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NOTE ON OZONE CORRECTION FOR THE TIROS-N STRATOSPHERIC SOUNDING UNIT

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NOTE ON OZONE CORRECTION FOR THE TIROS-N STRATOSPHERIC SOUNDING UNIT

D R Pick, J Nash and D E Warner, Met O 19 - April 1978

Preamble

The Stratospheric Sounding Unit (SSU), which is to be launched on the TIROS-N series of operational satellites, measures radiation emitted from the atmosphere in the spectral region 630-710 cm^{-1}. The radiometer utilizes a pressure modulation technique and its difference transmission, or chopped spectral response, is complex. While most of the radiation in this spectral region originates from the ν_2 band of carbon dioxide, ozone also has a fundamental ν_2 band centred at 710 cm^{-1} extending over the spectral range 550-850 cm^{-1} (see McCaa & Shaw 1967, McClatchey et al 1973). Figure 1 illustrates the calculated transmission for .5 atm cm path of ozone at 1 cm^{-1} resolution; typical atmospheric amounts vary between .2 and .5 atm cm. Also shown in Figure 1 is the calculated spectral response at 1 cm^{-1} resolution for the high pressure modulator of the SSU. The actual transmission due to ozone is the result of weighting the ozone curve by the pressure modulation curve.

Since there is no ozone in the pressure modulator, modulation arises from random coincidences between the high resolution spectra of ozone and carbon dioxide. A calculation of adequate accuracy is limited by the accuracy of the line positions in the two spectra and the complexity of the two spectra. Thus it was thought advisable to experimentally measure the effect on the three SSU channels.

The Experiment

Figure 2 shows an outline of the ozone generation and storage system. Basically oxygen is blown at $\sim$ 75 ml/min through phosphorus pentoxide (a drying agent) into a double walled container. The inside well is filled with copper sulphate to form a conducting electrode, while the outside sits in a bath of copper sulphate, isolated from the previous electrode, to form the other electrode. These electrodes are maintained at 22 kV at 50 Hz and generate ozone by the silent electrical discharge method. Some 5-10% of the oxygen is converted to ozone. This is monitored by measuring the change in transmission in a 1 cm cell in the gas flow. The ozone is removed from the oxygen flow by absorption on to silica gel cooled by solid carbon dioxide (-80°C). After several hours, when the equivalent of a .7 atm cm for the white cell has been absorbed (ie a deep blue band $\sim$5 cm wide in the silica gel), the oxygen stream is turned off

and the system evacuated to remove the residual oxygen. The silica gel on warming to room temperature releases the ozone into the 5 l flask, The yield should be about a pressure of ~ 15 cm Hg. This ozone is then admitted into the evacuated while cell, buffered with oxygen and the transmission measured for the SSU using the 9.1 m path.

Several precautions are necessary when making ozone. Since the gas is toxic, the charcoal trap is put in the exhaust line to decompose surplus ozone during generation. As the gas is highly reactive, grease and flammable materials must be scrupulously avoided. The rotatory pump oil used to evacuate the white cell and the ozone system must be special oil for this purpose. The other main problem is to protect against flying glass if an explosion occurs, hence the system is encaged in a laminated glass sided box with 1" block board base and top. Tap control and jabjack motion are performed with a screw driver through small holes in the top or bottom.

The ozone amount in the white cell is monitored using the apparatus outlined in Figure 3. With no ozone in the measurement arm, the ratio between the ozone detecting diode output and the reference photodiode is monitored. As ozone is introduced this ratio changes and the amount is deduced from the absorption and a measurement of the absorption path. The type U2 filter is used to isolate the strong mercury line at 253 nm using a (base 10) absorption coefficient of 133.9 (cm NTP)$^{-1}$ (A S Hearn, 1961) from the low pressure mercury lamp.

Results and Interpretation

Figure 4 shows the experimental results obtained with the SSU development model D2. The absorption by ozone for the high pressure cell is about as expected, but the medium and low pressure cells are affected by carbon dioxide, presumably generated by ozone attacking the rubber O rings and various electronic equipment inside the while cell chamber. The low pressure cell absorption is used to estimate the carbon dioxide content appropriate to that measurement from which a correction to the high pressure cell absorption is produced. The high pressure cell absorption is relatively insensitive to carbon dioxide amount at these values.

In the atmospheric case the ozone layer is below the .1 transmission for the low pressure cell (cf Figure 7, high pressure is .7) and hence the ozone correction is a factor of 7 less sensitive for the low pressure cell (due to the overlying carbon dioxide).

The measurements and model calculation for the high pressure cell are plotted in Figure 5, and demonstrates that the model overestimates the experimental results. This is insignificant in the light of the effect on the atmospheric weighting function (qv).

