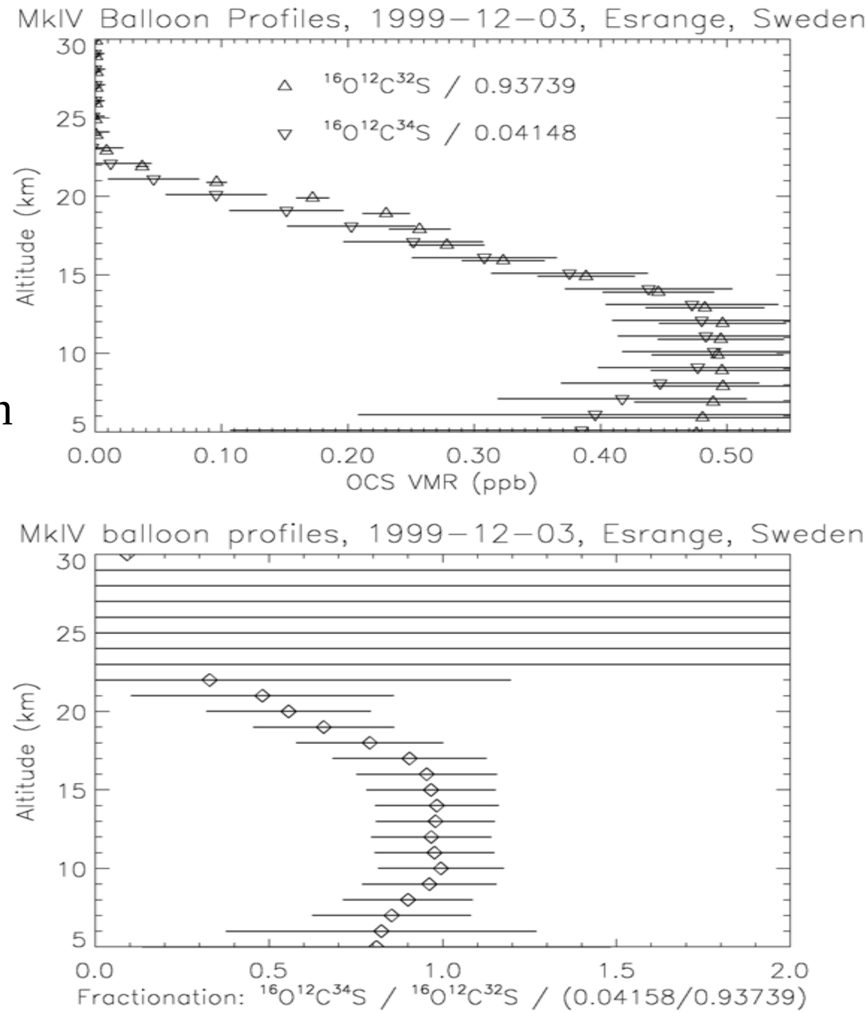


Balloon measurements of $^{34}S/^{32}S$ isotopic fractionation in OCS

Vertical profiles of $OC^{32}S$ and $OC^{34}S$ were retrieved from MkIV balloon spectra measured from Sweden, in December 1999 (upper panel).

These profiles were used to derive profiles of $^{34}S/^{32}S$ isotopic fractionation (lower panel). This is significantly lower than 1 in the 18-22 km altitude range, for this particular flight.

