

Aircraft Search for Millimeter-Wavelength Emission by Stratospheric ClO

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Three millimeter-wavelength transitions of ClO were searched for in the stratospheric emission spectrum during May–August 1977 using aircraft-based instruments. The measurements indicate that if stratospheric ClO has a vertical distribution of the form predicted by present photochemical models, then the ClO volume mixing ratio at the profile peak did not exceed 10^{-9} at the time and place of the measurements. The observed spectra suggest the presence of ClO in the stratosphere but do not provide a definitive detection.

INTRODUCTION

Photochemical theories predict that the ClO radical is produced in earth's stratosphere as part of a catalytic cycle by which stratospheric ozone can be depleted [e.g., *Molina and Rowland, 1974; Stolarski and Cicerone, 1974; Wofsy and McElroy, 1974; Crutzen et al., 1978; Wofsy, 1978*]. Chlorocarbons, which are industrially produced and used principally as propellants in spray cans and as coolants in refrigeration systems, are thought to be the major source of chlorine involved in this cycle. Because of the significance of stratospheric ozone in shielding the biosphere from damaging solar ultraviolet radiation and because of the economic significance of the chlorocarbons, there is considerable interest in verifying the theoretical predictions. One test of the theory is comparison of the predicted and measured distribution of certain trace gases in the atmosphere. In the case of ClO, perhaps the most crucial species in the chlorine cycle for ozone destruction, only *Anderson et al. [1977, 1979]*, have reported measurements to date. They used an in situ fluorescence detection system and obtained values in the general range predicted by the photochemical theories but with some values larger than can now be theoretically explained.

The ClO radical has a large electric dipole moment and rotational transitions at millimeter and submillimeter wavelengths [*Amano et al., 1969; Kakar et al., 1978*]. In principal, observations of these transitions in the stratospheric spectrum can provide remote measurement of ClO with some information on its altitude distribution [*Kakar and Waters, 1976*]. We here report results of a search for stratospheric emission from three millimeter-wavelength transitions of ClO using aircraft-based instruments. General references for microwave remote sensing of the atmosphere are by *Staelin [1969]* and *Schanda [1976]*.

THEORY

Our experiments, described below, measure the brightness temperature (equivalent black body temperature) of thermal

radiation from the stratosphere as a function of frequency for a particular observational geometry. This brightness temperature can be calculated from the radiative transfer equation, molecular absorption coefficient, and atmospheric models. Here we develop the expressions needed for the calculations; the calculated emission will then be compared with the measurements in order to interpret the results.

At stratospheric temperatures and millimeter wavelengths the Planck function is proportional to temperature to better than ~5% accuracy, scattering is negligible, and the radiative transfer equation simplifies to

$$T_B(\nu) = \int_S T(s) e^{-\tau_\nu(s)} d\tau_\nu(s) \quad (1)$$

where $T_B(\nu)$ is the brightness temperature of the radiation at frequency ν and at the point of measurement, the integral is evaluated along the observation path S , $T(s)$ is the temperature at point s on S , and $\tau_\nu(s)$ is the optical depth at frequency ν between the observation point and point s . The optical depth is related to the absorption coefficient k_ν by

$$d\tau_\nu(s) = k_\nu(s) ds \quad (2)$$

The general expression for the absorption coefficient due to a transition J can be written [*Gordy and Cook, 1970, p. 40*]

$$k_\nu = \frac{8\pi^3 N F \nu^2}{3ckT} \left[1 - \frac{h\nu}{2kT} \right] |\mu_J|^2 S(\nu, \nu_0) \quad (3)$$

where N is the molecular number density, F is the fraction of molecules in the lower state of the transition, μ_J is the dipole moment of the transition, $S(\nu, \nu_0)$ is the line shape function where ν_0 is the center frequency of the transition, c is the speed of light, k is Boltzmann's constant, and h is Planck's constant. For the ClO transitions of interest here the fraction of molecules in the lower state is

$$F = 0.755 F_e F_v F_J \quad (4)$$

where F_e is the fraction in the ground electronic state, F_v is the fraction in the ground vibrational state, F_J is the fraction in the lower rotational angular momentum state of the transition, and the factor 0.755 is the relative isotopic abundance of ^{35}ClO (we searched for only ^{35}ClO transitions). The two electronic states of ClO which have significant population at atmospheric temperatures are the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, with the $^2\Pi_{1/2}$ being higher in energy by 318 cm^{-1} [*Basco and Morse, 1973*]. The fraction in the $^2\Pi_{3/2}$ state is then

$$F_e = \left[1 + \exp\left(-\frac{458}{T}\right) \right]^{-1} \quad (5)$$

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TABLE 1. Hyperfine Components of ClO Transitions