Transmission Model for Ozone

Rather than do elaborate line by line calculations it was decided to try modelling the ozone absorption by evaluating $\Sigma_\nu (\bar{\tau}_{cell} \times \tau_{ozone})$ $\Sigma_\nu \bar{\tau}_{cell}$, where the summation step is 1 cm^{-1} and the $\bar{\tau}$ are the mean transmission at 1 cm^{-1} resolution for the cell pressure modulation (τ_{cell}) and ozone (τ_{ozone}). The pressure modulation spectral shape has been previously claculated, while calculating the atmospheric transmission tables using a modified Drayson line by line programme. The ozone transmission is estimated using a Goody Randon model of the form

$$\bar{\tau}_{ozone} = \exp(-1./\mathrm{SQRT}(1./(\Sigma S.m)^2 + 1/(2(\Sigma\sqrt{Sd})^2 \times u)))$$

where ΣS is the sum of line strengths in the 1 cm^{-1} interval, $\Sigma\sqrt{Sd}$ is the sum of the square root of the product of line strength and line width (at one atmosphere). These were calculated from the McClatchey (1973) line data (at 300K for tank conditions, 220K for the atmospheric correction). m is the total amount in the path (g/cm^2 units used) while u is the pressure (in atmospheres) weighted amount.

The programming and scaling factors were readily checked by calculating the band equivalent width ($\Sigma_\nu (1 - \bar{\tau}_{ozone})$) for various experimental conditions used by McCaa and Shaw (1967), see Figure 6.

Effect of Ozone on the SSU Atmospheric Transmission Tables

A large series of ozone profiles measurements over the USA have been documented by Herring and Bowden (1964). Comparison of the profiles indicate that probably the distribution most likely to effect the SSU is the Canal Zone profiles (total ozone .28 atm cm) rather than the Goose Bay type (.5 atm cm) (see Figure 7). This is because of the higher ozone concentration at 30 mb. Ozone transmission tables for the three pressure modulators and angles 0, 5, 15, 25 and 35 were generated for a "worst case" equatorial case, and a maximum ozone amount case. These tables are then used to correct a similar transmission table for atmospheric carbon dioxide. The perturbation due to the ozone is obviously reduced due to the fact that the ozone occurs in a broad layer which is below the bulk of the carbon dioxide absorption.

The largest effect is $\Delta\tau$ of .005 for the high pressure cell at 35° off nadir for a canal zone profile, and .004 for the Goose Bay profile. This is equivalent to a systematic radiance error of up to .18 and .13 mW/m^2 st cm^{-1}, as found by calculating radiation with and without ozone correction for a set of rocket observations.

Error of Estimate

The agreement of the model with experiment is about .015 in a transmission change of .05 ie 30%, while the total equivalent width from McCaa and Shaw agrees to $\sim$ 2%. The most likely theoretical problem is modelling at 1 cm^{-1} resolution the correlation between the different line spectra, where line widths are $\sim$ .1 cm^{-1}/atm or up to 4×10^{-3} cm^{-1} during the tank run. Positional accuracy of ozone lines of $\pm$ .03 cm^{-1} will cause problems for a more elaborate CO_2/Ozone line by line calculation. The effort is not justified by the smallness of the effect in this case.

Conclusion

The variation and size of the ozone correction makes seasonal or latitude/longitude adjustments unnecessary. A mean of the two ozone corrections is applied to the high pressure channel transmission table for the SSU. However for a filter radiometer such as HIRSII viewing the lower atmosphere with 14 cm^{-1} filters at 716 cm^{-1} the ozone transmission correction is large ($\sim$ .07) and variable.

References

1. R A McClatchey, W S Benedict, S A Clough, D E Burch, R F Calfee, K Fox, L S Rothman & T S Garing — 1973 — AFCRL Atmospheric Absorption Line Parameters Compilation, AFCRL TR 73 0096, Environmental Research Papers No 434.
2. D J McCaa & J H Shaw — 1967 — Infrared bands of ozone. AFCRL 67 0237.
3. W S Herring & T R Borden — 1964 — Ozone Observations over North America. AFCRL-64-30/2 and follow on pubs.
4. A S Hearn — 1961 — Proc. Phys. Soc. 78 p 832.

Acknowledgements

The sketch design of D R Pick was elaborated by P M Kent and D E Warner; the glass system was built by C Gazzard. The electronics system for monitoring the ozone content (using U.V. absorption of the mercury line at 254 nm) was designed and built by G A Robinson and P Westbury. J Nash and D E Warner finally got the system to work and made the measurements. D R Pick provided the model calculations.

