−1.02°C and 34.91 per mil at station 88. We have assumed a temperature dependence of −4 percent per degree Celsius and a salinity dependence of −0.6 percent per part per thousand in the CFM solubilities, based on the behavior of gases with similar ranges of solubilities [R. F. Weiss and T. K. Kyser, *J. Chem. Eng. Data* **23**, 69 (1978); R. F. Weiss and B. A. Price, *Mar. Chem.* **8**, 347 (1980)].
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Is There Any Chlorine Monoxide in the Stratosphere?

Abstract. *A ground-based search for stratospheric chlorine monoxide was carried out during May and October 1981 with an infrared heterodyne spectrometer in the solar absorption mode. Lines due to stratospheric nitric acid and tropospheric carbonyl sulfide were detected at about 0.2 percent absorptance levels, but the expected 0.1 percent lines of chlorine monoxide in this same region were not seen. Stratospheric chlorine monoxide is less abundant by at least a factor of 7 than is indicated by in situ measurements, and the upper limit for the integrated vertical column density of chlorine monoxide is 2.3 × 10^{13} molecules per square centimeter at the 95 percent confidence level. These results imply that the release of chlorofluorocarbons may be significantly less important for the destruction of stratospheric ozone than is currently thought.*

Chlorofluorocarbons are important and widely used industrial chemicals, but current photochemical models of the stratosphere indicate that their release ultimately depletes the O_3 layer (*1*). Chlorine monoxide (ClO) is thought to be a key tracer of this process, and measurements of its stratospheric abundances are therefore particularly important. Anderson and his colleagues have reported (*2*) a series of in situ measurements of stratospheric ClO, based on its chemical conversion to chlorine atoms, which are then detected by resonance fluorescence. Their results show large variations from flight to flight.

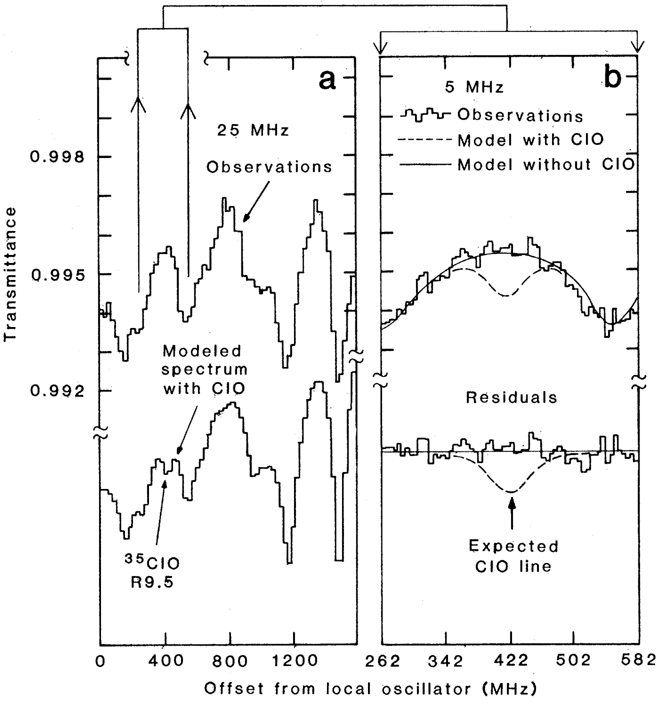

Fig. 1. (a) Observed and modeled spectra of the terrestrial atmosphere near the P12 $^{14}CO_2$ laser line. The frequency resolution is 25 MHz, and the spectra are displayed as transmittance versus the frequency difference from 856.515 cm^{-1}. The modeled spectrum is displaced downward for clarity, and the expected line of ^{35}ClO (R9.5) is indicated. (b) Observed and modeled spectra centered on the R9.5 ClO line. The frequency resolution in the observed spectrum is 5 MHz, and the modeled spectrum is displayed with infinite resolution. The residual differences between the observations and the modeled spectrum without ClO are shown and are compared with the expected ClO line.