$J' \rightarrow J = \frac{3}{2} \rightarrow \frac{1}{2}$			$J' \rightarrow J = \frac{13}{2} \rightarrow \frac{11}{2}$			$J' \rightarrow J = \frac{15}{2} \rightarrow \frac{13}{2}$		
$F' \rightarrow F$	Relative Intensity	Frequency, MHz	$F' \rightarrow F$	Relative Intensity	Frequency, MHz	$F' \rightarrow F$	Relative Intensity	Frequency, MHz
3 → 2	0.156	167221.6	5 → 4	0.188	241501.6	6 → 5	0.196	278636.0
4 → 3	0.201	167213.4	6 → 5	0.220	241497.8	7 → 6	0.226	278633.2
5 → 4	0.257	167204.8	7 → 6	0.259	241494.2	8 → 7	0.259	278630.6
6 → 5	0.325	167195.5	8 → 7	0.304	241490.1	9 → 8	0.297	278627.53
3 → 3	0.0182	167201.7	5 → 5	0.00881	241495.4	6 → 6	0.00663	278633.6
4 → 4	0.0241	167175.2	6 → 6	0.0117	241473.5	7 → 7	0.00881	278612.5
5 → 5	0.0183	167138.2	7 → 7	0.00883	241442.8	8 → 8	0.00664	278583.4
3 → 4	0.00052	167163.6	5 → 6	0.00011	241471.2	6 → 7	0.00006	278613.0
4 → 5	0.00042	167108.7	6 → 7	0.00010	241422.1	7 → 8	0.00006	278565.2

The fundamental vibrational frequency of ^{35}ClO in the $2\pi_{3/2}$ state is $\omega = 844 \text{ cm}^{-1}$ [Menzies *et al.*, 1977], which leads to [e.g., Gordy and Cook, 1970, p. 110]

$$F_v = 1 - \exp\left(-\frac{1215}{T}\right) \quad (6)$$

Using $B_{02} = 18.5798 \text{ GHz}$ for the effective rotational constant of ^{35}ClO in the $2\Pi_{3/2} v = 0$ state [Kakar *et al.*, 1978], we obtain

$$F_J = \frac{0.89}{T} (2J + 1) \exp\left[-\frac{0.89}{T} \left(J + \frac{1}{2}\right)^2\right] \quad (7)$$

by manipulation of standard expressions [e.g., Gordy and Cook, 1970, p. 56].

The millimeter-wavelength spectrum of ClO is due to electric dipole transitions corresponding to changes $J \rightarrow J + 1$ in the angular momentum quantum number. ClO is a Hund's case (a) molecule for which the dipole matrix elements corresponding to these transitions are

$$\begin{aligned} |\mu_J|^2 &= \mu^2 \frac{(J + 1)^2 - \Omega^2}{(J + 1)(2J + 1)} \\ &= 1.54 \times 10^{-36} \frac{(J + 1)^2 - 2.25}{(J + 1)(2J + 1)} (\text{esu cm})^2 \end{aligned} \quad (8)$$

where Ω , the resultant angular momentum along the molecular axis, equals $\frac{3}{2}$ for the $2\Pi_{3/2}$ electronic state and μ is the permanent dipole moment of the molecule, $1.24 \times 10^{-18} \text{ esu cm}$ [Amamo *et al.*, 1969]. Each $J \rightarrow J + 1$ transition of ClO consists of several hyperfine components arising from the chlorine nuclear moment. The frequencies and relative intensities of these hyperfine components for the three transitions we searched for in the stratospheric spectrum are given in Table 1. The frequencies are from either measurements or theoretical ex-

pressions of Kakar *et al.*, [1978]. Their uncertainty is $\sim 0.1 \text{ MHz}$ for the $J = \frac{3}{2} \rightarrow \frac{1}{2}$ transitions, $\sim 0.3 \text{ MHz}$ for the $J = \frac{11}{2} \rightarrow \frac{9}{2}$ transitions and $\sim 1.0 \text{ MHz}$ for the $J = \frac{13}{2} \rightarrow \frac{11}{2}$ transitions. The relative intensities of the hyperfine components are from well-known expressions [e.g., Gordy and Cook, 1970, p. 299].