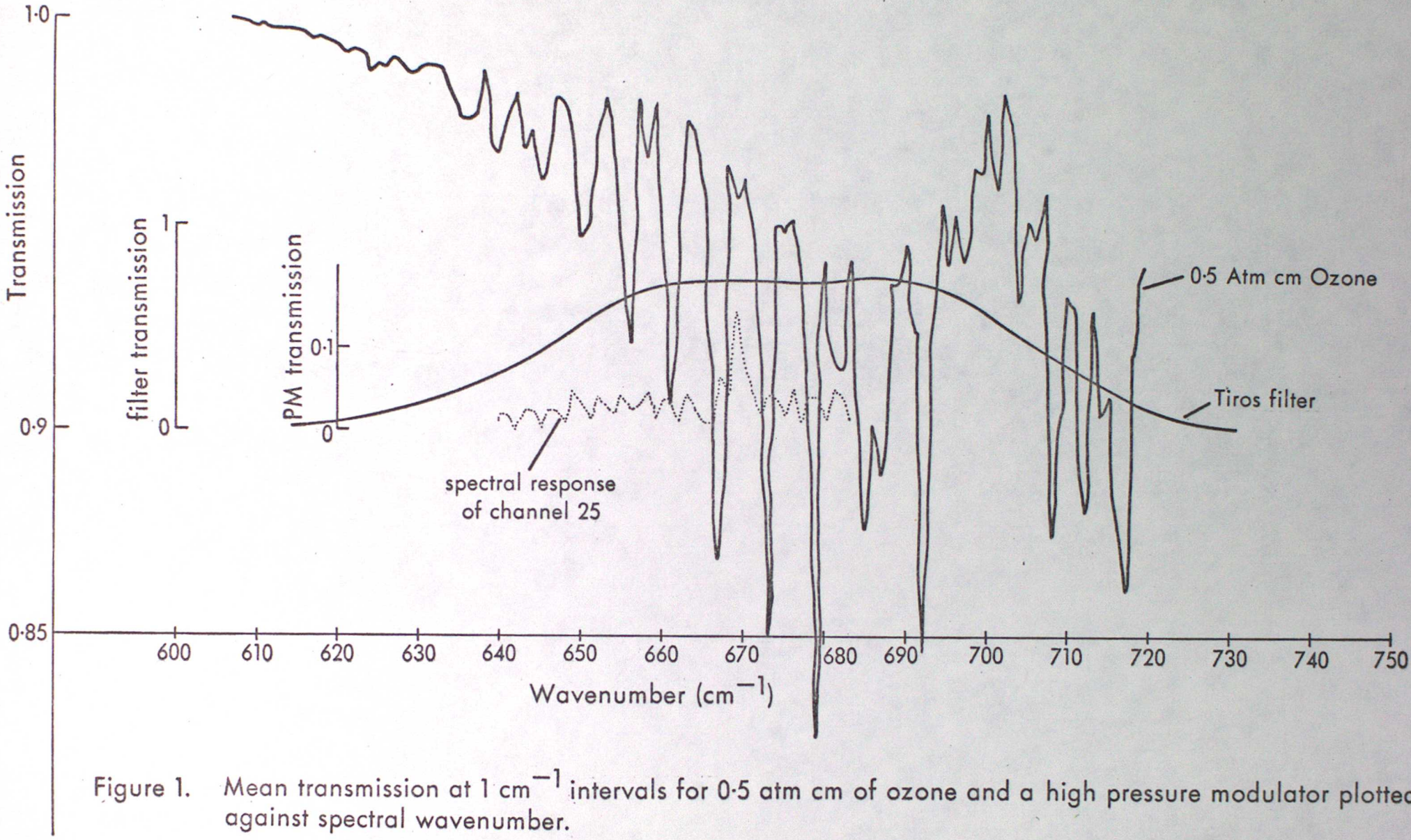

Figure 1. Mean transmission at 1 cm^{-1} intervals for 0·5 atm cm of ozone and a high pressure modulator plotted against spectral wavenumber.

