SUBMILLIMETERWAVE HETERODYNE MEASUREMENTS OF STRATOSPHERIC ClO, HCl, O$_3$, and HO$_2$: FIRST RESULTS

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Abstract. The vertical profiles of ClO, HCl, HO$_2$ and O$_3$ were determined from thermal emission measurements by a balloon-borne spectrometer operating near 640 GHz. Results are in broad agreement with previous measurements and models, but differ significantly with model photochemistry for the ratio of ClO to HCl.

Introduction

Chlorine-catalyzed odd-oxygen loss in the stratosphere occurs by reaction of ClO and Cl with O and O$_3$. The available chlorine for this cycle is determined by the partitioning between the reactive odd chlorine species, ClO + Cl + (ClO)$_2$, and the HCl/ClONO$_2$ reservoirs. The chemistry controlling this ratio includes reactions involving OH, O, HO$_2$, NO, NO$_2$, CH$_4$, and, in the lower stratosphere, particulate surfaces. The validation of photochemical models, essential to predict the effect of the increasing chlorine burden, requires concerted vertical profile measurements of Cl$_x$, HO$_x$, NO$_x$ species, chlorine reservoirs, O$_3$, CH$_4$ and water vapor.

We report here the first simultaneous measurements of stratospheric O$_3$, HCl, ClO, and HO$_2$. The measurements were made with a new instrument which is the first use of submillimeter heterodyne spectroscopy for upper atmospheric measurements. The theory and advantages of atmospheric remote sensing in this spectral region are discussed by Waters [1992].

Experimental Method

The Submillimeterwave Limb Sounder (SLS) is a heterodyne radiometer measuring thermal molecular emission spectra near 640 GHz. The instrumental field of view (FOV) is 0.35° full width at half maximum (2–3 km vertical resolution at the limb tangent point) as defined by scannable optics. Signals are downconverted to an intermediate frequency (IF) band 2.5 GHz wide centered at 11.6 GHz by an uncooled Schottky diode harmonic mixer [Erickson, 1992]. The radiometer is operated double sideband (DSB), i.e., spectral features occurring symmetrically above and below the effective local oscillator frequency of 637.050 GHz appear together in the IF output spectrum. The relative sideband response is near unity

and is measured as part of the instrument calibration. The second harmonic mixer is pumped at 318.525 GHz from a tripled 106.175 GHz phase-locked InP Gunn oscillator waveguide coupled to the mixer block. The IF spectrum is split into 7 overlapping 0.5 GHz wide bands centered on spectral lines. Signals are further downconverted and input to 5 spectrometers. (Measurements of H^{35}Cl and one HO$_2$ line are time-shared with those of H^{37}Cl and one O$_3$ line, respectively.) The spectrometers each contain 15 filters and square-law detector diodes, filter widths range from 2 MHz at line center to 128 MHz at the band edge.

Spectra are recorded as the antenna FOV is scanned vertically through the atmospheric limb. Limb scans consist of observations at elevation angles from +1.0° to -6.0° in 0.2° steps, 'cold' sky reference views (+47°) and blackbody calibration target measurements.

The data presented here are from midday portions of balloon flights launched from National Scientific Balloon Facility sites at Daggett CA (35°N 115°W) on 09 April 1991 and from Ft. Sumner NM (34°N 104°W) on 01 October 1991. Measurements on 09 April 1991 are from 20:20–23:00 UT (30°–54° solar zenith angle); the balloon height was 38.5 km and the mean 35 km tangent point was 36.9 N latitude, 114.8 W longitude. The October 1991 measurements are from 17:30–21:26 UT (41°–59° solar zenith angle); the balloon height was 38.3 km; the mean 35 km tangent point location was 34.5 N latitude, 101.7 W longitude. On both flights, the gondola also carried the Far Infrared Limb Observing Spectrometer (FILOS) [Peterson and Pickett, 1991] and O$_3$ photometer instruments.

