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Abstract

A ground-based search for the 856.50137 cm^{-1} R(9.5) and for the 859.76765 R(12.5) transitions of stratospheric ^{35}ClO was made in the solar absorption mode using an infrared heterodyne spectrometer. Measurements were made in May and October of 1981, and lines due to stratospheric HNO_3 and tropospheric OCS were detected, at about 0.3% absorption levels. The expected lines of ClO in this same region were not detected, even though the optical depth of the ClO lines should be on the order of 0.2% using currently accepted ClO abundances. These infrared measurements suggest that stratospheric ClO is at least a factor of 7 less abundant than is indicated by indirect in situ fluorescence measurements, and our upper limit of 2.4×10^{13} molecules cm^{-2} to the integrated column density of ClO is a factor of over 4 less than is indicated by microwave measurements. Our results imply that the release of fluorocarbon precursors of ClO may be significantly less important for the destruction of stratospheric ozone (O_3) than was previously thought.

Current photochemical models of the stratosphere indicate that chlorofluoromethanes (CFMs) released into the earth's atmosphere from the manufacture and use of refrigerants and propellants are active in the depletion of the ozone layer (1). The CFMs undergo photodissociation in the stratosphere to produce free chlorine atoms which then react with ozone to form chlorine monoxide (CℓO) and molecular oxygen. The CℓO reacts further with atomic oxygen in the upper stratosphere to produce chlorine atoms and molecular oxygen. The CℓO free radical is thus a catalyst in the removal of odd oxygen species from the stratosphere, and measurements of stratospheric CℓO abundances are particularly important in understanding the chemistry of the chlorine cycle and its importance for long-term trends in the earth's ozone layer.

Stratospheric CℓO abundances and volume mixing ratio profiles have been measured both by in situ resonance fluorescence techniques (2) and by ground-based (3) and balloon-borne (4) microwave measurements on the $J=11/2\rightarrow9/2$ emission line of ^{35}CℓO at 204.352 GHz. It is, however, important to note that both measurement techniques suffer from a lack of uniqueness. The UV fluorescence method is indirect because chlorine atoms are measured directly and the precursor (CℓO) molecule is inferred. The microwave experiments clearly measure an emission line at the correct frequency and strength to be CℓO if current abundance models are correct, but it cannot be shown rigorously that the detected line is not due to some other species. The apparent detection of stratospheric CℓO based on infrared heterodyne measurements (5) using a $^{14}CO_2$ laser has subsequently been shown (6) to be in error since the frequency of the reported atmospheric line does not correspond to a vibration-rotation transition of CℓO; however, a reexamination (7) of the experimental data of Ref. 5 does show the presence of a weak line at the correct frequency to be CℓO.

Infrared absorption measurements of stratospheric CℓO abundances are important for two reasons: first, because they provide an independent check on the results of the fluorescence and microwave measurements on CℓO, and second, the presence of an absorption line with the correct frequency and strength is a necessary condition for CℓO to be confirmed. We report here an attempt to detect stratospheric CℓO in the infrared using heterodyne spectroscopy with a $^{14}CO_2$ laser as the local oscillator. The spectral line searched for is the R(9.5) infrared absorption line in the $^2\pi_{3/2}$ $v=0\rightarrow1$ vibrational mode of ^{35}CℓO.

The frequency of this absorption line is calculated by Maki et al. (6) to be 856.50137±0.00018 cm^{-1}, based on molecular constants derived from precision laser spectroscopy of this band. Other atmospheric species expected to absorb near this frequency include OCS, HNO_3, NO_2, and perhaps O_3, although the spectroscopic parameters for ozone and nitric acid are not precisely known in this spectral region. A search was also made for the R(12.5) line of ^{35}CℓO known to be at 859.76765 cm^{-1} from direct laboratory measurements (6).

Measurements of the terrestrial atmospheric absorption lines formed against the solar continuum were made at the Kitt Peak National Observatory (32°N, 112°W) using the infrared heterodyne spectrometer system developed (8) at Goddard Space Flight Center. The P(12) line at 856.51545 cm^{-1} (9) of a line-by-line tunable $^{14}CO_2$ laser was used as the local oscillator for the measurements reported here. The double-sideband solar absorption spectrum, null-balanced against a reference blackbody source, was recorded at 25 MHz (0.00083 cm^{-1}) resolution with a 64 channel rf filter bank extending 1.6 GHz from the laser local oscillator frequency. The absorption region near the expected frequency of the CℓO transition was also measured over a range of 320 MHz using 5 MHz bandwidth filters. The 25 MHz resolution of the spectrometer system is sufficient to resolve fully the lineshapes of the observed atmospheric absorption lines. Several individual scans were averaged to obtain the spectra analyzed. Measurements were made before sunset 23 May 1981, just after sunrise 24 May 1981, and before sunset 14 October 1981 and are summarized in Table 1.