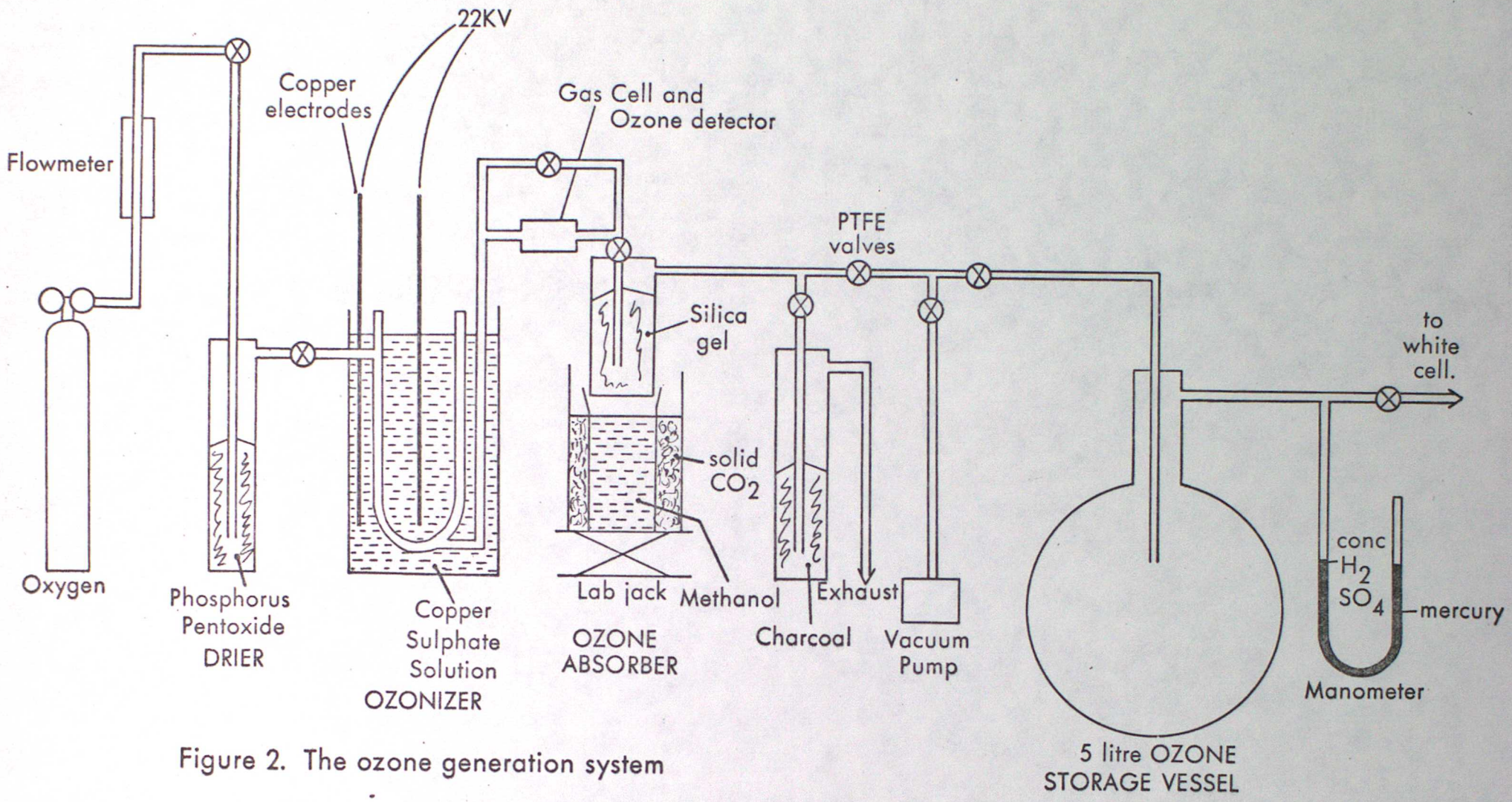

Figure 2. The ozone generation system

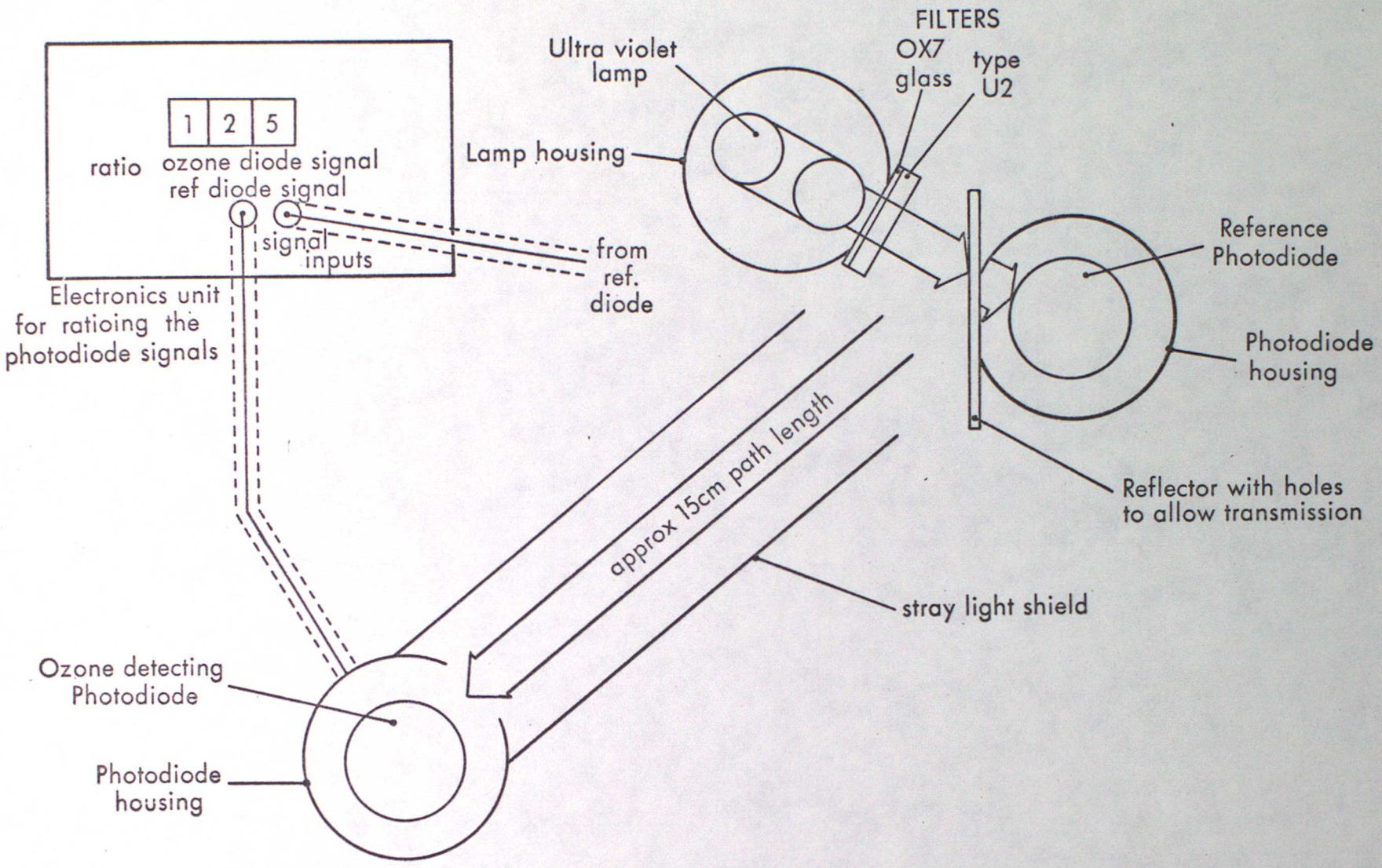

Figure 3. The white cell ozone measuring system.