Mixing ratio vertical profiles were inferred using sequential estimation [Rodgers, 1976]. Simulated atmospheric ra-
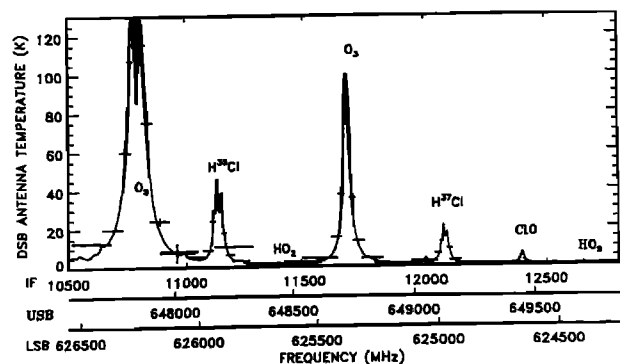

Fig. 1. Midday 35 km tangent height measured (crosses) and calculated (smooth line) spectra. Abcissa axes give the frequencies of upper and lower sideband spectral features (denoted by IF, USB and LSB, respectively).

diance used in the retrieval process was calculated using line positions and intensities from the JPL Submillimeter, millimeter, and microwave spectral line catalog [Poynter and Pickett, 1985] and National Metrological Center temperature profiles. The radiance calculation also evaluated nearby lines from all significant atmospheric species in the JPL catalog. Triangular basis functions (linear segments) were used to model constituent vertical profiles. Retrieval coefficients (partial derivatives) were calculated by finite differences using climatological values as the initial linearization point. Non-linearities were handled by iteration. Retrieval error budget includes random and systematic components from radiometric calibration, instrument pointing, spectroscopic parameters and residuals.

Results

Observed Spectra

Figure 1 is a portion of the spectral data (limb view tangent height 35–37 km) from the 01 October 1991 flight showing the full 2.5 GHz instrument bandpass. Measurements are points with vertical and horizontal extents equal to the estimated 1σ noise and the filter width, respectively. Spectral features for ^{35}ClO, O_3 and HO_2 (12,700 MHz) occur in the radiometer upper sideband; HCl (both isotopes), HO_2 (11,400 MHz IF), O_3 (11,679 MHz IF) features are in the lower sideband. The smooth curve is a calculated spectrum using retrieved abundances for O_3, ClO, HCl and HO_2. The ClO line, measured and calculated, (35 km tangent height) from the 09 April 1991 flight is shown in Figure 2a. Figure 2b shows the partially resolved $H^{35}Cl$ hyperfine triplet. Figure 2c shows the observed HO_2 emission at 625,661 MHz averaged from +1° elevation angle views during the 01 October 1991 flight.

ClO results below 35 km show only small variations, within uncertainty bounds, between the April and October flights. At the profile peak near 40 km, however, we find ~25% greater ClO abundance in April. Between these flights in June 1991, the volcano Pinatubo (15°N, 121°E) erupted and injected large amounts of SO_2 into the lower stratosphere producing aerosols which may sup-

press NO_x through heterogeneous reactions and increase ClO [Prather, 1992]. Comparison of the April and October ClO profiles shows no significant ClO increases following Pinatubo and may imply that the volcanic aerosol cloud had not yet reached 34°N by October 1991 or that the effect was confined to a layer below ~18 km.

Our ClO results are compared with in situ reel-down profiles [Brune and Anderson, 1986; Brune et al., 1985], in situ aircraft (flight 881015 41°N 490K Θ) [Toohey et al., 1991] and our balloon 204 GHz microwave (BMLS) measurements [Waters et al., 1988 and unpublished results] in Figure 3a. The variations among these profiles are within the range of seasonal and local variability [Solomon and Garcia, 1984] and, although together spanning 7 years, these measurements exhibit no clear trend in stratospheric ClO abundance.

HCl profiles are shown in Figure 3b with ATMOS results (29° N) [Zander et al., 1990] from May 1985 and the May 1988 in situ measurement by May and Webster [1989]. ATMOS and SLS vertical gradients are similar, however, our results and those of May and Webster [1989] indicate an overall increase in stratospheric HCl since the 1985 ATMOS measurements. Integrated column HCl abundances above 20 km from our data for April and October 1991 are 1.74 ± 0.22 and $1.71\pm0.25 \times10^{15}cm^{-2}$. These values, relative to the corresponding 1985 ATMOS HCl column of $1.34\times10^{15}cm^{-2}$ [Zander et al., 1990], give a linear increase rate of $4.7\pm0.8\%$ year^{-1}. This value is in good agreement with values in the recent review by Rinsland et al. [1991] of the HCl column trend from the period 1977 to 1990.