A representative scan is shown in Fig. 1 for sunset 14 October 1981. The spectrum shows the frequency offset in MHz from the P(12) $^{14}CO_2$ laser line frequency <u>vs.</u> the double-sideband absorption intensity. The resolution is 25 MHz per channel, and the range of the absorption intensity corresponds to about 1% of the solar continuum.

Atmospheric absorption lines due to carbonyl sulfide and nitric acid are identified in Fig. 1. The broad tropospheric OCS line spans the full 1600 MHz range of the spectral scan. Several features due to stratospheric HNO_3 are seen as much narrower absorption lines. The molecule responsible for the narrow absorption line offset 1525 MHz from the local oscillator frequency has not been identified (10). The position of the expected R(9.5) absorption line of CℓO is shown by the arrow in Fig. 1. No absorption due to $C\ell O$ is obvious at this frequency position, even though currently accepted stratospheric $C\ell O$ abundances (2-4) predict a double-sideband optical depth on the order of 0.2% at five air masses for this line.

Synthetic atmospheric spectra were calculated for comparison with the measured spectra, using accepted volume mixing ratio profiles for OCS, HNO_3, NO_2, and various $C\ell O$ model profiles. Atmospheric absorption line shapes were computed by dividing the atmospheric region for each molecule into ten equal-thickness layers covering approximately two decades of molecular abundances. Mid-latitude atmospheric temperature and pressure profiles as a function of altitude were taken from the 1976 U.S. Standard Atmosphere (11). The volume mixing ratio profile used for OCS was the average of the measurements of Mankin et al. (12) and Inn et al. (13) and the modeled profiles of Turco et al. (14) and Sze and Ko (15). Line positions and intensities for OCS were taken from Wells et al. (16) but were also measured in the laboratory using the field heterodyne spectrometer. The volume mixing ratio profile used for HNO_3 is the average of the profiles obtained by Barker et al. (17) below about 20 km, and the average of the theoretical profiles summarized by Hudson and Reed (18) above 20 km. Relative intensities and accurate line positions were measured (19) for HNO_3 in the laboratory using the same heterodyne system since the spectrum of HNO_3 has not been analyzed adequately in this spectral region. The NO_2 molecule contributes a small amount ($\lesssim$10%) to the absorption feature offset 575 MHz from the P(12) $^{14}CO_2$ laser line, and it is included in the synthetic spectra. The volume mixing ratio profile for NO_2 is an average profile representing measurements summarized by Hudson and Reed (18). Line positions for NO_2 were measured in the laboratory using the field heterodyne system and were found to agree with those given by Flaud et al. (20) to within experimental error. Ground state energies and absolute line strengths were taken from Flaud et al. (20). The volume mixing ratio profiles for all these molecules are shown in Fig. 2, and the line parameters used in the fits are given in Table 2.

Absorption frequencies for the vibration-rotation transitions of $^{35}C\ell O$ and $^{37}C\ell O$ have been determined by Maki et al. (6), and line strengths have been calculated by Gillis and Goldman (21) from the band strength measured by Rogowski et al. (22). Currently accepted volume mixing ratio profiles for $C\ell O$

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(2-4) were used to compute the optical depth expected for the R(9.5) line of ^{35}ClO. The volume mixing ratio profile used for ClO is included in Fig. 2. This profile represents the average of nine measurements made by Anderson et al. (2) below about 40 km and the average of the range of the theoretical models summarized by Hudson and Reed (13) above 40 km. A hard-sphere pressure broadening coefficient of 0.07 cm^{-1}/atm was used for the ClO molecules.

A typical modeled spectrum, excluding the line due to ClO, is compared with observations (May, sunrise) in Fig. 3(a). The synthetic spectrum is displaced downward for clarity and the residuals are displayed as well. Perfect agreement between the synthetic spectrum and the experimental spectrum is not obtained, not only because we do not directly iterate on the volume mixing ratio profile shapes, but also because there are a few lines not included in our line atlas in Table 2 for this region. Ozone, for example, has at least two lines in this spectral region, one near 1003± 150MHz, and one near 526±450 MHz offset from P(12) of $^{14}CO_2$ (23). Absolute intensities are not known for these two lines; however, they are expected to be very weak since they do not appear in high air-mass ground-based spectra taken by Goldman et al. (24) in which the HNO_3 and OCS lines do appear. Layering of the HNO_3 as a function of altitude, such as that observed by Barker et al. (17), could also change somewhat the computed HNO_3 line profiles, since we used the simpler volume mixing ratio profile shown in Fig. 2. In spite of these limitations, the synthetic spectra do reproduce reasonably well the observed spectra.