Since direct detection of the ClO electronic resonance bands is not practical, confirmation of the chemical kinetic results has been directed toward detection by rotational and vibrational spectroscopy. Ground-based (*3*) and balloon-borne (*4*) measurements of the (J = 11/2 → 9/2) rotational line of ^{35}ClO at 204.352 GHz have been reported. The balloon-borne detection (*5*) by infrared vibrational spectroscopy near 12 μm is incorrect (*6*). Precise laboratory spectroscopy shows that the atmospheric line reported by Menzies and his co-workers (*5*) does not correspond to a transition of ClO; a reexamination of these experimental data (*5*) does show the presence of a weak absorption line at the correct frequency to be ClO (*7*).

We report the results of a search for stratospheric ClO, based on the use of a ground-based infrared heterodyne spectrometer. Three vibrational lines were searched for near 12 μm, two from the $^2\pi_{3/2}$ fundamental of $^{35}Cl^{16}O$ and one from the $^2\pi_{3/2}$ fundamental of ^{37}ClO. These lines should have been detected if currently accepted abundances are correct, yet none was found. We present a detailed comparison of the observed and synthetic atmospheric spectra near 856.515 cm^{-1}. The upper limit to the stratospheric ClO abundance that we derive is significantly smaller than the abundances obtained from the (independent) chemical kinetic and rotational spectroscopic methods.

Infrared absorption measurements of stratospheric ClO are important (i) because the detection of vibrational absorption lines with the correct frequencies and relative strengths is a necessary condition for the confirmation of ClO and (ii) because quantitative analysis of the line strengths and shapes provides an independent check on the results obtained by other methods. The vibrational fundamental band ($v = 0 \rightarrow 1$) of ClO lies near 12 μm, overlapping both a particularly favorable window in the terrestrial atmosphere and the (00°1)-(10°0, 02°0)$_I$ band of the $^{14}C^{16}O_2$ laser. The fact that there are close coincidences for lines of ClO (*6*) with the P8 and P12 transitions of the $^{14}C^{16}O_2$ laser (*8*) suggests that it might be possible to detect stratospheric ClO by infrared heterodyne spectroscopy (*9*) using these local oscillator transitions. Furthermore, recent stratospheric infrared spectra (*10*), taken at 12.8 air masses and at moderately high resolving power, show weak atmospheric absorption lines with only a

Table 1. Observing parameters during searches for stratospheric ClO.

Date (1981)	Local oscillator	^{35}ClO line searched	Range of solar zenith angle* (deg)	Range of stratospheric air mass†
23 May, afternoon	P12	R9.5	78.6 to 88.8	4.5 to 10.3
24 May, morning	P12	R9.5	89.4 to 79.5	10.4 to 4.9
25 May, morning	P8	R12.5	89.1 to 78.2	10.3 to 4.4
25 May, afternoon	P8	R12.5	69.6 to 81.8	2.8 to 5.8
14 October, afternoon	P12	R9.5	77.0 to 88.9	4.1 to 10.3
15 October, afternoon	P8	R12.5	75.8 to 88.8	3.8 to 10.2

*The solar zenith angle is the true angle of the sun from the vertical, measured from the ground. †The stratospheric air mass is defined to be the ratio of the (refracted) slant-path length to the vertical path length between two spherical boundaries at 20 and 40 km, as seen by an observer at the ground.

few scattered strong lines of tropospheric water vapor in this spectral region. Atmospheric path lengths of this order can readily be obtained from the ground and strong H_2O lines can be avoided, thus setting the stage for a ground-based search for stratospheric ClO by ultrahigh-resolution infrared spectroscopy.

We measured the atmospheric spectra at Kitt Peak National Observatory (32°N, 112°W) during May and October 1981, using the McMath solar telescope and an infrared heterodyne spectrometer (*9*) developed at Goddard Space Flight Center. The observing parameters are given in Table 1. The sun was chopped against a precision blackbody source (typically 1100 K), and their intensities were adjusted until the mean heterodyne signal (5 to 1600 MHz) was null-balanced. The difference spectrum was then measured with a 128-channel spectral line receiver. Subsequent measurement of the blackbody reference spectrum, chopped against the room, established the differential transmittance scale and provided an absolute optical calibration for all channels simultaneously.