Our calculations of stratospheric ClO emission, which are compared with measurement below, used the Voigt line shape for the function $S(\nu, \nu_0)$. Individual hyperfine components with the frequencies and relative intensities shown in Table 1 were included. The standard expression was used for the Doppler line width parameter [e.g., Gordy and Cook, 1970, p. 45]. The line width parameter for collisional broadening of ClO lines has not yet been measured. Two diatomic molecules for which nitrogen-broadened line widths have been measured are CO and HF; their respective dipole moments, $0.11 \times 10^{-18} \text{ esu cm}$ [Burrus, 1958] and $1.8 \times 10^{-18} \text{ esu cm}$ [Muentner and Klempner, 1970], bracket that of ClO. At $T = 300^\circ\text{K}$ the collisional line width parameter for N_2 broadening of CO is 2.4 MHz/mbar [Draegert and Williams, 1968] and for HF is 3.7 MHz/mbar , based on Meredith's [1972] measurements at $T = 373^\circ\text{K}$ with extrapolation to 300°K , using $T^{-0.75}$ temperature dependence; we believe these values bound the uncertainty in the ClO line width parameter. An estimated value of 3.2 MHz/mbar for the stratospheric ClO collisional line width parameter at $T = 300^\circ\text{K}$ and a temperature dependence $T^{-0.75}$ was used in our calculations. Our assumed temperature dependence is intermediate between that for broadening due to dipole-quadrupole and dipole-induced dipole interactions [Townes and Schawlow, 1955, p. 349]; we expect that such interactions are the dominant collisional broadening mechanism for the millimeter lines of stratospheric ClO.

The expressions and values above are sufficient for calculating stratospheric ClO emission with given models of ClO distribution and atmospheric temperature and pressure. They

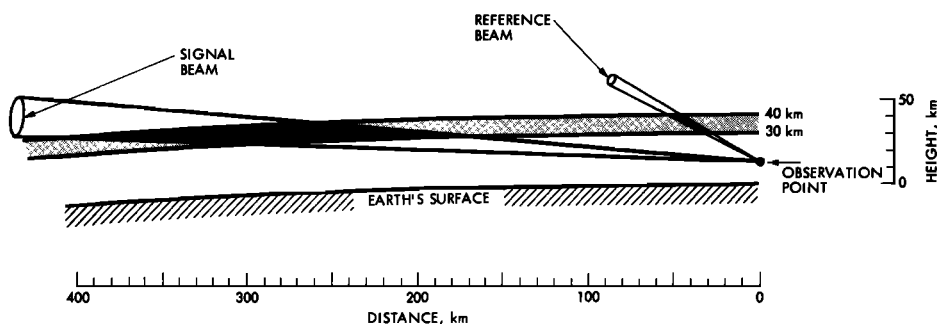


Fig. 1. Observational geometry; The figure is drawn to scale and illustrates the intersection of the signal and reference beams with a stratospheric layer between 30- and 40-km altitude (the approximate altitude range at which maximum ClO mixing ratio is expected to occur).

were used, with similar expressions for absorption coefficients of H_2O , O_3 , and O_2 , in computer programs to give the results described below. To ensure that these computer results are reasonable, it is worthwhile to make simplifying approximations that expedite manual evaluation of the expressions. Since the Doppler line width parameters for the ClO lines of interest here are ~ 0.1 to 0.2 MHz, collisional broadening of the lines will dominate at pressures above ~ 0.1 mbar or altitudes up to ~ 65 km. We are interested in ClO at altitudes much below this, so the Voigt line shape can be replaced by the collisional line shape. At line center the collisional line shape reduces to $S(\nu_0, \nu_0) = (\pi\Delta\nu_c)^{-1}$, where $\Delta\nu_c$ is the collisional line width parameter. Now, since $\Delta\nu_c$ is proportional to total pressure and thus total number density, (3) at line center is proportional to the number density of ClO divided by the total number density. Combining expressions (3)–(8), using a collisional line width parameter as discussed above and the fact that the ClO line frequencies are given, approximately, by $\nu_0 = 2B_{02}(J + 1)$, and evaluating these expressions on line center at $T = 230^\circ\text{K}$ (the approximate temperature expected for ClO in the stratosphere) yields

$$k_\nu = 1.2 \times 10^{-3} f_{\text{ClO}} (J + 1) [(J + 1)^2 - 2.25] \cdot \exp[-0.004(J + \frac{1}{2})^2] \text{ cm}^{-1}$$

where f_{ClO} is the ClO volume mixing ratio and hyperfine splitting is neglected. For small optical depths (the case for stratospheric ClO) and an isothermal atmosphere (an approximation) the radiative transfer equation reduces to $T_B = Tk_\nu L$, where L is the path length through the emitting gas. A ClO volume mixing ratio of $\sim 5 \times 10^{-10}$ is expected over the altitude range of 30–40 km (see Figure 4) and a path length of ~ 100 km is expected for the observation geometry (see Figure 1). These values with the above approximate expressions for the brightness temperature and absorption coefficient yield ClO brightness temperatures of $\sim 0.1^\circ\text{K}$ at 167 GHz, $\sim 0.4^\circ\text{K}$ at 241 GHz, and $\sim 0.6^\circ\text{K}$ at 278 GHz. At 35 km, the approximate mean altitude for expected peak ClO mixing ratio, the pressure is ~ 5 mbar, and the line width parameter will be ~ 20 MHz, corresponding to a full line width at half-power points of ~ 40 MHz. Such approximate values agree quite well with results of the computer calculations shown below.