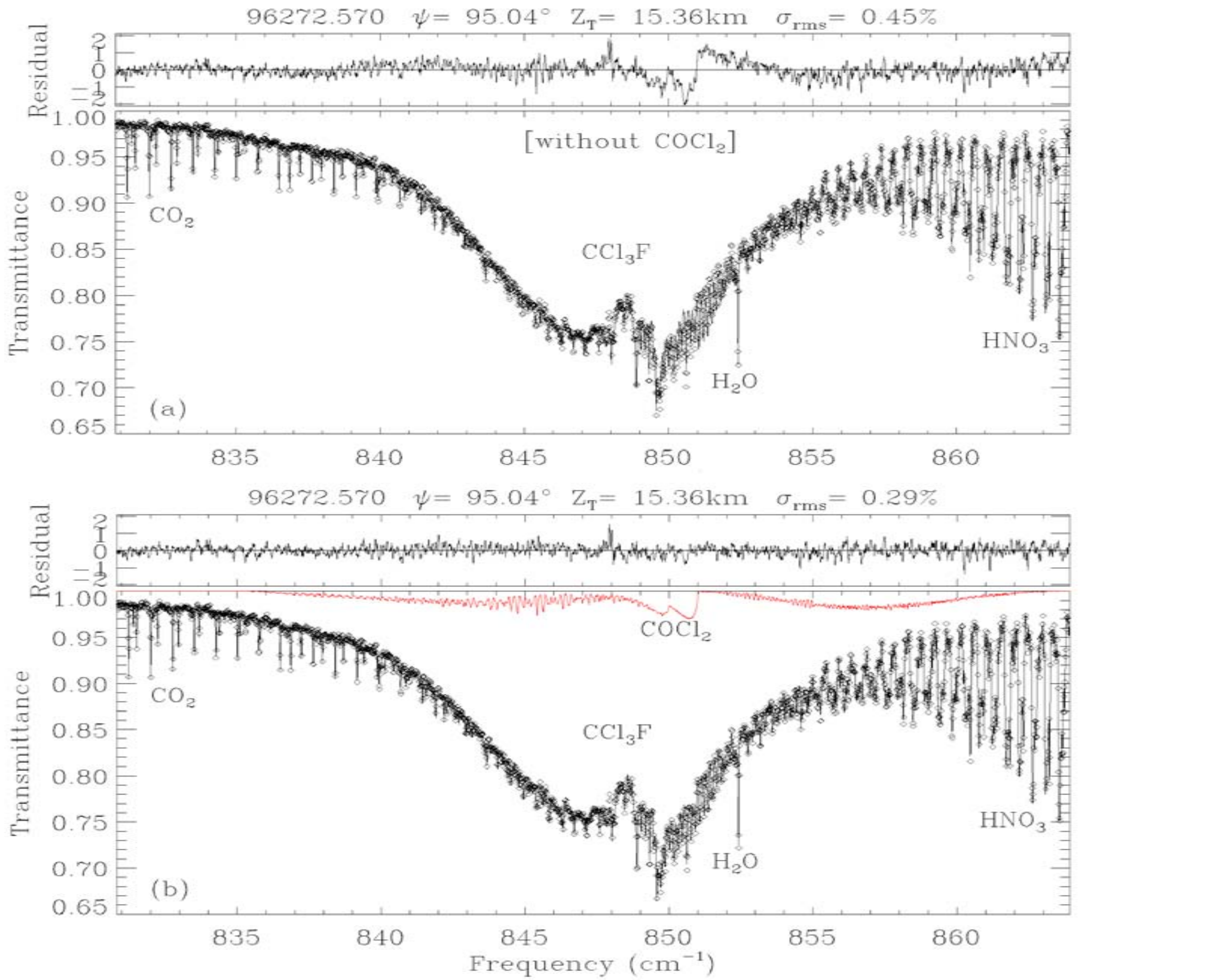
These, along with results from earlier balloon flights, were used by Leung et al.[2002] to demonstrate that OCS cannot be the primary source of stratospheric sulphate aerosol, because their $^{34}S/^{32}S$ratios are quite different.



MkIV balloon measurements of $COCl_2$

Upper Panel: Spectral fit to a MkIV limb spectrum using the HITRAN linelist. Main absorption band is due to CCl_3F (CFC-11). At first we thought that the persistent systematic residuals around 850 cm^{-1} were due to errors in the CCl_3F cross-sections.