Our HO_2 profiles from 01 October, shown in Figure 3c, generally agree well with previous mid-day mid-latitude in situ [Stimpfle et al., 1990] and FTIR emission [Park and Carli, 1991; Traub et al., 1990] measurements. Our results tend to confirm the observation of Traub et al. [1990] that model photochemistry is consistent with measurements below 40 km, but underestimates HO_2 in the upper stratosphere. We expect improved sensitivity ($\times$ 2) for HO_2 on future balloon flights and will be better able to investigate the apparent ~30% discrepancy between measurements and model results in this region.

Figure 4 compares retrieved O_3 results with the in situ O_3 photometer profiles recorded during each balloon ascent [J.J. Margitan, private communication]. These measurements are in good agreement and confirm the tendency of photochemical models to underestimate O_3 abundance in the upper stratosphere [WMO, 1985]. This discrepancy, ~35% at 40 km, is illustrated in Figure 4 by the shaded region showing the range of model results from WMO Report 16 [1985].

ClO, HCl Partitioning

Figure 5 shows ratio of ClO to HCl from these measurements compared to the California Institute of Technology one-dimensional model for May 30°N, 50° solar zenith angle, [M.Allen, private communication] and to the range of 2-D model calculations (30° N summer mid-day conditions) given in WMO Report 16 [1985] . We find significantly less ClO relative to HCl than predicted by the majority of these models throughout the middle stratosphere (25–40 km). The Caltech model shows slightly better agreement, but still implies ~60% more ClO (or less HCl) at 37 km than we observe.
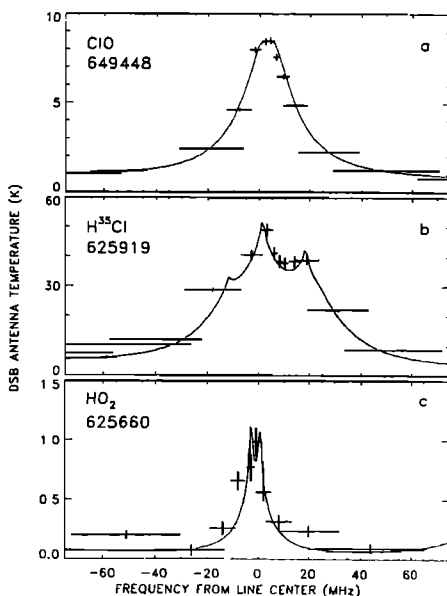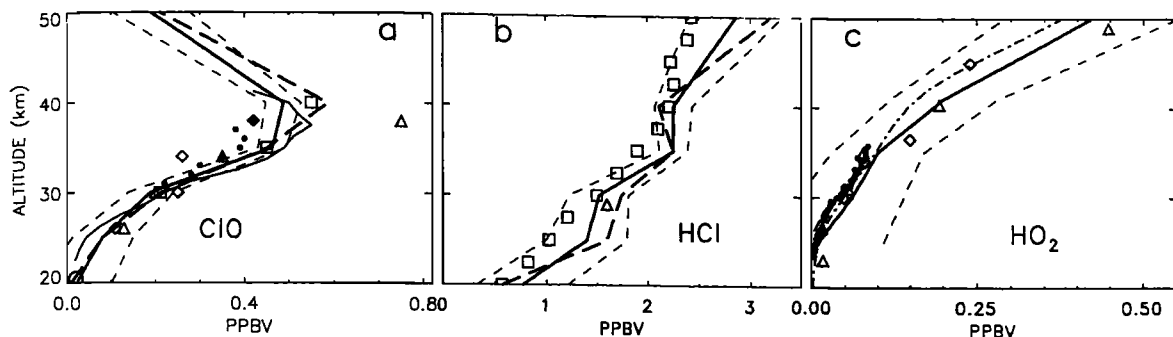

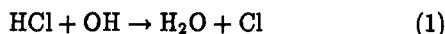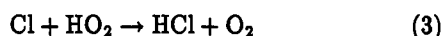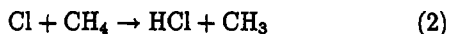Fig. 2. ^{35}ClO, $H^{35}Cl$ and HO_2 spectra.