MEASUREMENTS

Our measurements were performed from altitudes of 11–13 km with aircraft-based instruments. Two NASA aircraft, both operated by the Ames Research Center, were used: the Convair 990 Flying Laboratory and the C-141 Kuiper Airborne Observatory. Measurements from these altitudes avoid the problem of tropospheric absorption, principally by H_2O , and allow observations at lower elevation angles with longer path lengths than can be achieved with ground-based measurements.

The geometry for the aircraft observation is sketched in Figure 1. Stratospheric emission was observed at an elevation angle of 4° with an instrument 'signal' beam $\sim 3^\circ$ width. The difference between the stratospheric spectrum at 4° and a 'reference' spectrum at $\sim 30^\circ$ elevation was taken to reduce instrumental spectral responses. (Such differencing is required for the weak ClO signals, although it does reduce the observed signal by 15–20%.) Knowledge of the observation angles was accurate to approximately $\pm 0.5^\circ$, as determined by alignment on the ground and the measured pitch and roll of

the aircraft during flight. Observations were performed through standard aircraft window ports with the conventional windows replaced by a material (polyethylene or TPX) transmissive at millimeter wavelengths. The window geometry prevented using reference beam elevation angles larger than $\sim 30^\circ$. An elevation angle of 4° was chosen for the signal beam because this was the lowest elevation (determined by experiment) at which there was not substantial variation observed in the background tropospheric emission. Such variation was due principally to the small ($\sim \pm 0.5^\circ$) aircraft roll, which has a larger effect at lower elevation angles. It was found in practice that the difference in emission between the signal and reference beams varied by less than $\sim 2^\circ\text{K}$ in brightness temperature. Because this variation is due to tropospheric emission having a broad spectral character quite distinct from stratospheric emission with the resolution of our instruments, the variation had negligible effect on our 167- and 241-GHz measurements, which required no spectral scanning. For the 278-GHz measurement, which required spectral scanning, individual scans were monitored and discarded when there was obvious variation due to aircraft roll. The remaining scans ($\sim 90\%$) were averaged to obtain the final result; for this result to have been affected by undetected variations due to roll these variations would have had to be significantly correlated with the spectral scan, which is highly unlikely.

Superheterodyne receivers were used for the measurements. Such receivers 'mix' the incoming stratospheric radiation with a local oscillator signal and downconvert its frequency so that low noise amplification and spectral analysis can be performed using conventional electronic techniques.

Schottky barrier diodes fabricated at the University of Virginia were used as the mixing element for measurements at 167 and 241 GHz. At 167 GHz the diode was mounted in a wave guide structure [Kerr *et al.*, 1977]; at 241 GHz a quasi-optical structure [Gustincic, 1976] was used for the mount. A reflex klystron was the local oscillator at 167 GHz, and a backward wave oscillator ('carcinotron') was used at 241 GHz. Frequency stability of the 167-GHz phase-locked oscillator system was ~ 0.001 MHz, and that of the free-running 241-GHz oscillator was ~ 2 MHz. The oscillator frequency was measured by observations of harmonics generated from a 10-GHz frequency synthesizer. With the exception of the mixer and local oscillator the receiver was identical at 167 and 241 GHz and has been described by Gustincic [1977]. At 167 GHz it had an equivalent single side band noise temperature of $\sim 3000^\circ\text{K}$, and at 241 GHz it was $\sim 7000^\circ\text{K}$. The receiver

TABLE 2. Dates, Locations, and Solar Elevation Angles for ClO Measurements

Date (1977)	Solar Elevation, deg	Latitude, °N	Longitude, °W
<i>ClO Transition $\frac{3}{2} \rightarrow \frac{7}{2}$ (167 GHz)</i>			
May 30	–28 to –18	40 to 36	110 to 94
May 31	+72 to +63	40 to 46	75 to 67
June 1	+61 to +37	53 to 49	26 to 3
June 13	+8 to +40	53 to 43	–3 to –9
June 15	–8 to –18	52 to 44	–8 to 10
<i>ClO Transition $\frac{13}{2} \rightarrow \frac{11}{2}$ (241 GHz)</i>			
June 26	51 to 52	54 to 49	36 to 49
June 27	67 to 71	43 to 41	81 to 97
<i>ClO Transition $\frac{15}{2} \rightarrow \frac{13}{2}$ (278 GHz)</i>			
Aug 1	70 to 30	43 to 37	126 to 153

