DAYTIME ClO OVER McMURDO IN SEPTEMBER 1987: ALTITUDE PROFILE RETRIEVAL ACCURACY

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During the 1987 National Ozone Expedition, mm–wave emission line spectra of the 278.6 GHz rotational stratospheric ClO were observed at McMurdo Station, Antarctica (deZafra et al., these proceedings). The results confirm the 1986 discovery (deZafra et al., Nature **328**, 408, 1987; Solomon et al., Nature **328**, 411, 1987) of a lower stratospheric layer with ~100 times the normal amount of ClO; our 1987 observations, made with a spectrometer bandwidth twice that used in 1986, make possible a more accurate retrieval of the altitude profile of the low altitude component of stratospheric ClO from the pressure broadened line shape, down to ~16 km. The accuracy of the altitude profile retrievals is discussed, using the "daytime" (09:30 to 19:30, local time) data from 20 to 24 September, 1987 as an example. The signal strength averaged over this "daytime" period is ~85% of the midday peak value. We also discuss the rate of ozone depletion implied by the observed ClO densities.

Figures 1 & 2 show the derived ClO profile in units of mixing ratio and number density respectively. For the initial guess at the altitude profile required by the deconvolution algorithm, we used a constant 0.5 ppbv at altitudes above 18 km. Below 18 km, we assumed that the ClO mixing ratio declined rapidly as found in the in situ aircraft measurements (NASA Press Release, October, 1987) over the Palmer Peninsula during August and September, 1987.

The distribution is bimodal with maxima at 19 km and at about 36 km. The uncertainty in the derived profile is much greater for the upper stratospheric ClO, which depends on the intensities over narrow frequency intervals near the line center, while the lower stratospheric mixing ratio depends on intensities averaged over wide frequency intervals in the spectral line wings. In this paper we will focus on the lower stratosphere, which is the location of the Antarctic ozone depletion.

The sources of error include 1) system calibration, 2) statistical noise in the data, 3) baseline curvature due to variations in instrumental response across the spectrum, 4) the effect of the initial guess on the retrieved profile and 5) the bias introduced by the retrieval technique.

1) The instrumental calibration has an uncertainty of ±12%. Since this results in an uncertainty in the overall scaling of the profile which is independent of altitude, we have not included it in the error bars in Figures 1 & 2.

2) The largest errors, particularly in the upper stratosphere, are from the statistical noise in the spectral line data. Monte Carlo tests of the retrieval algorithm were carried out to determine the magnitude of the expected errors. The noise–free spectral line shape that

would be observed if our derived altitude profile were the actual ClO profile was calculated. Gaussian noise at the same level as that in our data was then added to this line shape, and the result fed into the deconvolution algorithm to produce an output profile. This was done many times, with different noise spectra added, producing an ensemble of output profiles. Figure 3 shows the the two profiles from this ensemble which give the extreme high and low values of the ClO mixing ratio at 20 km. This ensemble was analyzed statistically, and the error bars in Figures 1 & 2 represent plus and minus twice the standard deviation (95% confidence interval) obtained in this analysis.

3) As can be seen in Figure 4, the spectral line appears symmetrical with little evidence of baseline curvature. It is possible to derive altitude profiles using only the low frequency or only the high frequency side of the line. These are shown in Figure 5, along with the profile derived using the whole line (which also appeared in Figure 1). The differences are very small for the lower stratosphere, consistent with those expected just from differing statistical noise in the two sides of the spectrum.

4) We have found that within a wide range of initial guesses at constant mixing ratio (0.1 to 1.0 ppbv from 16 to 50 km), the retrieved profile varied only slightly and the possible errors were small compared to those from statistical noise. The effect of the fixed ClO mixing ratio below 15 km is also small, providing that the true mixing ratio at 14 km is less than that of the peak.

5) In interpreting the altitude profile we note that the retrieval cannot recover any small scale layering in the ClO profile. We have carried out Monte Carlo tests to determine the accuracy with which the retrieval algorithm can recover model altitude profiles of varying width from the corresponding spectral line shapes with noise added; these show that if the layer is at least 6 km thick (full width at half maximum), the thickness will be successfully recovered. We find that the ClO layer over McMurdo has half of the peak mixing ratio at 16 and 23 km or a thickness of 7 km. (see Figure 1).