Fig. 3. ClO, HCl and HO$_2$ profiles from 09 April 1991 (bold dashed line) and 01 October 1991 (bold solid line). Error bounds for 01 October 1991 data are thin dashed lines. (a), ClO from BMLS May 1985 ($\Diamond$), Oct 1986 ($\triangle$), and May 1989 ($\square$)[Waters et al., 1988 and unpublished data] and in situ ClO by Brune et al.[1985] ($\bullet$), Brune and Anderson [1986] (thin line) and Toohey et al. [1991] (o) are shown. (b), ATMOS HCl profile ($\square$) [Zander et al., 1990] and ($\triangle$) May and Webster [1989]. (c), HO$_2$ profiles of Traub et al. [1990] ($\triangle$), Stimpfle et al. [1990] ($\bullet$), Park and Carli [1991] ($\Diamond$) and (dash-dot) Caltech model [M.Allen, private communication].

The partitioning of total inorganic chlorine (Cl$_y$) between HCl and the sum of Cl+ClO+HOCl+ClONO$_2$ is principally controlled [Solomon and Garcia, 1984], in the absence of heterogeneous chemistry, by the relative rates of odd chlorine, Cl$_x$, production

$$HCl + OH \rightarrow H_2O + Cl \qquad (1)$$

and loss by

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (2)$$

$$Cl + HO_2 \rightarrow HCl + O_2 \qquad (3)$$

Models and measurements of ClONO$_2$ [Zander et al., 1990] and HOCl [Chance et al., 1989] show that Cl$_x$ is largely ClO above ~35 km. ClO dimer is not expected to be significant above ~30 km due to thermal instability and photolysis [DeMore et al., 1990]. Equating ClO with Cl$_x$ gives, at steady-state,

$$\frac{ClO}{HCl} \approx \frac{k_1[OH]}{k_2[CH_4] + k_3[HO_2]} \times \frac{ClO}{Cl} \qquad (4)$$

Examining quantities on the right of Equation(4), values for [OH] from FILOS measurements during these flights [H.M. Pickett, private communication] and [HO$_2$] from our results are comparable to Caltech model values in the 35 to 40 km region. CH$_4$ abundances required to fully account for the discrepancy are ~1.3 ppmv, outside the 0.5-0.9 ppmv range measured by rocket and balloon in the upper stratosphere [WMO, 1985]. The ClO to Cl ratio is dominated by "fast chemistry" reactions with O$_3$, O, and NO. Since uncertainties associated with the rate constants for these reactions are small (<20%) [DeMore et al., 1990], significant changes in the model value for [ClO]/[Cl] must occur by altering model abundances of O and NO which would also affect the predicted HO$_2$ to OH partitioning. Park and Carli [1991] and Wennberg et al. [1990] show convergence of measurements and model prediction for [HO$_2$]/[OH] above 35 km. We conclude that the ClO to Cl ratio is unlikely to be the source of the [ClO]/[Cl] discrepancy. The uncertainty in the rate constant for Cl + CH$_4$, ~10%, is inadequate to significantly affect the model result and Cl+HO$_2$ is a minor Cl$_x$ loss channel below 45 km. The lower uncertainty bound for the OH+HCl reactions is ~30% below the mean value [DeMore et al., 1990]

at upper stratospheric temperatures. This lower value for k$_1$ together with moderately increased CH$_4$ levels appear sufficient to shift model results into agreement with our observations. Other modifications to photochemical models that would reduce the ClO/HCl discrepancy have
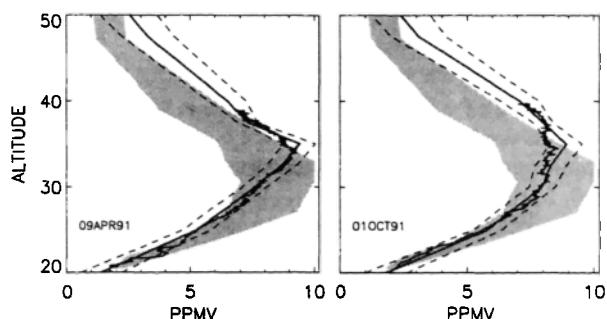