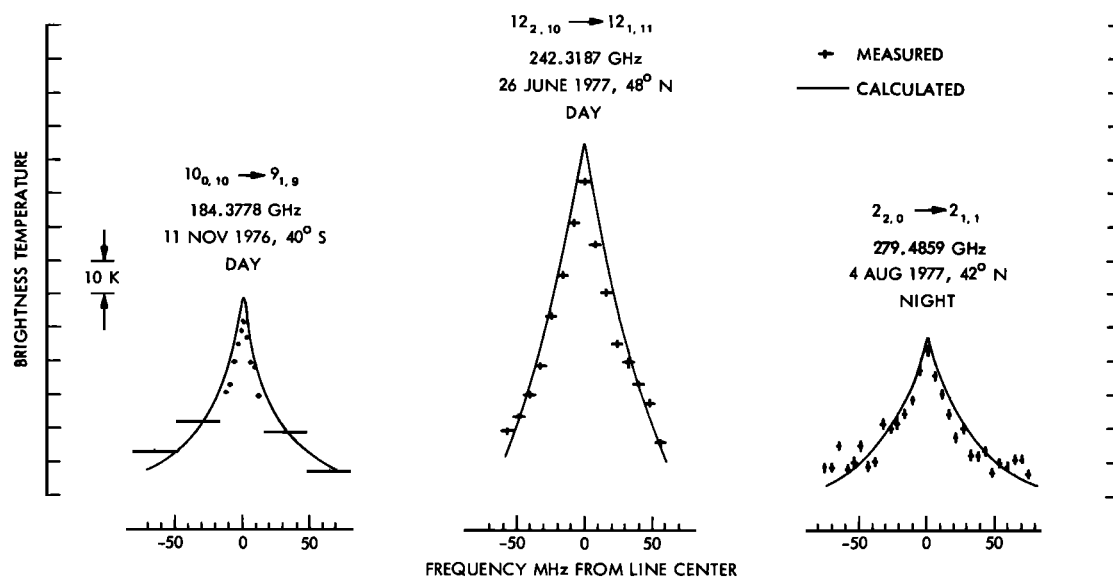


Fig. 2. Observed and calculated emission lines of stratospheric O_3 . The vertical axis is the brightness temperature of the emission, and the horizontal axis is the frequency from line center ($1 \text{ MHz} = 10^{-3} \text{ GHz}$). The center frequencies, quantum numbers, dates, and latitudes of the measurements are indicated. The vertical extent of the measurement bars gives the $\pm 1\sigma$ random measurement noise; the horizontal extent gives the spectral resolution. The calculated lines are for the ozone profile in Figure 4.

operated at ambient temperature and had no rejection of the image side band. The input to the receiver was chopped at 4 Hz between the signal and reference beams. The receiver output was a 100-MHz band width signal centered at 1.42 GHz. This signal was further downconverted to a center frequency of 160 MHz, where spectral analysis was performed by a bank of 15 electronic filters such that no spectral scanning was required. Each filter had a resolution of 8 MHz and overlapped its neighbor at the half-power point. The filter outputs were individually detected, demodulated synchronously with the chopping of the receiver input, averaged for ~ 1 min, and then digitized and passed to a programmable calculator for calibration and further averaging.

For measurements at 278 GHz a receiver constructed at Bell Laboratories for astrophysical observations was used. The mixing element of this receiver was a liquid helium-cooled InSb hot electron bolometer [Phillips and Jefferts, 1973], and its local oscillator was the tripled output of a reflex klystron. The instantaneous spectral resolution was 1 MHz, which was scanned over a range of ~ 150 MHz in 31 steps by computer control of the local oscillator. The time required for each scan was approximately 1 min. Frequency stability at each step was better than ~ 0.01 MHz. Absolute knowledge of the frequency was obtained by observing phase lock points at different harmonics of a crystal reference. The noise temperature of this receiver was $\sim 500^\circ\text{K}$. The input to the receiver was chopped at ~ 70 Hz between signal and reference beams. (For this system the elevation of the reference beam was 22° .) The output was detected, demodulated synchronously with the chopping of the input for each local oscillator frequency, digitized, and passed to the small computer for calibration and averaging.

Calibration of both systems was performed by observations of ambient and liquid nitrogen targets. (The Schottky diode receiver also had a third calibration target at a temperature 25°C above ambient.) During measurements the calibration targets were observed periodically after intervals of approximately 0.5–1 hour. Window losses were inferred to be approx-

imately 10% at 167 GHz, 15% at 241 GHz, and 20% at 278 GHz. The overall calibration of the measurements is expected to be accurate to about 10%. Operation of the instruments was checked by observations of stratospheric emission from millimeter-wavelength ozone lines that are near the ClO lines searched for.