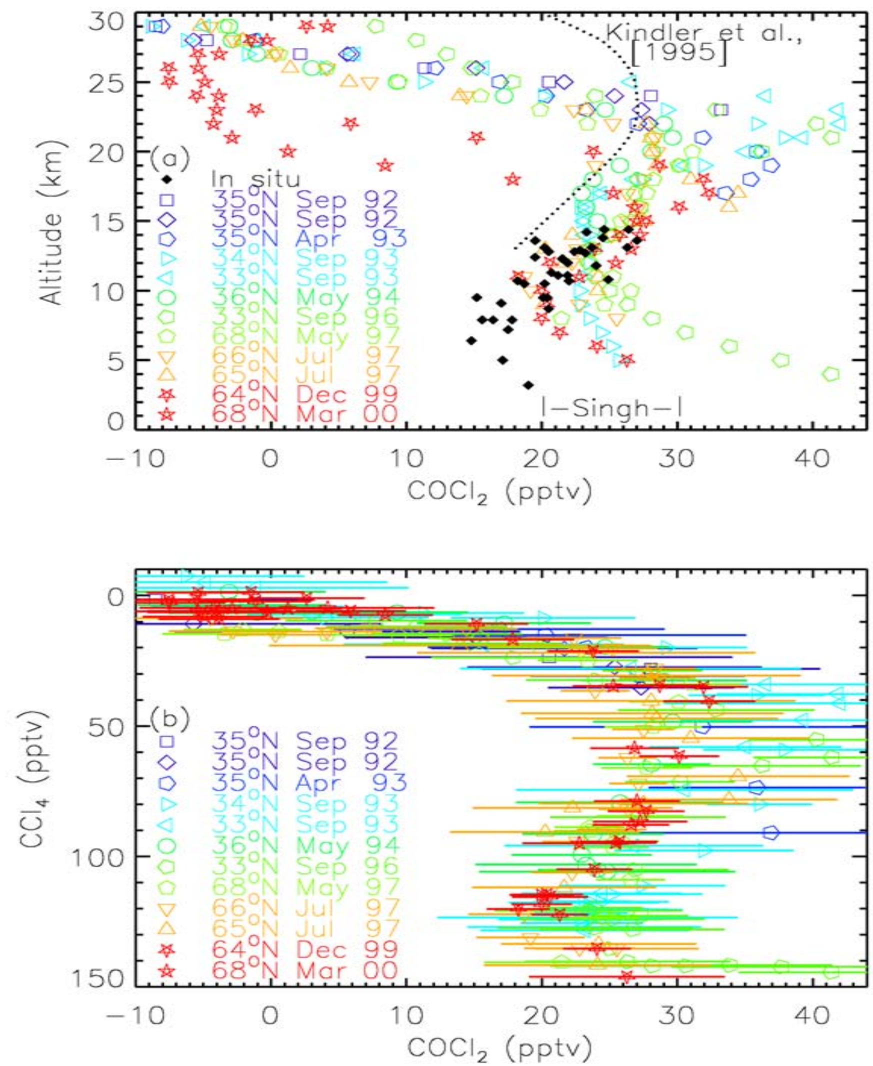
Lower Panel: Spectral fits after including $COCl_2$ linelist (from Brian Drouin, JPL). Red line shows contribution from $COCl_2$ alone.
Despite the much stronger overlapping absorption of the CCl_3F, $COCl_2$ is easily detected, from its unique absorption signature.