Fig. 4. (a) O$_3$ volume mixing ratios from 09 April 1991 and (b) 01 October 1991. Error bounds are shown as thin dashed lines. O$_3$ photometer profiles [J.J.Margitan, private communication] are shown as thin lines. The shaded region (same in both panels) is the model range [WMO, 1985].
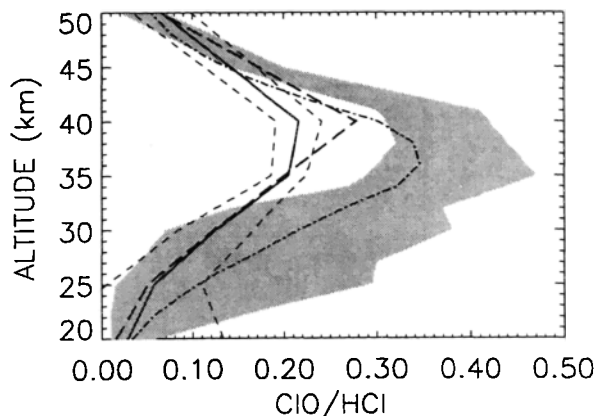

Fig. 5. ClO/HCl ratio from 09 April 1991 (thick dashed line) and 01 October 1991 (solid line). Error estimates for the 01 October data are thin dashed lines. Caltech model [M. Allen, private communication] is the dash-dot line. The shaded region shows the range of various 2-D models for ClO/HCl [WMO, 1985].

been mentioned: Allen and Delitsky [1991] found improved agreement between calculations and ClO measurements by increasing the model rate of HCl formation by Cl+HO$_2$; McElroy and Salawitch [1989] have suggested that the reaction of ClO with OH forming HCl as a minor product may be a significant sink for odd chlorine. These suggested changes in current model chemistry to reduce the calculated ClO/HCl ratio may help alleviate the discrepancy between the measured and model O$_3$ trend in the upper stratosphere. Current chemistry substantially ($\sim$2×) overestimates the O$_3$ changes around 40-45 km as compared to SAGE-II minus SAGE-I observations [WMO, 1988].

Full understanding of the partitioning of stratospheric chlorine ($\sim$3 ppbv from these results) requires additional measurements, especially profiles of CH$_4$ and ClONO$_2$.

References

Allen, M. and M.L. Delitsky. Inferring the abundances of ClO and HO$_2$ from Spacelab 3 Atmospheric Trace Molecule Spectroscopy observations. *J. Geophys. Res.*, 96, 2913-2919, 1991.

Brune, W.H. and J.G. Anderson. In situ observations of midlatitude stratospheric ClO and BrO. *Geophys. Res. Let.*, 13, 1391-1394, 1986.

Brune, W.H., E.M. Weinstock, M.J. Schwab, R.M. Stimpfle, and J.G. Anderson. Stratospheric ClO: In situ detection with a new approach. *Geophys. Res. Let.*, 12, 441-444, 1985.

Chance, K.V., D.G. Johnson, and W.A. Traub. Measurement of stratospheric HOCl: concentration profiles including diurnal variation. *J. Geophys. Res.*, 94, 11,059-11,069, 1989.

DeMore, W.B., S.P. Sander, D.M. Golden, M.J. Molina, R.F. Hampson, M.J. Kurylo, C.J. Howard, and A.R. Ravishankara. *Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling.* Jet Propulsion Laboratory, Pasadena, CA, 1990. JPL Publication 90-1.

Erickson, N.R. Low noise submillimeter receivers using single diode harmonic mixers. to be published in *Proc. IEEE*, 1992.