In the lower stratosphere, the peak daytime ClO mixing ratio is 1.55 ± 0.3 ppbv, centered at an altitude of 19 ± 1 km, falling to half peak at 16 and 23 km, and falling below 0.3 ppbv above 24 km. Thus, during the day, a half of the available chlorine is in the active form, ClO. For the purposes of determining the ozone depletion rate due to chlorine it is more convenient to look at the ClO density profile in Figure 2. This shows a layer centered at 18 km, with a peak density of $[ClO] = 2.9 \times 10^9 \ cm^{-3}$, and extending from 22 km at the top down to about 15 km. The altitude of this layer corresponds very closely to the altitude range of ozone depletion found above McMurdo during the same time period (Hofmann et al., Preprint, January, 1988), which shows strong ozone depletion extending from 15 to 22 km.

These very high ClO densities are favorable for a depletion mechanism which depends on the square of the ClO density (Molina and Molina, J. Phys. Chem. 91, 433, 1986). In this mechanism the rate limiting step is the formation of the ClO dimer through the reaction:

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$

If we assume that the preferred destruction channels of Cl_2O_2 release two free chlorine atoms, either by photodissociation or thermal decomposition, then the rate of ozone destruction is twice the rate of formation of the ClO dimer. Letting $t_{1/2}$ be the ozone half

life, K be the rate constant for the dimer formation and $MR(O_3)$ the mixing ratio of ozone,

$$t_{1/2} = \frac{0.69\, MR(O_3)}{2\, K\, [ClO]^2}$$

Using $K = 6.1 \times 10^{-32}\ cm^6 s^{-1}$ (Hayman *et al.*, *GRL* **13**, 1347, 1986), $[ClO] = 2.9 \times 10^9\ cm^{-3}$ and $MR(O_3) = 1.5 \times 10^{-6}$ gives $t_{1/2} = 1.0 \times 10^6$ seconds. Since these numbers are representative of the twelve hours of daylight, the actual time scale for the ozone depletion is

$$t_{1/2} = 23\ days$$

This time scale is also in approximate agreement with observed rate of ozone depletion.

These ClO observations thus demonstrate that both the altitude and rate of ozone depletion can be accounted for by chlorine acting through the ClO dimer mechanism.

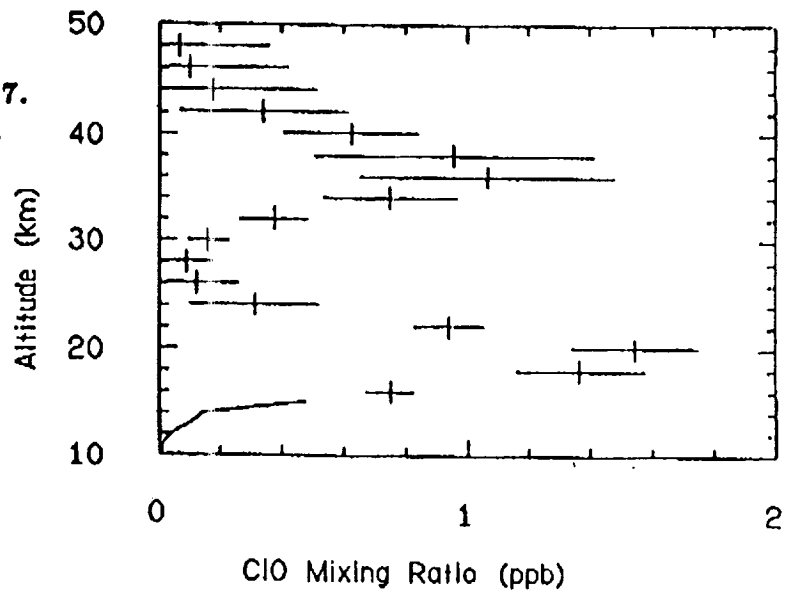Figure 1. 20 – 24 SEPT, 1987. AVERAGE DAYTIME ClO.

Figure 2. 20 – 24 SEPT, 1987. AVERAGE DAYTIME ClO.

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