MkIV balloon measurements of $COCl_2$

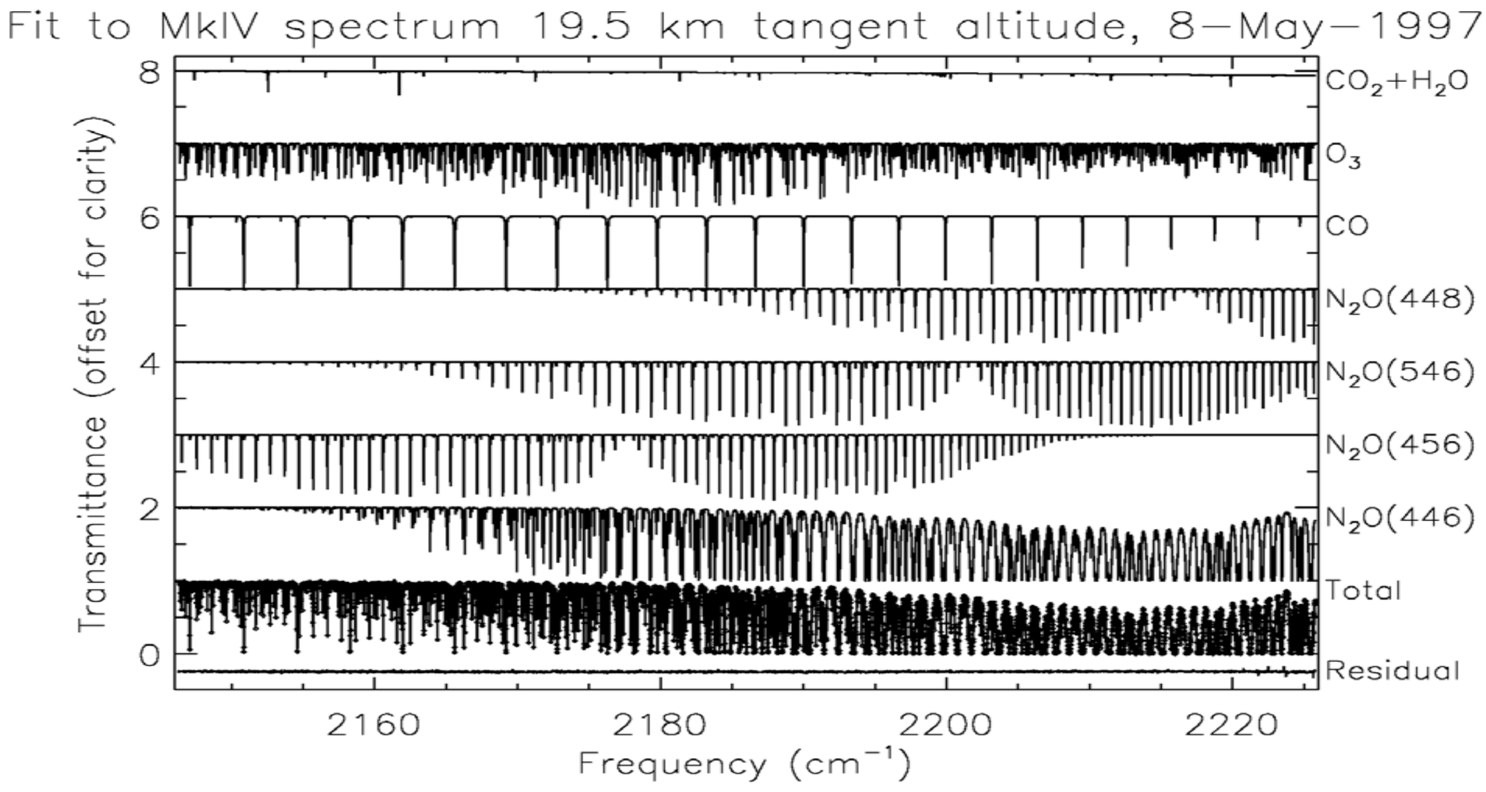
Upper Panel: Profiles of $COCl_2$ were retrieved from 12 different MkIV occultations (open colored symbols). These are compared with airborne in situ observations (solid black symbols), and model prediction (black dotted line). Substantial vortex descent is apparent in the Dec 1999 and Mar 2000 profiles (red stars).

Lower Panel: Plotting the same $COCl_2$ profiles versus CCl_4 (a long-lived tracer) rather than altitude, removes variations due to transport. For example, the Dec 1999 and Mar 2000 profiles now fall into line with the others.