May, R.D. and C.R. Webster. In situ stratospheric measurement of HNO$_3$ and HCl using the balloon-borne laser in situ sensor tunable diode laser spectrometer. *J. Geophys. Res.*, 94, 16,343-16,350, 1989.

McElroy, M.B. and R.J. Salawitch. Changing composition of the global stratosphere. *Science*, 243, 763-770, 1989.

Park, J.H. and B. Carli. Spectroscopic measurements of HO$_2$, H$_2$O$_2$, and OH in the stratosphere. *J. Geophys. Res.*, 96, 22,535-22,541, 1991.

Peterson, D.B. and H.M. Pickett. Far-IR Fabry-Perot spectrometer for OH measurements. In McElroy, J. and R.J. McNeal, editors, *Remote Sensing of Atmospheric Chemistry*, 1491, pages 308-313, Soc. Photo-Opt. Eng., 1991.

Poynter, R.L. and H.M. Pickett. Submillimeter, millimeter, and microwave spectral line catalog. *Appl. Opt.*, 24, 2235-2240, 1985.

Prather, M. Catastrophic loss of stratospheric ozone in dense volcanic clouds. *J. Geophys. Res.*, 97, 10,187-10,191, 1992.

Rinsland, C.P., J.S. Levine, A. Goldman, N.D. Sze, M.K.W. Ko, and D. W. Johnson. Infrared measurements of HF and HCl total column abundances above Kitt Peak, 1977-1990: Seasonal cycles, long-term increases, and comparisons with model calculations. *J. Geophys. Res.*, 96, 15,523-15,540, 1991.

Rodgers, C.D. Retrieval of atmospheric temperature and composition from remote measurements of thermal radiation. *Rev. Geophys. Space Phys.*, 14, 609-624, 1976.

Solomon, S. and R.R. Garcia. On the distribution of long-lived tracers and chlorine species in the middle atmosphere. *J. Geophys. Res.*, 89, 11,633-11,644, 1984.

Stimpfle, R.M., P.O. Wennberg, L.B. Lapson, and J.G. Anderson. Simultaneous, in situ measurements of OH and HO$_2$ in the stratosphere. *Geophys. Res. Let.*, 17, 1905-1908, 1990.

Toohey, D.W., W.H. Brune, K.R. Chan, and J.G. Anderson. In situ measurements of midlatitude ClO in winter. *Geophys. Res. Let.*, 18, 21-24, 1991.

Traub, W.A., D.G. Johnson, and K.V. Chance. Stratospheric hydroperoxyl measurements. *Science*, 247, 446-449, 1990.

Waters, J. Submillimeter wavelength heterodyne spectroscopy and the remote sensing of the upper atmosphere. to be published in *Proc. IEEE*, 1992.

Waters, J.W., R.A. Stachnik, J.C. Hardy, and R.F. Jarnot. ClO and O$_3$ stratospheric profiles: Balloon microwave measurements. *Geophys. Res. Let.*, 15, 780-783, 1988.

Wennberg, P.O., R.M. Stimple, E.M. Weinstock, A.E. Dessler, S.A. Lloyd, L.B. Lapson, J.J. Schwab, and J.G. Anderson. Simultaneous in situ measurements of OH, HO$_2$, O$_3$ and H$_2$O: a test of modeled stratospheric HO$_x$ chemistry. *Geophys. Res. Let.*, 17, 1909-1912, 1990.

WMO, World Meteorolgical Organization. *Atmospheric Ozone, 1985.* Technical Report Report No. 16, Global Ozone Research and Monitoring Project, 1985.

WMO, World Meteorolgical Organization. *Report of the International Ozone Trends Panel, 1988.* Technical Report Report No. 18, Global Ozone Research and Monitoring Project, 1988.

Zander, R., M.R. Gunson, J.C. Foster, C.P. Rinsland, and J. Namkung. Stratospheric ClONO$_2$, HCl and HF concentration profiles derived from Atmospheric Trace Molecule Spectroscopy Experiment Spacelab 3 observations: An update. *J. Geophys. Res.*, 95, 20,519-20,525, 1990.

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