# Diurnal Variation of Stratospheric Chlorine Monoxide: A Critical Test of Chlorine Chemistry in the Ozone Layer

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Chlorine monoxide (ClO) has for some years been recognized as a key tracer of the stratospheric ozone depletion cycle arising from natural and anthropogenic injection of chlorine-containing compounds, principally halocarbons, into the atmosphere (1, 2). The reactions

$$O_3 + Cl \rightarrow ClO + O_2 \tag{1}$$

$$ClO + O \rightarrow Cl + O_2$$

and

constitute the catalytic cycle by which chlorine atoms convert ozone,  $O_3$ , to diatomic  $O_2$ .

There is a strong diurnal variation expected in the concentration of ClO. After the recombination of atomic oxygen at sunset, reaction 2 ceases. At night, ClO is believed to combine in a three-body reaction with  $NO_2$  to form chlorine nitrate,

$$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClONO}_2$$
 (3)

which is thought to be the dominant reservoir of chlorine in the absence of sunlight. During daylight hours, free chlorine is again produced from this reservoir by the photolysis of chlorine nitrate:

$$\text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_3$$
 (4)

The rate of nighttime removal of ClO via reaction 3 is dependent on the NO<sub>2</sub> concentration and the total density, both of which decrease with altitude above 30 km: thus high-altitude ClO is expected to last through the night, while ClO at lower levels (altitude  $\leq$  35 km) disappears. Earlier measurements by in situ resonance fluorescence (3), infrared heterodyne spectroscopy (4), balloon-borne (5) and ground-based (6) millimeter-wave spectroscopy have established the presence, approximate quantity, and vertical distribution of daytime stratospheric ClO. A more critical test of the full complex of reactions of stratospheric chlorine may be obtained from measurements of the diurnal variation of ClO. Such observations avoid the complications and uncertainties introduced by vertical and lateral transport and longer receiver with a noise temperature of 1100 K, approximately 21/2 times more sensitive than our earlier detector (6). Use of this more sensitive detector, combined with an increase by a factor of 2.4 in the theoretical line intensity for the higher frequency 278-GHz line as compared with the 204-GHz line, has led to a sixfold increase in observational sensitivity. For a fixed signal-to-noise ratio, the required measurement duration is reduced by about a factor of  $6^2$  or 36, allowing a relatively high time resolution to be achieved. The "back-end" spectrometer consists of a filter bank with 256 channels, each with a bandwidth of 1 MHz. The measurement technique, calibration method, and instrumental configuration described earlier (6) remain unchanged.

Our observations were carried out at the summit of Mauna Kea, Hawaii (elevation, 4250 m; latitude, 19.5°N) during

Abstract. This article reports measurements of the column density of stratospheric chlorine monoxide and presents a complete diurnal record of its variation (with 2hour resolution) obtained from ground-based observations of a millimeter-wave spectral line at 278 gigahertz. Observations were carried out during October and December 1982 from Mauna Kea, Hawaii. The results reported here indicate that the mixing ratio and column density of chlorine monoxide above 30 kilometers during the daytime are  $\sim 20$  percent lower than model predictions based on 2.1 parts per billion of total stratospheric chlorine. The observed day-to-night variation of chlorine monoxide is, however, in good agreement with recent model predictions, confirms the existence of a nighttime reservoir for chlorine, and verifies the predicted general rate of its storage and retrieval. From this evidence, it appears that the chlorine chemistry above 30 kilometers is close to being understood in current stratospheric models. Models based on this chemistry and measured reaction rates predict a reduction in the total stratospheric ozone content in the range of 3 to 5 percent in the final steady state for an otherwise unperturbed atmosphere, although the percentage decrease in the upper stratosphere is much higher.

term seasonal trends. Earlier balloonbased millimeter measurements over a limited portion of the diurnal cycle have shown a decrease in ClO at sunset and an increase after sunrise (5). In this article we present a complete diurnal record of ClO variation, with a time resolution of 2 hours, acquired by ground-based remote sensing of millimeter-wave line emission.

### **Observations of Emission Lines**

The ClO molecule has millimeterwave rotational spectral lines spaced approximately every 37 GHz. We have reported measurement (6) of the line at 204.352 GHz from the  $J = 11/2 \rightarrow 9/2$ levels. Our current measurements are based on the  $J = 15/2 \rightarrow 13/2$  transition at 278.630 GHz. We use a cryogenically cooled millimeter-wave heterodyne mixtwo periods, from 8 to 11 October and from 9 to 16 December 1982. The atmospheric water vapor content, which dominates the tropospheric absorption of stratospheric emission lines at millimeter-wave frequencies, was very low and generally stable around the clock during these observation periods (7).