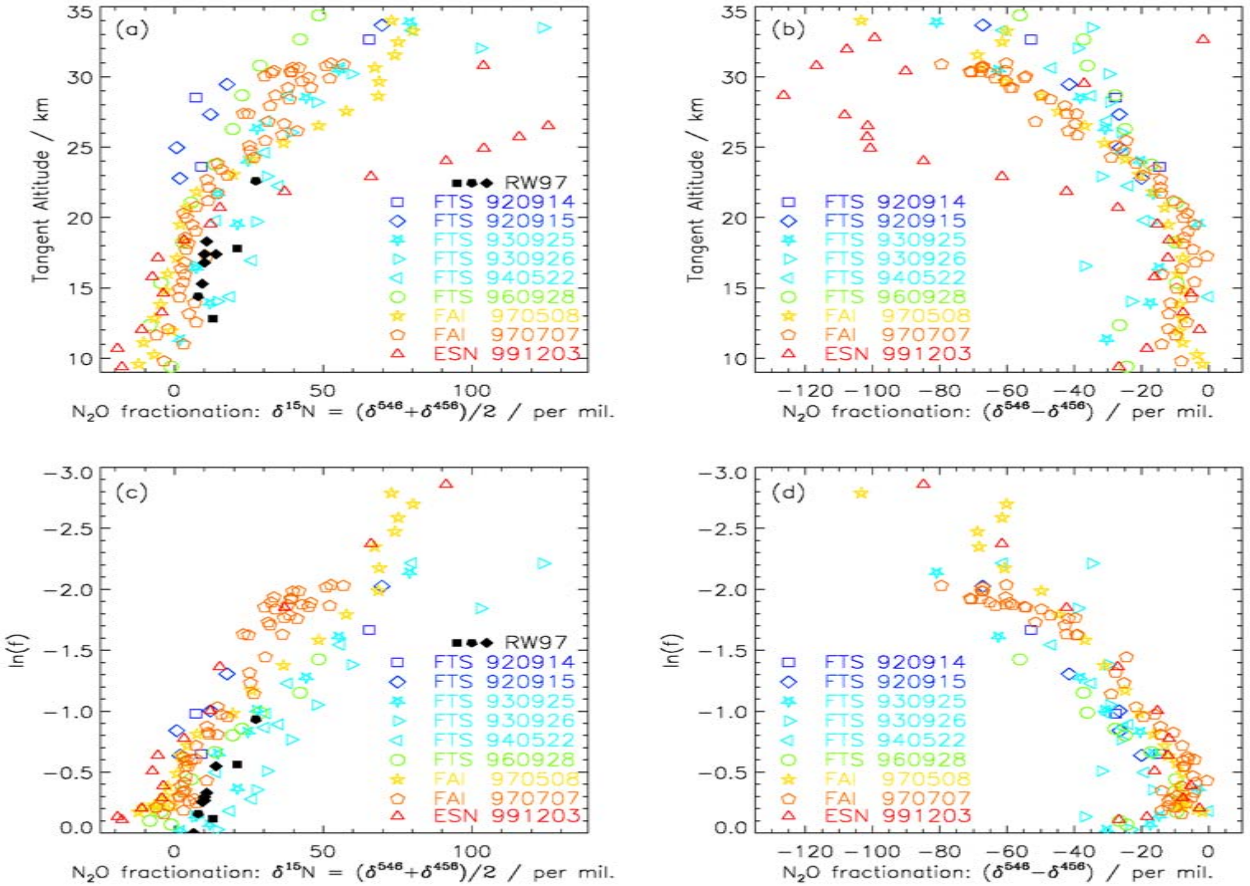
Isotopic Fractionation in N_2O

Griffith et al., [2000] measured the fractionation in stratospheric N_2O from MkIV balloon spectra, such as the one fitted below. Four different N_2O isotopologues can be measured in the 2140-2210 cm^{-1} region.