A synthetic spectrum including the ClO absorption line predicted by the accepted stratospheric abundance of ClO (2-4) is compared in Fig. 3(b) with the experimental scan of 14 October 1981. The simulation uses the volume mixing ratio profiles shown in Fig. 2, including that shown for ClO. Stratospheric ClO abundances at the levels indicated by this particular volume mixing ratio profile are obviously not confirmed by our infrared data.

Although ClO is not detected in our measurements, an upper limit can be placed on the stratospheric ClO abundance which is consistent with the infrared data. This is done by reducing the volume mixing ratio profiles for ClO shown in Fig. 2 by a constant of proportionality until the R(9.5) line of ^{35}ClO becomes barely visible in the residuals. This procedure gives the volume mixing ratio profile shown by the dashed line in Fig. 2 as the upper limit for the acceptable stratospheric CℓO abundance profile and is a factor of 6.7 less than the average of the profiles measured by Anderson et al. (2). Our profile is a factor of 2.3 less than their minimum CℓO profile (measured on 8 December 1976) and a factor of 51 less than their maximum CℓO profile (measured on 14 July 1977).

Our infrared data place an upper limit of 0.12 ppbv on the abundance of CℓO at the volume mixing ratio peak near 40 km if we assume the profile shape described above. The average volume mixing ratio measured by Anderson et al. (2) is about 0.8 ppbv at this altitude. Our upper limit on the volume mixing ratio profile also yields CℓO mixing ratios 5.1 times less at 36 km, 5.7 times less at 31 km, and 6.7 times less at 23 km than are indicated by the measurements by Waters et al. (4). We find an upper limit to the integrated column density of CℓO above 23 km to be 2.39×10^{13} molecules/cm^2. This is a factor of over 4 less than the total column density of 1.05×10^{14} molecules/cm^2 reported by Parrish et al. (3), and it is a factor of 6.7 less than the column density derived from the accepted profile shown in Fig. 2 for CℓO. Our results imply that the abundance of CℓO in the earth's stratosphere is much less than is indicated by the measurements by Anderson et al. (2), by Parrish et al. (3), and by Waters et al. (4). Menzies (7) reports a weak atmospheric line at the correct frequency to be the R(6.5) absorption line of ^{35}CℓO and has derived a new volume mixing ratio profile for CℓO. This profile peaks at about 0.5 ppb at 38-40 km and then rapidly decreases to less than 0.1 ppbv near 35 km. This much more rapid fall-off in the CℓO volume mixing ratio compared to other measurements (2-4) suggests a smaller integrated CℓO column density than is currently accepted.

The two possible sources of error in our infrared measurements are in the frequency and the intensity of the R(9.5) line of ^{35}CℓO. The frequency of this line is 856.50137±0.00018 cm^{-1} (6). The uncertainty in this frequency represents 5.4 MHz; this is much less than the width of one of the 25 MHz filters in the heterodyne spectrometer, and the frequency accuracy should therefore not be a problem at the resolution used here. Menzies (7) has measured the frequency of the R(6.5) line of CℓO with a $^{14}CO_2$ laser heterodyne spectrometer in the laboratory, and finds the line center frequency to be within

5 MHz of Maki's value. Perturbations are not expected to play a role for this state, so we regard Menzies' results for the R(6.5) line as an independent confirmation of Maki's results for the R(9.5) and R(12.5) line frequencies. The intensity used for the $C\ell O$ line is from Gillis and Goldman (21), who calculated line intensities for $C\ell O$ from the band intensity of 11.8 cm^{-2} atm^{-1} at 296 K (22). Any errors in this band intensity will certainly affect our results, but if this experimental band intensity is in error, it is likely to be too low since high-quality ab initio quantum mechanical calculations accounting for electron correlation in $C\ell O$ predict (25) a band intensity of 32 cm^{-2} atm^{-1} at 296 K. The line parameters for $C\ell O$ are thus not likely to be in error sufficiently to account for our nondetection of $C\ell O$. Furthermore, the atmospheric spectral region near the P(8) laser line of $^{14}CO_2$ at 859.78513 cm^{-1} (9) was examined as well. The R(12.5) line of the $^{2}\pi_{3/2}$ $v=0\rightarrow1$ transition of $^{35}C\ell O$ should appear 511 MHz offset from the P(8) laser line but was not observed in the atmospheric spectra. Two somewhat weaker lines of $^{37}C\ell O$ would also be seen in our spectra if current stratospheric models were correct, but we do not see any evidence for those lines either.