Each spectrum (*9*) was recorded double side-band at 25-MHz (0.00083 cm^{-1}) resolution with a 64-channel radio-frequency filter bank extending 1600 MHz from the laser local oscillator. We measured the spectral region near the expected frequency of the ClO transition simultaneously over a range of 320 MHz with a second 64-channel filter bank, using filters with a 5-MHz bandwidth. The P12 line at 856.51545 cm^{-1} and the P8 line at 859.78513 cm^{-1} of a line-by-line tunable $^{14}CO_2$ laser were used as local oscillators in searching for the R9.5 and R12.5 lines of ^{35}ClO, respectively (Table 1). The R16.5 line of ^{37}ClO also lies near the P12 line of $^{14}CO_2$; however, it is expected to be only ~1/3 as strong as the corresponding line of ^{35}ClO (Table 2). Preliminary results for P8 agree with the results presented here for P12.

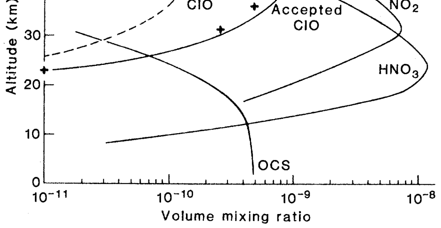

Fig. 2. Volume mixing ratio profiles for OCS, HNO_3, NO_2, and ClO used in simulating the experimental spectra. The three ClO measurements indicated by crosses are from Waters *et al.* (*4*). The dashed line represents an upper limit to a stratospheric ClO abundance profile consistent with our infrared data.

A typical spectrum of the measured atmospheric transmittance versus the frequency offset from the P12 laser line is shown in Fig. 1. The observed spectrum was acquired on 14 October 1981 and represents the average of 16 scans (each representing 89 seconds of integration), centered on a time 47 minutes before stratospheric sunset (*11*) (Table 1). The spectral resolving power ($\nu/\Delta\nu$) is 1×10^6 in Fig. 1a and 5×10^6 in Fig. 1b. All channels were acquired simultaneously.

Synthetic atmospheric spectra were calculated for comparison with the measured spectra, including spectral lines of OCS, HNO_3, NO_2, "nano-gen" (see below), and ClO. Since the atmosphere is optically thin in this spectral region, the absorptances were modeled for each molecule individually and later combined linearly, giving the overall atmospheric transmittance to a good approximation. A multilayered spherical atmosphere was constructed, consisting of ten equally thick layers for each species. The layers differed for each species and were chosen to cover approximately two decades of molecular abundances in each case. We calculated Voigt lineshape functions for each layer, using mid-latitude temperature and pressure profiles (*12*). The modeled spectrum is shown at 25-MHz resolution in Fig. 1a and at infinite resolution in Fig. 1b (solid and dashed curves). The model atmosphere used in calculating the synthetic spectra is shown in Fig. 2.

The volume mixing ratio profile used for OCS was the average of the measurements of Mankin *et al.* (*13*) and Inn *et al.* (*14*) and of the modeled profiles of Turco *et al.* (*15*) and Sze and Ko (*16*). Line positions and intensities for OCS were taken from Wells *et al.* (*17*); we also confirmed these in the laboratory, using the field heterodyne spectrometer. The compound OCS contributes a single line to this spectrum, centered only 25 MHz from the local oscillator (Table 2). Because OCS is tropospheric, this line is strongly pressure-broadened and appears in Fig. 1a as a gradually increasing transmittance as the offset from the local oscillator increases (compare modeled transmittances near 25, 750, and 1400 MHz).

Several features due to stratospheric HNO_3 are seen in Fig. 1a as much narrower absorption lines due to the much lower local pressures. The most obvious HNO_3 absorptions are centered near 156, 554, 963, and 1186 MHz (Table 2).

Table 2. Spectral line atlas for the 856.5-cm^{-1} region.