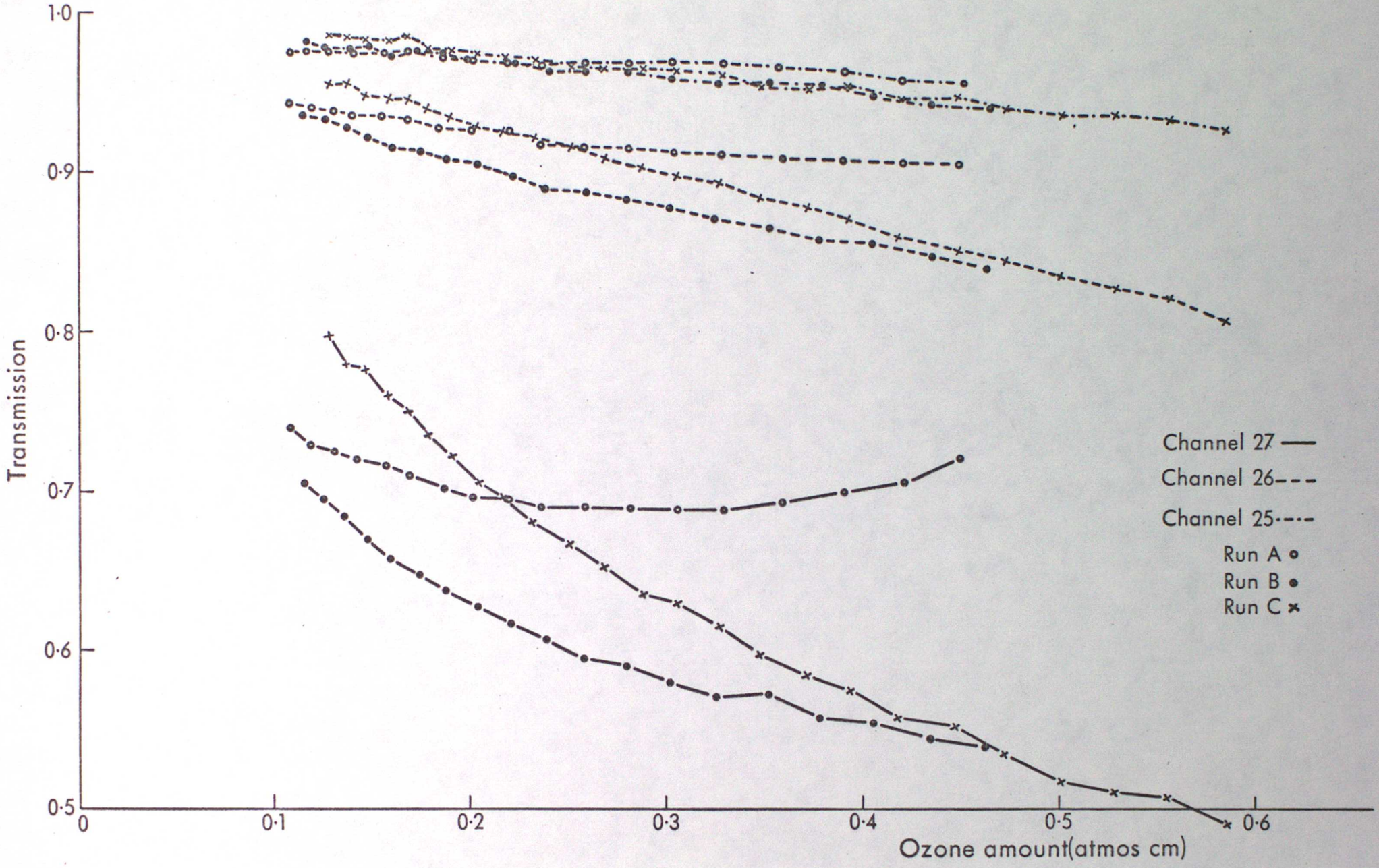

Figure 4. Absorption measurements for development model SSU, with ozone/oxygen mixture