In the following discussion, we present emission intensities as brightness temperatures in kelvins. This custom, commonly used in radio astronomy, is derived from the Rayleigh-Jeans approximation for blackbody radiation, in which emitted power per unit frequency is linearly proportional to temperature. All intensities represent the values that would be observed if one were looking through one stratospheric air mass toward the zenith after removing the effect of tropospheric attenuation.

In Fig. 1, we present a sample of midday (1230 to 1630) and nighttime

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(0030 to 0630) stratospheric emission spectra between 278.55 and 278.78 GHz. These data are averaged over the appropriate time blocks for all the days from 9 to 16 December 1982. In addition to the diurnally varying ClO line centered at 278.630 GHz, the unprocessed data contain emission from other stratospheric spectral lines. The strong slope arises from the wing of the  $18_{1,17} \rightarrow 18_{0,18}$  rotational transition of vibrationally excited  $(v_2 = 1)^{16}O_3$  centered at 278.522 GHz. Not directly visible is the weak  $14_{4,10} \rightarrow 15_{3,13}$  rotational transition of <sup>16</sup>O<sub>3</sub> in the  $v_1 = 1$  vibrational state, at a frequency of 278.634 GHz (8). This line, only 4 MHz away from the ClO line center, has a predicted integrated intensity of  $\sim 8$  percent of the observed total integrated midday signal and must be taken into account when determining the spectral line shape and total intensity of the overlving ClO line.

In order to extract as much information as possible concerning the pressurebroadened CIO line in a spectral region that is somewhat complicated by nearby O<sub>3</sub> lines, we have used a two-step background subtraction technique. From the raw data (for example, curve A in Fig. 1) we first subtract the calculated line shape and intensity for the  $v_1 = 1$ ,  $14_{4,10} \rightarrow 15_{3,13}$  ozone line which, because it is almost coincident in frequency with the ClO transition, cannot otherwise be separated from the data (9). We then obtain the remaining ClO emission (for example, Fig. 2) by subtracting a base line consisting of the nighttime spectrum (10) after removal of the narrow (in frequency) nighttime ClO signal near the line center. This base line is shown in Fig. 1, curve C. The only other correction applied to the data in Fig. 2 is to remove a small residual linear slope across the full band pass. The subtraction process successfully removes the emission from the ozone line wing and the instrumental feature at 278.72 GHz while preserving the detailed ClO line wing shape. The resulting line shape yields a good fit when compared to the pressure-broadened line shape computed from the model vertical profile predicted by Sze and Ko (11) after a small scaling adjustment of 0.86 to the model.

The identification of the signal in Fig. 2 as arising from stratospheric ClO is unambiguous since the frequency of the line center matches the laboratory value to within 1 MHz (the resolution of the spectrometer); the intensity is very close to 2.4 times that of the previously measured 204-GHz line (6), in agreement with the theoretical ratio of these line intensities at stratospheric temperatures;

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data (0030 to 0630) during the same period. (Curve C) Same as curve B with suppression of nighttime ClO over a span  $\pm 20$  MHz around the line center. The upper abscissa scale shows offsets from the ClO line center. The strong underlying slope represents the wing of the  $18_{1,17} \rightarrow 18_{0,18}$  rotational transition of  $\nu_2 = 1$  vibrationally excited ozone centered at 278.522 GHz. The feature at 278.72 GHz is instrumental. Fig. 2 (right). Midday ClO signal (1230 to 1630) averaged over the period 9 to 16 December 1982 at Mauna Kea, Hawaii. This line has been obtained by subtracting curve C from curve A, Fig. 1. For comparison, a theoretical line shape derived from the vertical distribution for ClO predicted by Sze and Ko [see (11) and Fig. 5] based on the chemistry of (14), has been least-squares fitted (in amplitude only) against the data. The required scaling factor for the theory was 0.86. The full hyperfine splitting is included in the line shape. The measured pressure-broadening coefficient of 3.35 MHz/torr at 317 K with a  $T^{-0.75}$  temperature dependence was used in this calculation.

there is a strong day-night variation, which is an expected signature of ClO; and the line becomes narrower at night, signifying a diminution of ClO concentration at lower altitudes. In addition, the absolute intensity is close to that expected for ClO from current models. We stress these independent identifying features, since the measurable presence of ClO in the stratosphere has been questioned by Mumma *et al.* (12). Their conclusions are based on a null result, which is in clear conflict with other reported ClO measurements obtained by various independent techniques (3-6) and with the present results.