Frequency (cm^{-1})	Offset* (MHz)	Line strength (cm/molecule, 296 K)†
	HNO_3 (20)	
856.5102	156	2.82×10^{-21}
856.5339	554	1.42×10^{-21}
856.4970	554	1.42×10^{-21}
856.4926	685	5.78×10^{-22}
856.4833	963	2.82×10^{-21}
856.4759	1186	1.69×10^{-21}
856.5550	1186	5.00×10^{-21}
856.5680	1575	1.09×10^{-21}
	$NO_2\ ^pP_6 15$ (21)	
856.4967	563	2.36×10^{-22}
	OCS P6 (17)	
856.5146	25	6.24×10^{-21}
	^{35}ClO R9.5	
856.50137 (*6*)	422	6.99×10^{-21} (*23*)
	^{37}ClO R16.5	
856.54146 (*6*)	780	2.16×10^{-21} (*23*)
	Nano-gen	
	275	0.16 percent‡
	688	0.09 percent
	1038	0.30 percent
	1500	0.61 percent

*Absolute frequency difference relative to the local oscillator transition. The local oscillator is P12 $^{14}CO_2$ at 856.51545 cm^{-1}. †These line strengths were scaled to the local temperature for each atmospheric layer in our model atmosphere. ‡Four lines were observed (see text). Absorptances are given in place of strengths.

The volume mixing ratio profile used for HNO_3 is the average of the profiles obtained by Barker *et al.* (*18*) below about 20 km and the average of the theoretical profiles summarized by Hudson and Reed (*19*) above 20 km. Weaver *et al.* measured relative intensities and accurate line positions (*20*) for HNO_3 in the laboratory, using a similar heterodyne system.

Stratospheric NO_2 contributes a small amount (≤ 10 percent) to the absorption feature offset 563 MHz from the P12 $^{14}CO_2$ laser line (Table 2), and it is included in the synthetic spectra. The volume mixing ratio profile used for NO_2 is an average of measurements summarized by Hudson and Reed (*19*). Weaver *et al.* measured line positions for NO_2 in the laboratory (*20*), using a similar heterodyne system; these line positions were found to agree with those given by Flaud *et al.* (*21*) to within the experimental error. Ground-state energies and absolute line strengths were taken from Flaud *et al.* (*21*).

The molecule responsible for the absorption line offset 1500 MHz from the local oscillator frequency has not been identified. This line is not listed on the trace gas atlas of the Air Force Geophysics Laboratory, and our laboratory heterodyne spectroscopy rules out ClO, OCS, HNO_3, H_2O, NO_2, $COCl_2$, Freon-11, Freon-12, CCl_4, CH_3Cl, and C_2H_6 as possibilities for this absorption feature (*20*); O_3 is eliminated on the basis of Barbe's results (*22*). The observed line displays a full width at half-maximum (FWHM) of ~125 MHz, consistent with a predominantly stratospheric location. Its double side-band depth is ~0.6 percent, comparable to that of the deepest HNO_3 absorption (near 1186 MHz). It grows with increasing air mass and is a real, terrestrial atmospheric line. Three other (weaker) lines are also present in the observations shown in Fig. 1a, and their widths are consistent with 125-MHz FWHM. These arguments suggest that all four lines are associated with a single molecular species of stratospheric origin with mixing ratio $\sim 10^{-9 \pm 1}$. We call this constituent nano-gen and list the line parameters in Table 2. Fortunately, none of the nano-gen lines falls near the ClO line position.

We calculated the absorptance expected for the R9.5 line of ^{35}ClO, using the profile labeled "accepted ClO" in Fig. 2, which represents the mean of nine profiles measured by Anderson and coworkers (*2*) below about 40 km and the mean of the theoretical profiles summarized by Hudson and Reed (*19*) above 40 km. The ClO line positions (Table 2) are given by Maki (*6*); these line positions are based on diode laser absorption spectroscopy and we confirmed them, using heterodyne spectroscopy in the laboratory. The ClO line strengths (Table 2) are taken from Gillis and Goldman (*23*), who renormalized the Boltzmann intensity distribution to the individual line intensities and total band strength measured by Rogowski *et al.* (*24*). The pressure-broadening coefficient (4.44 ± 0.23 MHz/torr at 218 K) measured by Pickett *et al.* (*25*) for broadening of ClO by N_2 was used.