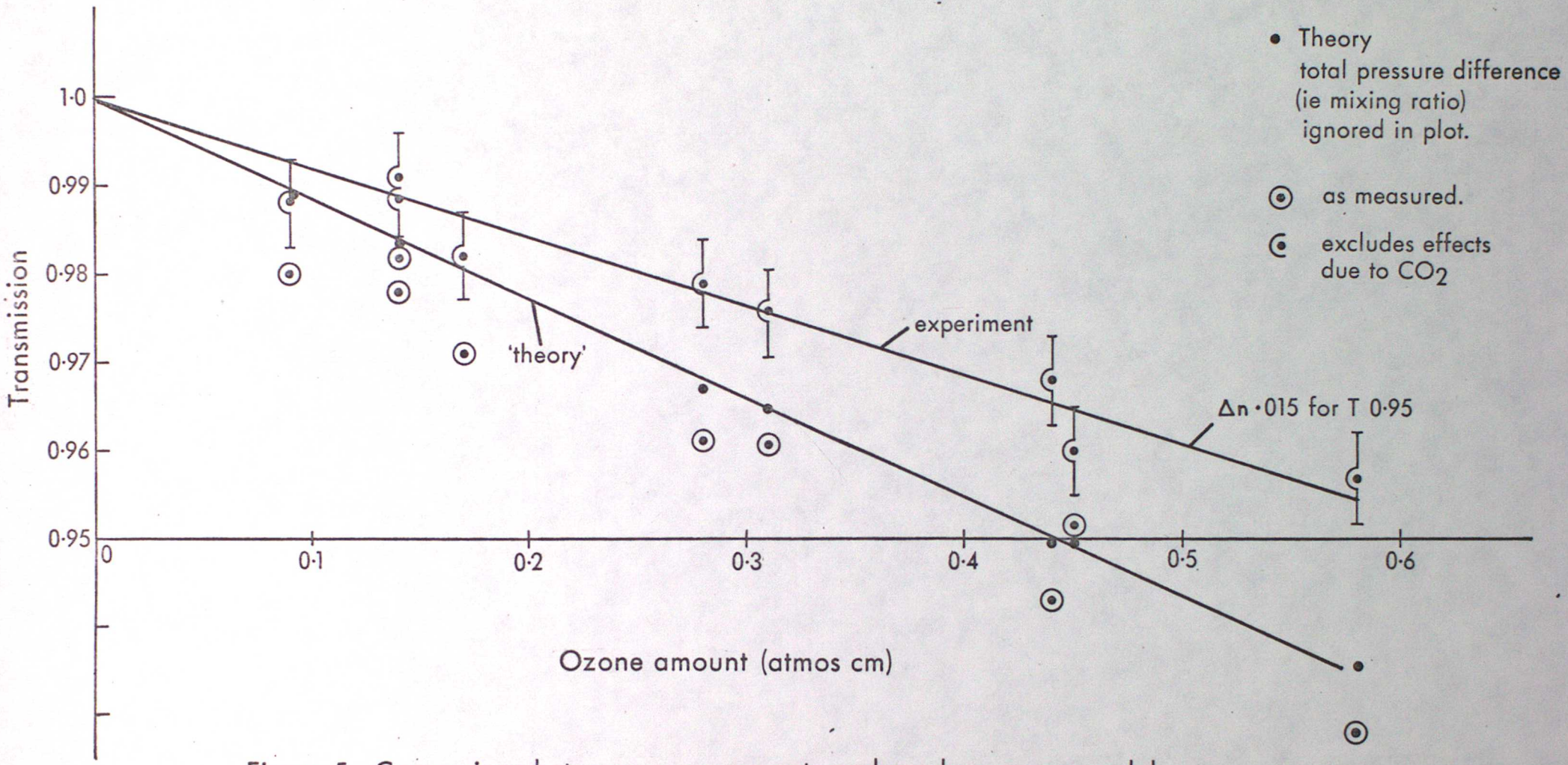

Figure 5. Comparison between measurements and random ozone model.