In Fig. 3 we present the observed ClO spectra for 9 to 16 December 1982, binned into 2-hour blocks. These results clearly demonstrate the diurnal variation, with a maximum in the afternoon and a minimum shortly before dawn.



Fig. 3. The 24-hour variation of CIO signal intensity in 2-hour time intervals, averaged over the period 9 to 16 December 1982. Signal width as well as amplitude diminishes during nighttime hours.

Two effects are easily noticeable in the change from the midday maximum to the predawn minimum: both the intensity and the line width decrease. The decline in line width indicates that the remaining nocturnal ClO is at a lower ambient pressure (higher altitude) than most of the daytime ClO since the line width from a given altitude layer is directly proportional to the pressure. The experimental results thus confirm the diurnal variation of ClO concentration as a function of altitude.

Figure 4a is a plot of the average integrated intensity of ClO emission during October and December 1982 over a span  $\pm 50$  MHz from the line center (after subtraction of the underlying ozone contribution) for 2-hour time intervals around the clock. Stratospheric sunrise and sunset (altitude, 35 km) in

early October at 19.5°N occur at ~ 0530 and 1805, respectively, and have shifted to ~ 0601 and 1745, respectively, by early December. Given the 2-hour time resolution, we have chosen to average the two data sets without a time adjustment. Our two data sets do show some differences in average midday CIO column density (~ 20 percent higher in December than in October). We have combined them in a linear average to improve the signal-to-noise ratio for the diurnal variation.

The integrated intensity is proportional to the column density above ~ 30 km. The proportionality factor is somewhat dependent on the altitude distribution of the ClO: for example, over 90 percent of the ClO at  $\geq$  40 km emits within  $\pm$ 50 MHz of the line center whereas less than 60 percent of the emission from  $\leq$  30 km is contained within the same frequency span. Different trial methods of data base-lining and analysis indicate that the uncertainty associated with the derived integrated intensity in each time bin is about  $\pm 15$  percent for daytime data and about  $\pm 30$  percent for nighttime data.

## Line Intensities Compared with Model Predictions

In order to quantitatively compare the diurnal variation that we observed with that predicted from modeling efforts, we have generated synthetic ClO spectra from model ClO concentrations as a function of altitude for each of the 12 time bins and have subjected the resultant line shapes to the same procedure as the real data to calculate the model-

Table 1. Column densities and mixing ratios of CIO measured from Mauna Kea, Hawaii, as compared with model predictions. Column densities were determined from the observed spectral lines by three methods, M1, M2, and M3 (see text).

Measurement	Midday peak (1200 to 1600)				Night minimum (0000 to 0600) column density $(10^{13} \text{ cm}^{-2})$			
	Column density $(10^{13} \text{ cm}^{-2})$			Mixing ratio				
	Above 30 km		Above	$(10^{-9})$	Above 30 km			Above 40 km,
	M1	M2	40 km, M1	M2	M1	M2	M3	M1
Our observations 8 to 11 October 1982 9 to 16 December 1982 Average of October and December	$7^{+2}_{-1} \\ 7^{+2}_{-1} \\ 7$	$6.9 \pm 1 \\ 8.0 \pm 1 \\ 7.5$	$\begin{array}{c} 1.3 \ \pm \ 0.06 \\ 2.0 \ \pm \ 0.06 \\ 1.6 \end{array}$	$0.40 \pm 0.06$ $0.47 \pm 0.06$ 0.44	$1.2 \pm 0.3$	$\begin{array}{c} 1.1 \pm 0.2 \\ 1.4^{+0.2}_{-0.3} \\ 1.3 \end{array}$	$\begin{array}{c} 0.9 \pm 0.2 \\ 1.2 \pm 0.3 \\ 1.1 \end{array}$	$1.0 \pm 0.3$
Model predictions Sze and Ko (11) (total chlorine, 2.1 ppb)		9.2	1.6	0.55			1.3	1.0
Froidevaux (13) (total chlorine, 2.6 ppb)		12	2.0	0.70			1.9	1.3



Fig. 4. (a) Diurnal variation of ClO intensity integrated to  $\pm 50$  MHz from the line center for the combined October and December 1982 measurements from Mauna Kea, Hawaii. Typical errors bars ( $\pm 15$  percent for day and  $\pm 30$  percent for night) are indicated. For comparison, we present the diurnal intensity variation predicted by the models of Sze and Ko (11) and Froidevaux (13) after treating their models as data and deriving the integrated intensity that would be observed with our data reduction method (see text). (b) Same as (a) except that data and models are normalized to 1.0 near midday (1300) in order to directly compare the percentage diurnal variation. Shaded area represents the error limits around the mean values presented as a histogram in (a).