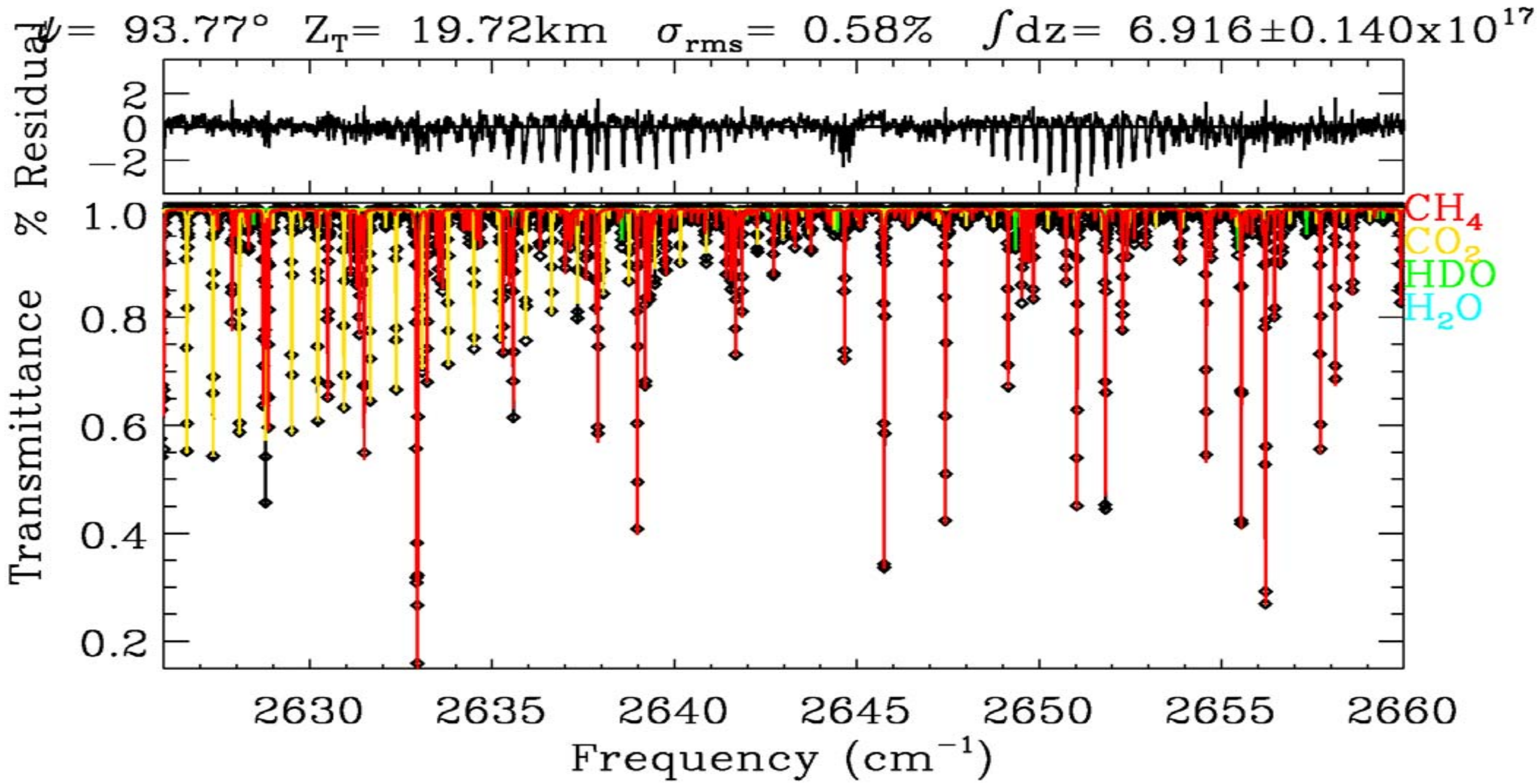
Isotopic Fractionation in N_2O

The results showed that atmospheric N_2O becomes progressively enriched in the heavy isotopologues with increasing altitude. This is due to their lower photolysis cross-sections cause by their zero point energy shifts.



Missing $2v_4$ band of HNO_3 ?