The 167-GHz ClO measurements were performed on five flights of the NASA Convair 990 between May 30 and June 15, 1977, on an expedition from Moffett Field, California, to Cologne, Germany. Two of these flights occurred at night. At Cologne, the 241-GHz local oscillator and mixer were installed, and measurements at 241 GHz were performed on June 26 and 27, 1977, during the two daytime flights returning to California from Europe. The 278-GHz ClO measurement was made from the NASA C-141 observatory during a daytime flight on August 1, 1977, from Moffett Field west over the Pacific. A window port toward the rear of the C-141 was used.

Table 2 gives the date, solar elevation ranges, latitude, and longitude for the individual measurements. Night measurements are identified by negative solar elevations. The latitudes given include the fact that the stratospheric region observed was ~ 250 km from the aircraft.

RESULTS

Figure 2 shows three millimeter-wavelength stratospheric ozone emission lines which were measured to check the instrument operation. (There are many such ozone lines having intensities large in comparison to instrumental sensitivity [Waters, 1976], and we have measured 15. H_2O lines at 183 and 380 GHz and an N_2O line at 251 GHz were also measured.) The 242-GHz O_3 line was observed on the same flight as the 241-GHz ClO measurements. The 279-GHz line was measured 3 days after the 278-GHz ClO measurement, with the identical instrumental configuration used for ClO. The 184-GHz O_3 line was observed on an earlier latitude survey mission with the NASA Convair 990; it is shown here because

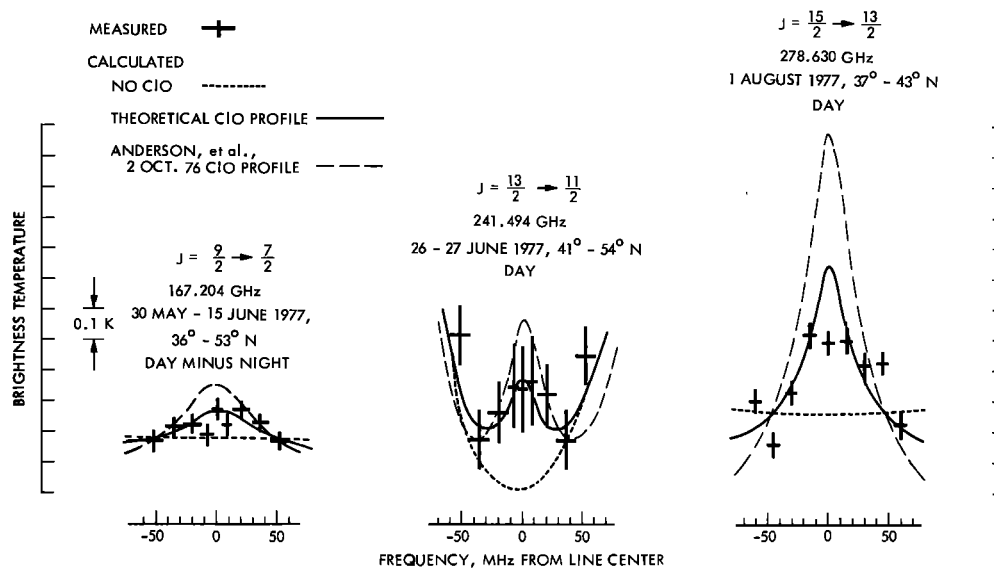


Fig. 3. Observed and calculated stratospheric emission at frequencies of ClO transitions. The horizontal and vertical axes are the same as for Figure 2. Frequencies, quantum numbers, dates, and latitudes of the measurements are indicated. Calculated emission is given for: no ClO, a theoretically calculated ClO profile from *Logan et al.* [1978], and the profile measured by *Anderson et al.* [1977] on October 2, 1976. The latter two profiles are given in Figure 4. The vertical extent of the measurement bars gives the $\pm 1\sigma$ random measurement noise, and their horizontal extent gives the spectral resolution. As discussed in the text, a straight line has been subtracted from both the measured and calculated emission.

the observation was made simultaneously with an ozonesonde measurement. Also shown in Figure 2 is the emission calculated for the particular observation geometry of each line. The calculations assume (1) the theoretical ozone profile shown below in Figure 4, (2) a water vapor mixing ratio of 5×10^{-6} in the mesosphere and upper stratosphere decreasing to 3×10^{-6} in the lower stratosphere, which was inferred from our aircraft measurements of H_2O emission at 183 GHz [*Waters et al.*, 1977], and (3) the 1976 U.S. Standard Atmosphere profiles of temperature and pressure [U.S. Government Printing Office, 1976]. Smearing due to the finite beam size of the instrument and the signal in the image side band of the Schottky receiver

has been accounted for. The relatively good agreement between measured and calculated O_3 lines gives us confidence in the operation of the instrument for ClO, since only the local oscillator tuning was changed between the O_3 and ClO measurements. These O_3 measurements are most sensitive to O_3 in the ~ 30 - to 50-km altitude region and indicate that the actual O_3 profile at these altitudes and at the time and place of the measurements agreed fairly well with the theoretical profile of Figure 4. Our O_3 , H_2O , and N_2O measurements will be discussed further in separate publications.