Diurnal or seasonal variability in the $C\ell O$ concentrations also do not appear to account for the much lower stratospheric $C\ell O$ abundances determined from our data. Although the measurements by Anderson et al. (2) do show large variability in the $C\ell O$ abundances, the measurements described here suggest $C\ell O$ concentrations that are at least a factor of 2.3 less than their reported minimum values. Also, our measurements were made during both morning and evening and in late spring and in early fall, yet none of the spectra indicate any $C\ell O$ absorption at all at the expected frequencies.

If uncertainties in the spectroscopic parameters or temporal variability do not account for our nondetection of infrared absorption by $C\ell O$, our results indicate that the role of $C\ell O$ in the destruction of the earth's ozone layer should be re-evaluated.

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26. J. D. Rogers is an NAS/NRC Resident Research Associate. M. J. Mumma, T. Kostiuk, D. Deming and D. Zipoy were Visiting Astronomers at Kitt Peak National Observatory, which is operated by the association of Universities for research in Astronomy, under contract with the National Science Foundation.

Table 1. Summary of measurements on stratospheric chlorine monoxide.

Date	Nominal Time[a]	Solar Zenith Angle[b]	Air Mass[c]
1. 23 May 1981	SS-48 min	78.55 - 80.92	4.5 - 5.4
2. 23 May 1981	SS-37 min	81.69 - 85.00	5.8 - 7.7
3. 23 May 1981	SS-28 min	85.63 - 88.81	8.2 - 10.3
4. 24 May 1981	SR+27 min	88.77 - 86.92	10.2 - 9.1
5. 24 May 1981	SR+33 min	86.27 - 83.75	8.7 - 6.9
6. 24 May 1981	SR+43 min	83.16 - 79.51	6.6 - 4.9
7. 14 Oct 1981	SS-47 min	76.98 - 83.33	4.1 - 6.7
8. 14 Oct 1981	SS-29 min	84.36 - 88.87	7.3 - 10.3

a. The nominal time is defined as the time after sunrise (SR) or before sunset (SS) at 40 km.

b. The solar zenith angle is the angle of the sun from the vertical, measured from the ground.

c. The air mass is the ratio of the slant-pathlength to the vertical pathlength between two spherical boundaries at 20 and 40 km.

Table 2. Line Atlas for the 856.5 cm^{-1} Region.

Molecule	Frequency (cm^{-1})	S (cm/molecule, 296K)[a]
HNO_3	856.511	$2.82x10^{-21}$
	856.533	$1.42x10^{-21}$
	856.497	$1.42x10^{-21}$
	856.491	$5.78x10^{-22}$
	856.483	$2.82x10^{-21}$
	856.553	$1.69x10^{-21}$
	856.476	$5.00x10^{-21}$
NO_2^{b} $^{P}P_6(15)$	856.496	$2.36X10^{-22}$
OCS^{c} P(6)	856.515	$6.24x10^{-21}$
$^{35}C\ell O^{d}$ R(9.5)	856.501	$6.99x10^{-21}$
$^{37}C\ell O$ R(16.5)	856.541	$2.16x10^{-21}$

a. These line strength values were scaled to the temperature for each atmospheric layer.

b. Spectroscopic parameters from Flaud et al. (20).

c. Spectroscopic parameters from Wells et al. (16).

d. Line position from Maki et al. (5), and line strength from Gillis and Goldman (21).