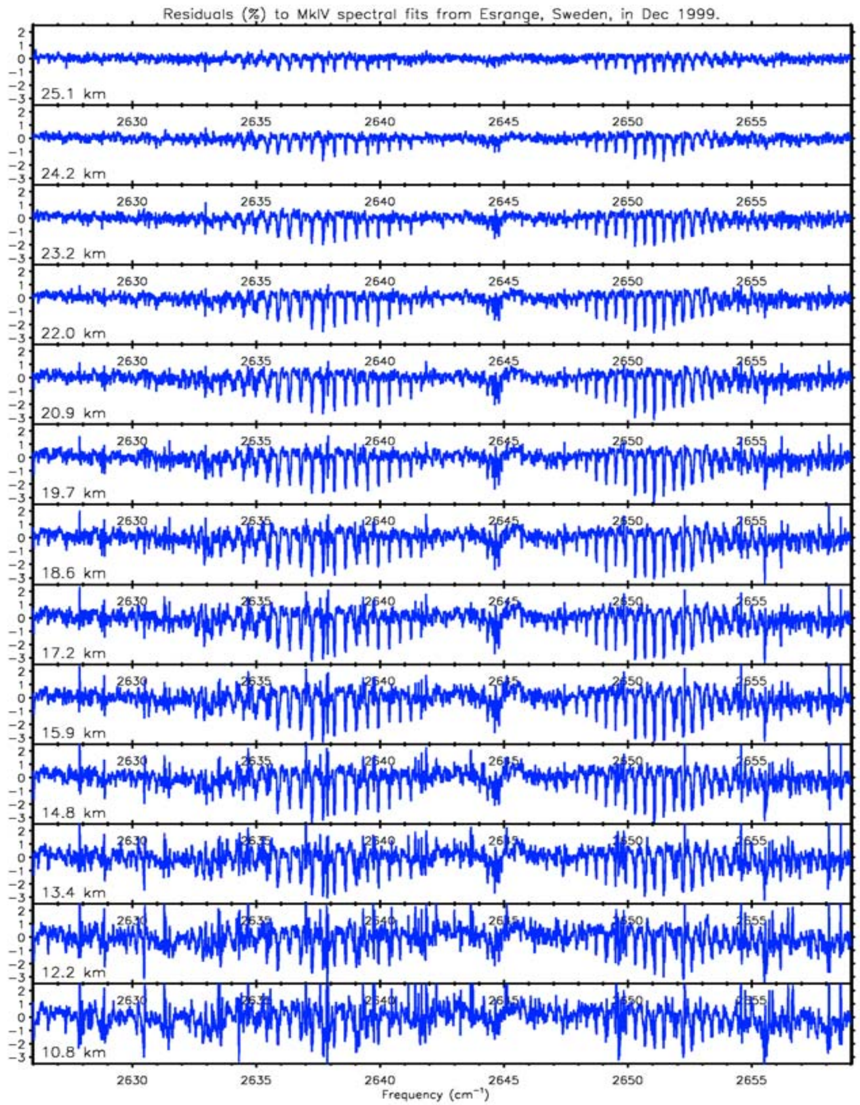
Fitting MkIV balloon spectra in the 2620-2660 cm^{-1} region show the presence of systematic residuals, that appear to exhibit P, Q, and R-branches. These residuals are up to 3% deep in spectra measured from Esrange, Sweden. in December 1999. The presence of these residuals can cause problems in fitting gases (e.g. HDO, HBr, H_2S, CO_2 isotopologues) in this region.



Missing $2v_4$band of HNO_3 ?

The altitude variation of the depths of these residuals confirms that the concentration of the responsible absorber peaks in the lower strato-sphere at ~16 km.

We believe that HNO_3 is the most likely candidate since the band looks like the longer wavelength HNO_3 bands and each of the absorption dips is a manifold containing several lines. Since the HNO_3 v_4 band is centered at 1326 cm^{-1}, a possibility is the $2v_4$ band.



Conclusions

Solar occultation spectrometry has the high SNR and spectral resolving power necessary to:

- Identify weak absorptions due to trace gases and minor isotopomers.

- Identify inadequacies in the spectroscopic database and pinpoint their cause.

In general, fits to MkIV balloon spectra are limited not by the measurement noise but by spectroscopic limitations.

To identify more weakly absorbing trace gases and minor isotopologues requires further spectroscopic improvement. Not just the trace species themselves, but more importantly, the major gases whose absorptions overlap the trace gas absorptions of interest.