Figure 3 shows the ClO measurement results and compares them with calculated ClO emission. The calculated emission is

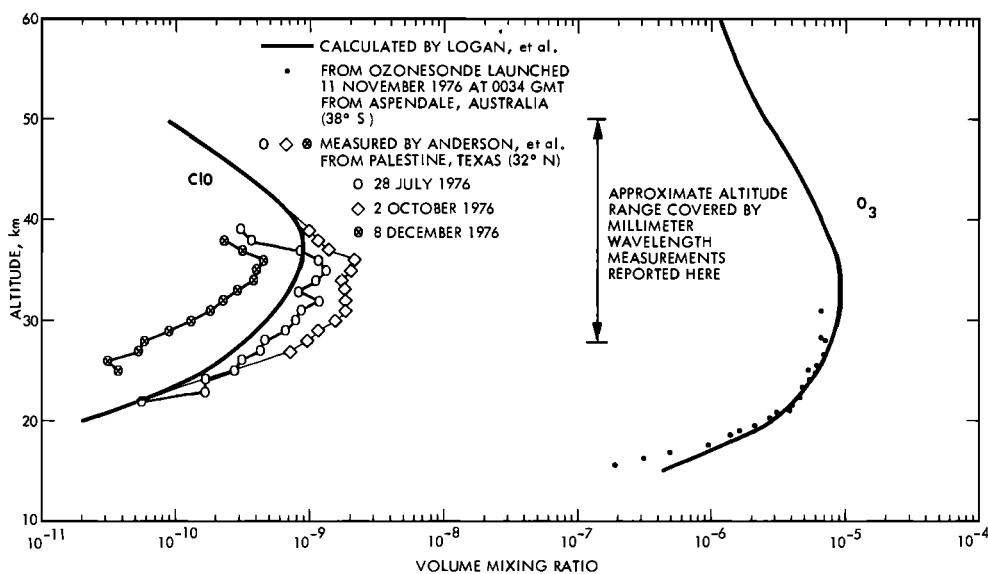


Fig. 4. Mixing ratio profiles of stratospheric ClO and O_3 . The ClO profile given by the solid line is midway between that calculated by *Logan et al.* [1978] for 'wet' (8×10^{-6} H_2O) and 'dry' (1×10^{-6} H_2O) stratospheres; the solid ozone profile was also calculated by them. Also shown are ClO profiles reported by *Anderson et al.* [1977]. For both ClO and O_3 the number densities given by the authors have been converted to mixing ratio using the 1976 U.S. Standard Atmosphere. The points below ~ 30 km for ozone are from an ozonesonde launched at the indicated time and location [*Kulkarni*, 1977].

shown for three cases: (1) no ClO, (2) a recent theoretical ClO profile from Logan *et al.* [1978], and (3) the ClO profile measured by Anderson *et al.*, [1977], on October 2, 1976. The ClO profiles used for the calculations are given in Figure 4. Absorption and emission by stratospheric O₃, H₂O, and O₂ were included in the calculations and the 1976 U.S. Standard Atmosphere was used for temperature and pressure profiles. As discussed below, a straight line has been subtracted from both the measurements and calculations of emission at 241 and 278 GHz. The residual curvature in the calculations for 'no ClO' is due to the wings of nearby O₃ lines. More spectral coverage of the measurements in the region of the ClO lines would have been desirable to determine the spectral base line; this was limited, however, by the instantaneous band width of the instrument and the available integration time.

Our measurements are relatively insensitive to ClO emission from altitudes below ~30 km, since such emission will have a line width greater than the ~100-MHz instrumental spectral band width. The measurements are also relatively insensitive to ClO emission from altitudes above ~50 km, since such emission will have line widths smaller than the ~8-MHz spectral resolution (after averaging) of the data.

The 167-GHz measurement result shown in Figure 3 is the difference between day and night spectra; approximately 3½ hours for day and for night taken within the intervals given in Table 2 are included. The individual day and night 167-GHz spectra showed a slope of ~0.3°K and a curvature downward of ~0.1°K brightness temperature over the 100-MHz spectral interval covered by the instrument. Such slope and curvature are approximately what we calculate owing to the wings of nearby ozone lines. However, slopes and curvature of this small amount could also be due to residual instrumental spectral responses.