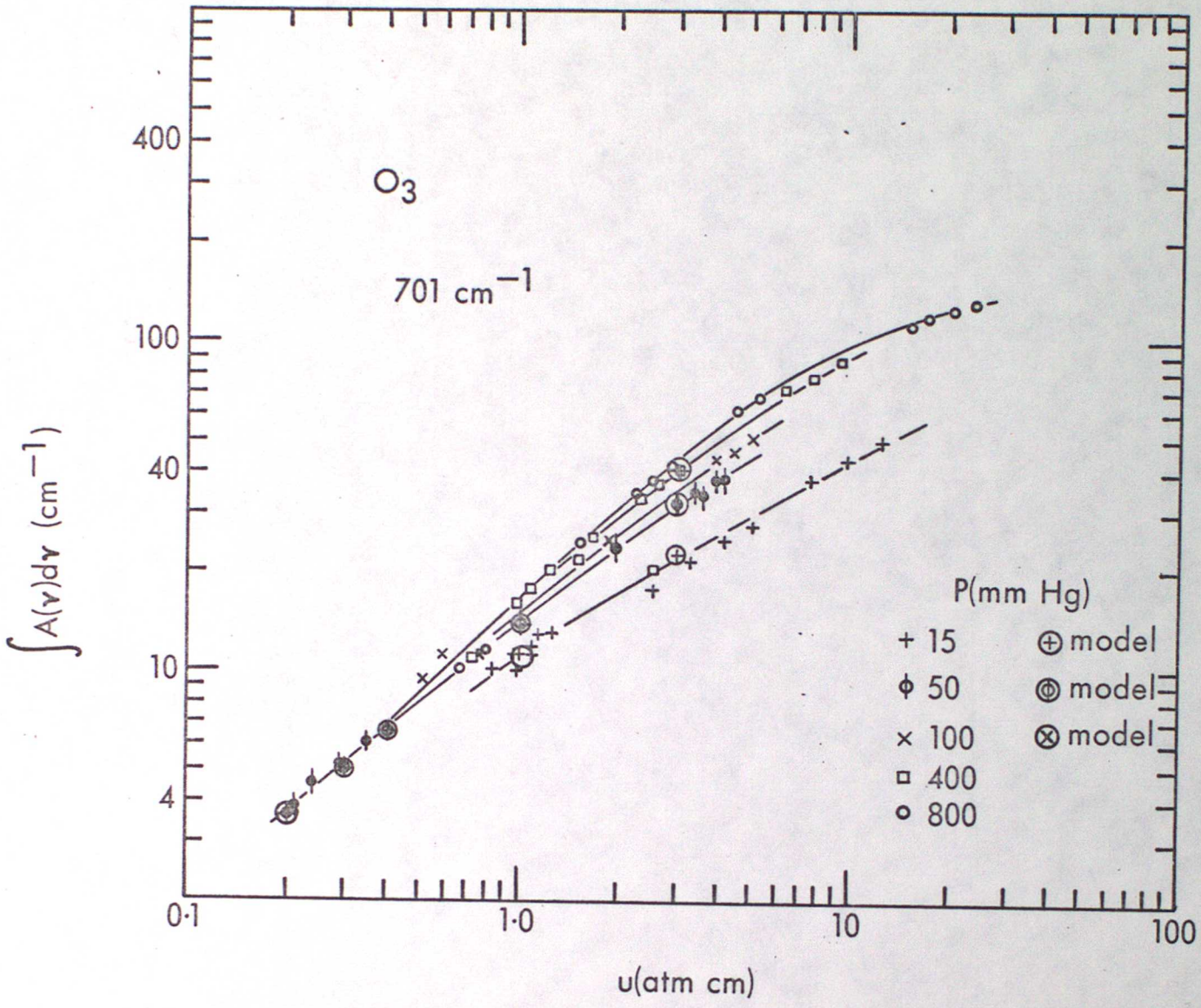

Figure 6. McCaa and Shaw ozone equivalent width data for the ν_2 band centred at 710 cm^{-1}.