predicted integrated intensities. The theoretical altitude distributions adopted for this comparison are from a two-dimensional model by Sze and Ko (11) and a one-dimensional model by Froidevaux (13) (see Fig. 5). Both models use recently recommended reaction rates (14) and include specific calculations for the latitude and times of our observation sets. The dashed and dotted curves in Fig. 4 show the results of this analysis. The average of the midday October-December observed integrated intensity is 0.73 times the value of the Sze and Ko model and 0.55 times that of the Froidevaux model. Although the solar declination at Mauna Kea changes from  $-4^{\circ}$  to  $-22^{\circ}$ during this time span, the predictions of the Sze and Ko model show a negligible variation in diurnal behavior or in integrated intensity; for the Froidevaux model, we have averaged the October and December predictions. The difference in predicted midday intensity (Fig. 4a) between the two models is primarily due to different assumptions about the total chlorine mixing ratio: Sze and Ko assume 2.1 parts per billion (ppb), and Froidevaux assumes 2.6 ppb. In order to remove this factor and to compare the observed change and the model percentage diurnal change, which tests the rate of conversion of ClO into and out of a nighttime reservoir, we have normalized the intensity to 1.0 at 1300 hours for each model and for our data (Fig. 4b).

The models are good at predicting the ratio of day/night CIO integrated intensity and the general form of the diurnal variation. The observed early morning (0000 to 0600) to midafternoon (1200 to 1600) ratio of 0.16  $\pm$  0.04 agrees with a predicted value of 0.16 for the two models. The observed diurnal variation demonstrates the existence of a nighttime reservoir for chlorine. Some discrepancy exists between the predictions of normalized model intensities (Fig. 4b) and our measurements of the postdawn increase of ClO, which appears to be slower than predicted. The modeled rise is driven by the photorelease of Cl from  $ClONO_2$  (reaction 4), which theoretically reaches 80 percent of maximum release by 2 hours after sunrise. This suggests that there may be an error in the adopted photodissociation rate of ClONO<sub>2</sub> or in other reaction rates which cumulatively determine the postdawn rise in ClO.

#### **Column Density and Mixing Ratio**

In our discussion of the comparison of the data with models, up to this point we have used the models to predict a ClO 15 JUNE 1984



Fig. 5. Vertical profile for CIO predicted by Sze and Ko (11) based on the chemistry of (14) including the "fast" formation rate for ClONO<sub>2</sub> (solid lines). Model predictions by Froidevaux (13) averaged for somewhat different predictions between October and December (dashed lines). Both models assume a latitude of  $\sim 19^{\circ}$ N.

integrated line intensity and have compared the model predictions with the observations. For a determination of the column density from the spectral line we have utilized three independent methods, two of which also yield information on the altitude distribution of CIO concentration or mixing ratio.

The first method (M1) utilizes a deconvolution of the observed line profile into contributions from several altitude bins. A multidimensional least-squares minimization routine fits the observed line profile by adjusting the ClO concentration in each bin to minimize the observed and generated line profile residuals. Although the quality of the data does not permit very high resolution in altitude, we find reliable and repeatable results for the two 10-km bins, 30 to 40 and 40 to 50 km.

In the second method for obtaining the column density (M2), one adopts a shape for the altitude distribution from a model and fits the predicted line profile by a single variable (scale factor for the amplitude) to the observed spectral line over the full range of available data. This is the method used to obtain the model line fit in Fig. 2. The column density can then be obtained from the scaled model. We find after experimenting with several models that, if the column density is restricted to altitudes  $\geq 30$  km, the bestfit column density is not very sensitive to the model, with a range of variation of less than 20 percent.