The 241-GHz measurement result includes 40 min of data taken on June 26 and 45 min taken on June 27. A straight line having -3.7°K slope over the 100-MHz spectral interval covered by the instrument has been subtracted from the measurements; our calculations using the ozone profile of Figure 4 predict a slope of -2.1°K (which has been subtracted from the calculations shown in the figure), due mainly to the 18_{2,16} → 18_{1,17} O₃ transition at 239.093 GHz, whose wing (440 MHz below line center) appeared in the image side band of the receiver. The emissionlike spectral feature that appears in the center of the 241-GHz spectrum was observed on both flights where the receiver was tuned for this ClO transition; on the June 26 flight this feature appeared stronger by approximately 1 standard deviation of the instrument noise given in Figure 3.

The 278-GHz ClO measurement result in Figure 3 includes approximately 3 hours of data. A straight line having slope of +0.5°K over the spectral range shown has been subtracted from the measurement. The calculated slope over this range is +0.3°K, which has been subtracted from the calculated emission. Whether the ~50% discrepancy between observed and calculated spectral slope for both 241- and 278-GHz results is due to inadequacies in our theoretical models of wing emission from stratospheric species (e.g., due to uncertainties in ozone line widths which have not yet been measured), to instrumental effects, or to natural variations in ozone below ~30-km altitude is not known at present.

Comparison of these measurements and calculations leads us to conclude that if the ClO vertical profile has the general shape predicted by present photochemical models of the stratosphere, then the ClO volume mixing ratio at the peak of

this profile does not exceed approximately 10⁻⁹, at least for the time and locations of the measurements. The 241-GHz measurement would be consistent with ~10⁻⁹ ClO at the peak, whereas the 278-GHz measurement would suggest less than ~0.6 × 10⁻⁹ at the peak. The 167-GHz measurement suggests that any nocturnal decrease in ClO amounts to less than ~10⁻⁹ in volume mixing ratio at the profile peak but that a nocturnal decrease of this amount is possible. Although an emission feature does appear in the spectra at the proper location for each of the three ClO transitions searched for, we do not claim a definitive detection of stratospheric ClO because spectral features of the observed amplitude can sometimes be introduced by systematic instrumental effects. Nevertheless, it is unlikely that such effects would produce the appearance of an emission feature located at all of the three ClO frequencies.

The largest uncertainty in the interpretation of these results, other than systematic instrumental features at the ~0.1°K level, is due to uncertainties in the ClO collisional line width parameter. If the line width parameter were as large as that measured for HF, then the calculated emission lines would have an amplitude 0.8 of that given in Figure 3; if the line width parameter were as small as that measured for CO, the calculated lines would be 1.2 times stronger. We believe these values bound the uncertainty in the ClO line width. As stated earlier, our instrument calibrations are believed accurate to about 10%. Since the measurements are of atmospheric thermal emission, they are also affected by the atmospheric temperature structure. To estimate the uncertainty in ClO emission due to this uncertainty, calculations were performed using 45°N model atmospheres for both January and July. The ClO lines calculated using these atmospheres differed from those calculated using the standard atmosphere by less than 10%. Uncertainties in the atmospheric temperature are thus not likely to be a major item in the error budget. On the basis of these considerations, we feel it quite unlikely that our conclusions are in error to as much as 50%, and that they are probably accurate to within 30%.

Our results are consistent with present theoretical predictions of the abundance and vertical distribution of ClO in the stratosphere, but they by no means confirm these predictions. We have not observed the relatively high abundances of ClO that have been occasionally observed by Anderson *et al.* [1977, 1979] in summer (including a measurement of large ClO abundances, 7 × 10⁻⁹ at 40 km, by them on July 14, 1977—2 weeks before our most sensitive 278-GHz measurement, which indicates much less stratospheric ClO). However, it should be noted that our measurements constitute a rather limited sample in time and that most of the measurements of Anderson *et al.*, are also consistent with present theoretical predictions of stratospheric ClO. Clearly, the problem of stratospheric ClO abundances and variations is far from resolved, and more measurements are certainly needed.

Note added in proof. Broadening of the 278-GHz ClO line by N₂ and the frequencies of the hyperfine components of this line have been recently measured in the JPL millimeter and submillimeter spectroscopy laboratory by H. M. Pickett and E. A. Cohen. Preliminary measured values agree with the values used in this paper to within the uncertainties estimated here. Menzies [1979] has also recently reported a balloon-borne laser heterodyne measurement of stratospheric ClO that yielded a ClO mixing ratio of ~2 × 10⁻⁹ at 37 km. We have calculated the 278-GHz emission for the Menzies ClO profile and obtain an emission line which is approximately twice as

large as our measured 278-GHz signal. This result further emphasizes the incompleteness of present knowledge of stratospheric ClO and its variations.

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J. J. Gustincic, a consulting engineer, was killed in a commercial jetliner crash on September 25, 1978. His pioneering efforts in millimeter and submillimeter receiver development helped make possible the measurements reported here, and this paper is dedicated to his memory.

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