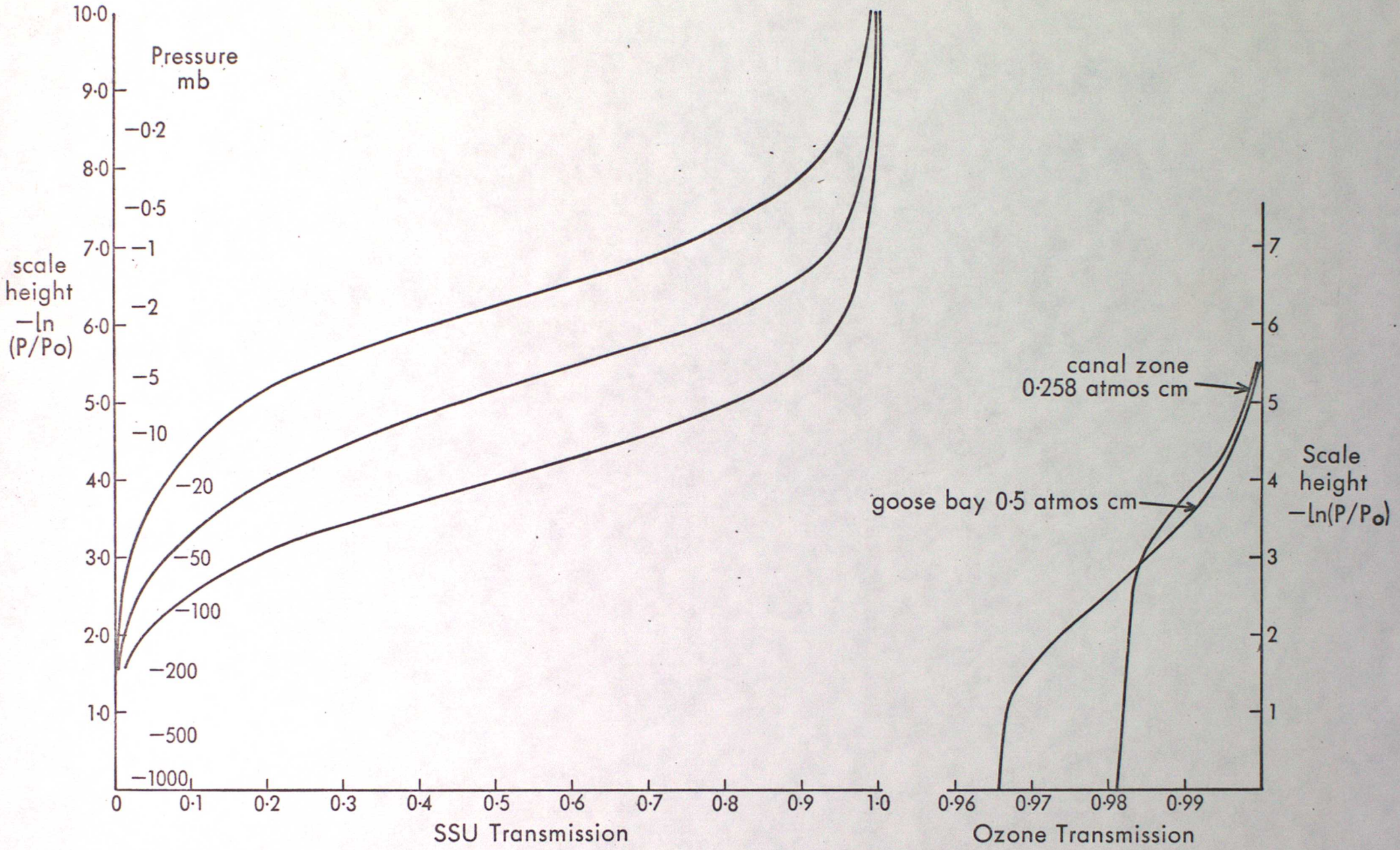

Figure 7.Transmission height profiles. for the the three SSU pressure modulators and two ozone transmission profiles