The modeled spectrum is compared with observations in Fig. 1. The ClO lines predicted in the synthetic spectrum are absent in the observed spectrum measured at both 25-MHz and 5-MHz resolution. Indeed, the data with a frequency resolution of 5 MHz show dramatically that the accepted stratospheric ClO abundances (*2–4*) are not supported by our infrared data.

Although we did not detect ClO, upper limits on the stratospheric abundance of ClO can be derived. We shall use both subjective and objective methods to derive upper limits from the data with 5-MHz resolution (Fig. 1b). One (subjective) approach is to add gaussian random noise to the noiseless synthetic spectrum and then to decrease the ClO line depth proportionally until its presence can just be discerned in the 5-MHz residuals. This procedure suggests an upper limit that is ~1/5 of the amount labeled "expected." We determine an objective upper limit by averaging channels symmetrically centered on the line. Abbas *et al.* (*26*) have shown that an optimum signal-to-noise ratio is achieved for gaussian-shaped lines when the ratio of spectral resolution to FWHM is 1.2. The FWHM of the expected ClO line is 60 MHz, but it departs from gaussian shape because of pressure-broadening. We thus expect optimum signal-to-noise ratio by adding roughly 15 channels. On this basis, we find that the abundance of ClO consistent with our data may not exceed 7.1 percent (1σ, where σ is the standard deviation) of the "accepted" ClO abundance. We shall take 14.2 percent as an upper limit, the value at the 95 percent confidence level (2σ). We thus find the stratospheric ClO abundance to be smaller by at least a factor of 7 than the currently accepted value (Fig. 2). If this were interpreted as a scaling factor to be applied to the "accepted" profile, we would formally derive an upper-limit profile as shown in Fig. 2. However, our data do not provide any justification for adopting a uniform scaling factor, valid throughout the stratosphere.

In view of our surprisingly small upper limit for ClO, we must carefully review possible sources of error. Let us consider first the effect of uncertainties in the frequency and intensity of the R9.5 line of ^{35}ClO. The frequency of this line is 856.50137 ± 0.00018 cm^{-1} (*6*). The 5.4-MHz uncertainty is much less than the width of one of the 25-MHz filters in the heterodyne spectrometer and should therefore not be a problem at the resolution used here. Furthermore, we have measured both the R9.5 line of ^{35}ClO and the R16.5 line of ^{37}ClO in a laboratory heterodyne spectrometer identical to the field instrument and find agreement with the values of Maki *et al.* (*6*). The intensity used for the R9.5 ClO line is based on the experimentally measured band intensity of 11.8 cm^{-2} atm^{-1} at 296 K (*23*). Margolis *et al.* (*27*) have independently measured the band strength to be 13.4 cm^{-2} atm^{-1}. Ab initio calculations of the band strength have been done at the self-consistent field level by Komornicki and Jaffe (*28*), who find 23 cm^{-2} atm^{-1}. Calculations at the SCF-CI level by Langhoff *et al.* (*29*), which include the effects of electron correlation, predict a band intensity of 32 cm^{-2} atm^{-1}. A systematic error in the line intensity will certainly affect our results, but there is reason to believe that the experimental line strengths may be too low rather than too high, and this woud only make the ClO upper limits even smaller.