In the third method (M3), one simply adds up the total integrated intensity over the entire observed band pass, setting zero base line near the edges at -70and +130 MHz from the line center. The use of this broad frequency width allows for inclusion of the maximum emission observable in the present data. The derived column density is related to the integrated intensity simply by the known line strength (15) and stratospheric temperature. For the 278-GHz ClO line we obtain a column density relation

$$N(\text{ClO}) = 0.28 \times 10^{14} \int_{-\infty}^{+\infty} T \, d\nu \quad (5)$$

where T is the brightness temperature of the spectral line, as defined earlier.

of Eq. Evaluation 5 vields  $N \ge 7 \times 10^{13} \text{ cm}^{-2}$  for the December midday maximum (1200 to 1600) and  $N = (1.2 \pm 0.2) \times 10^{13}$  for the nighttime minimum. This derivation is totally model-independent, but the daytime value must represent a lower limit only, since contribution to emission from lower altitudes is still only partially sampled. For example, at 30 km only  $\sim$  75 percent of the emission is included in the 200-MHz band pass used to determine zero base line, although at 40 km the fraction included is 95 percent. The nighttime value, however, should represent very nearly the true column density, given the narrow nighttime line. Even the lower limit on daytime column density from the present work exceeds by a factor of 3 the upper limit claimed in an unsuccessful infrared search for ClO (12).

The derived column densities and a comparison with unscaled models appear in Table 1. Averaging the observations during October and December, we find a midday column of ClO above 30 km of  $(7.5 \pm 1) \times 10^{13}$  cm<sup>-2</sup> and a nighttime minimum (0000 to 0600) of (1.2  $\pm$  $(0.2) \times 10^{13}$  cm<sup>-2</sup>. The measured daytime column densities above 30 km are 0.81 times that of the model of Sze and Ko and 0.62 times that of the model of Froidevaux. The average observed day/ night ratio of 5.8  $\pm$  1.3 agrees with both models to within the error. The only other published report that we know of [see note added in proof in (5)] on diurnal variation of ClO quotes a change in concentration of at least a factor of 10 between altitudes of 27 and 33 km from predawn hours to late morning. This is consistent with our measurements: the line width of our nighttime signal and a deconvolution of the spectral line show almost all of the predawn ClO lying above 40 km.

Use of the second method to obtain the ClO column density leads to a determination of the ClO concentration or mixing ratio near the peak of the distribution (between 35 and 40 km), which is only weakly dependent on the shape of the assumed altitude distribution. We find a mixing ratio of  $0.44 \pm 0.06$  ppb (see Table 1) for the average of October and December observations, about 20 percent less than the model of Sze and Ko and 37 percent less than the model of Froidevaux.

The midday density and mixing ratio of ClO is determined principally by the total chlorine content and the partition of chlorine, mainly (but not totally) through the reactions

$$Cl + CH_4 \rightarrow HCl + CH_3$$
 (6)

and

$$OH + HCl \rightarrow H_2O + Cl$$
 (7)

with the atomic chlorine being transformed to ClO through the very rapid reaction 1. The models quoted here have very close to 70 percent of the daytime chlorine at an altitude of 35 to 40 km in HCl and 30 percent in ClO.

The observations presented here indicate that, if this partitioning of chlorine is substantially correct, then the assumed total chlorine content may be too great: a reduction of total chlorine from the model range of 2.1 to 2.6 ppb to  $\sim 1.7$  ppb would give good agreement with our observations. Alternatively, small adjustments in the reaction rates or mixing ratios assumed for reactants in reactions 6 and 7 may be indicated.

#### Conclusions

In summary, we have observed the diurnal variation in stratospheric ClO above Mauna Kea, Hawaii, and find a decrease by a factor of  $5.8 \pm 1.3$  in the total column density above 30 km from the midafternoon maximum to the predawn minimum. The observed ratio of day/night ClO agrees well with predictions from diurnal models by Sze and Ko (11) and Froidevaux (13), and verifies the predicted storage and retrieval of ClO from a nighttime reservoir (reactions 3 and 4). The observed midday column densities are in moderately good agreement with these same models (11, 13)

and could be brought into better agreement by reducing their assumed total chlorine mixing ratio to  $\sim 1.7$  ppb. From this evidence it appears that in the stratosphere above 30 km the basic chemistry of chlorine and its compounds may now be close to being understood.

Earlier versions of this chemistry led to predictions for the eventual depletion of the ozone column density ranging as high as 15 to 18 percent, assuming a constant release of chlorofluorocarbons based on the 1977 production rate (2). These earlier versions also predicted a ClO column density and vertical distribution that were in conflict with earlier observations (3, 5, 6) as well as those reported here. Current models, incorporating several important changes in chemical reaction rates (14) that have resulted from improved laboratory measurements, predict an eventual reduction in the total ozone column density of only 3 to 5 percent (16) in an otherwise unperturbed atmosphere; this prediction is based on a constant release of chlorofluorocarbons based on the 1977 worldwide production rate. The vertical distribution of this reduction is by no means uniform, however, amounting to  $\geq 40$ percent at ~ 40 km (11, 17), with a possibly important impact on the thermodynamic structure of the stratosphere.

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