According to recent atmospheric models, diurnal variability of ClO does not account for the much lower stratospheric abundances determined from our data. For example, the diurnal model of Sze and Ko (*30*) indicates that the integrated ClO column density above 30 km at the time of day corresponding to Fig. 1 is about 85 percent of the noontime value, and the diurnal model of Herman (*31*) shows no appreciable change from noon to sunset in the integrated ClO column density above 25 km. It thus seems reasonable to compare our results with those obtained near local noon. The mean column density based on nine measurements by the chemical kinetic method (*2*) is 16.1×10^{13} cm^{-2}, and the result based on the use of ground-based millimeter-wave spectroscopy (*3*) is 10.5×10^{13} cm^{-2}. The upper limit reported here based on the infrared spectroscopic method is 2.3×10^{13} cm^{-2} at the 95 percent confidence level, which is considerably smaller. Menzies' (*7*) latest results also suggest much smaller ClO abundances. Our finding that the stratospheric ClO abundance is smaller by at least a factor of 7 than currently accepted values suggests that the role of ClO and chlorofluorocarbons in the destruction of the earth's O_3 layer may need to be reevaluated.

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Neptunium and Americium Speciation in Selected Basalt, Granite, Shale, and Tuff Ground Waters

Abstract. *Neptunium and americium are relatively insoluble in ground waters containing high sulfate concentrations, particularly at 90°C. The insoluble neptunium species is Np(IV); hence reducing waters should enhance its formation. Americium can exist only in the trivalent state under these conditions, and its solubility also should be representative of that of curium.*

Neptunium has been called "the neglected actinide" (*1*), and this characterization could apply to americium as well. Both are present in significant quantities in spent reactor fuel, and both pose potential threats to the environment. The "hazard index" for ^{237}Np, based on half-life, environmental mobility, biological activity, and other factors, has been estimated to equal that of ^{239}Pu (*2*). Nevertheless, in contrast to the case for plutonium, there is a paucity of information on the ground-water chemistry of these two elements. As far as we know, only a few papers on the environmental chemistry of these elements exist (*1, 3*), even though Foti and Freiling (*4*) did pioneering work in 1959.

Moreover, much of the research on plutonium reactions in ground water has suffered from a failure to determine its oxidation-state distribution and presence in complexes. Without such information for neptunium, the much-needed studies of its ground-water chemistry also are likely to yield meaningless data.

In an effort to correct these deficiencies, we have studied the chemical speciation of neptunium and americium in ground waters associated with rock types proposed as possible hosts for nuclear waste repositories. The four waters were from the Grande Ronde basalt from the Hanford reservation in Washington, Climax stock granite and tuff from the Nevada Test Site, and Cretaceous shale from a rural well near Rapid City, South Dakota. References to the hydrogeology of the sites have been cited (*5*). Their ground-water compositions are shown in Table 1. For comparison, the study also included deionized water. We made no attempt to control the atmosphere above the ground waters during the experiments, because similar studies with plutonium (*5*) had shown that within the time scale of this study the oxidation-reduction behavior of the waters was determined by ionic species rather than by dissolved oxygen.

The general procedure for the addition of neptunium or americium to the waters, equilibrations, and analysis was the same as that for plutonium (*5*). Sufficient ^{237}Np or ^{241}Am in $0.5M$ to $1.0M$ $HClO_4$ solution was added to achieve a concentration of approximately $10^{-8}M$ ($10^{-11}M$ for americium) in the waters; as in the plutonium study, the amount of this solution added was so small that *p*H adjustment after addition was required only in the case of the deionized water. After the specified equilibration periods, the solutions were mixed and sampled, both before and after filtration through 0.05-μm Nuclepore (*6*) filters. The filtrates were subjected to radiometric analysis for total neptunium or americium concentration as well as to praseodymium fluoride (PrF_3) carrier precipitation [for Np(III) and Np(IV) or Am(III)] in the presence of $K_2Cr_2O_7$ holding oxidant added just before HF addition, and thenoyltrifluoroacetone (TTA) extraction [also for Np(IV)], as described (*5*). (Because the tetravalent state was absent, TTA extraction was omitted in the americium study.) Whereas plutonium was extracted with TTA from $1M$ acid, neptunium extraction was found to be most efficient from $0.5M$ acid; otherwise, the procedures used were the same. Neptunium and americium were determined on all samples by radiometric alpha counting.

To assess the effect of initial oxidation state, we conducted separate experiments using reduced [primarily Np(IV)] and oxidized [primarily Np(V)] neptuni-