Figure Captions

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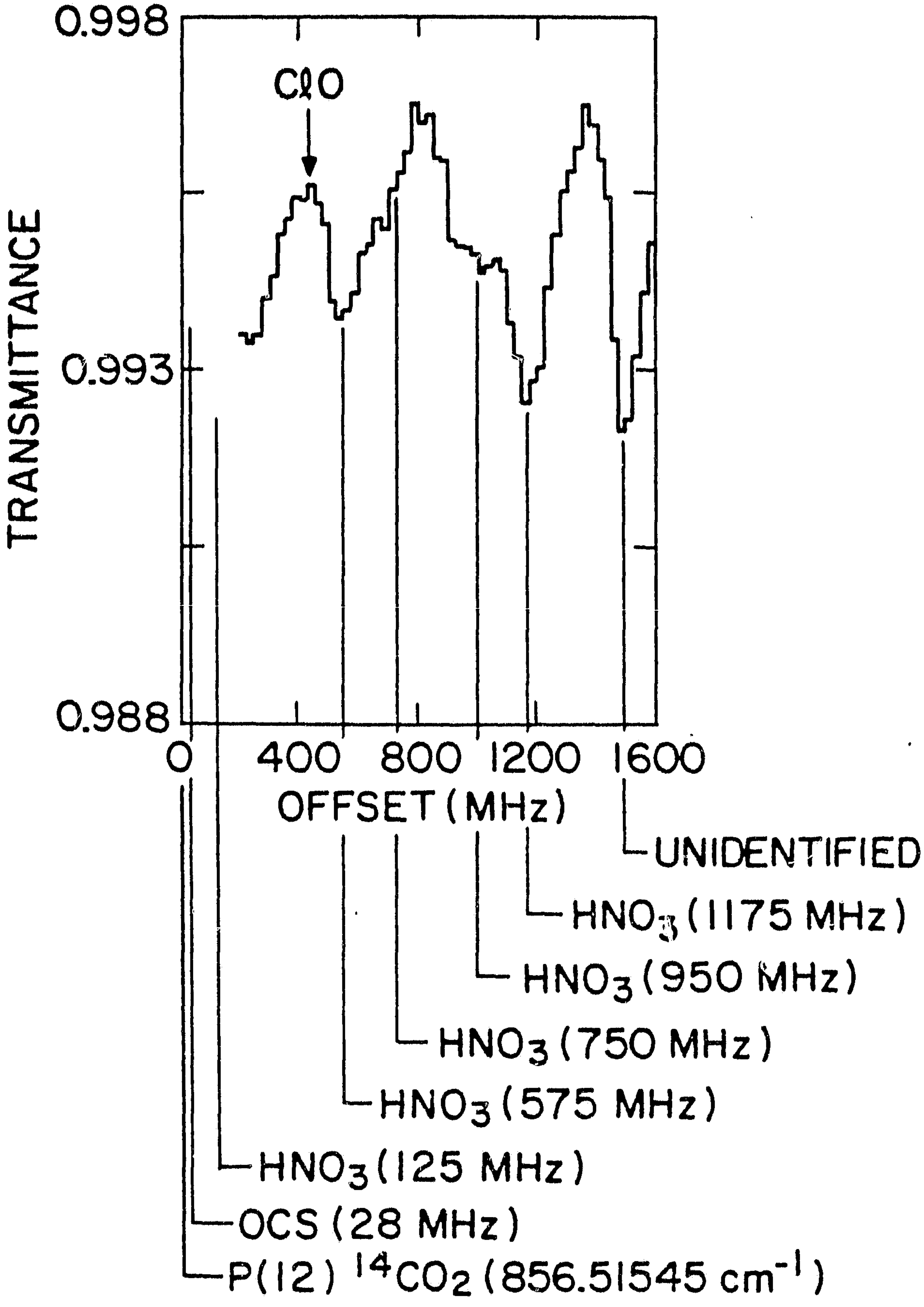
Fig. 1. Typical atmospheric infrared heterodyne absorption spectrum near the P(12) $^{14}CO_2$ laser line, taken before sunset 14 October 1981 at 5.3 average air masses. Atmospheric absorption lines due to OCS and HNO_3 are identified, and the position of the expected R(9.5) absorption line of $^{35}C\ell O$ is indicated by the arrow.

Fig. 2. Volume mixing ratio profiles for OCS, HNO_3, NO_2 and $C\ell O$ used in the simulations of the experimental spectra. The three measurements on $C\ell O$ indicated by the crosses are from Waters et al. (4). The dashed profile represents the upper limit to a stratospheric $C\ell O$ abundance profile consistent with the infrared data.

Fig. 3(a). Comparison of the atmospheric absorption spectrum and simulation for sunrise on 24 May 1981 at 5.7 average air masses. The synthetic spectrum is displaced downward by 0.002 for clarity. Here the synthetic spectrum does not include the R(9.5) line of $^{35}C\ell O$. The residuals are displayed as well.

Fig. 3(b). Comparison of the atmospheric absorption spectrum shown in Fig. 1 with the synthetic spectrum. The synthetic spectrum is displaced downward by 0.002. The absorption line expected for the R(9.5) line of $^{35}C\ell O$ at the abundance levels indicated by the "Accepted $C\ell O$" profile shown in Fig. 2 is included in this simulation.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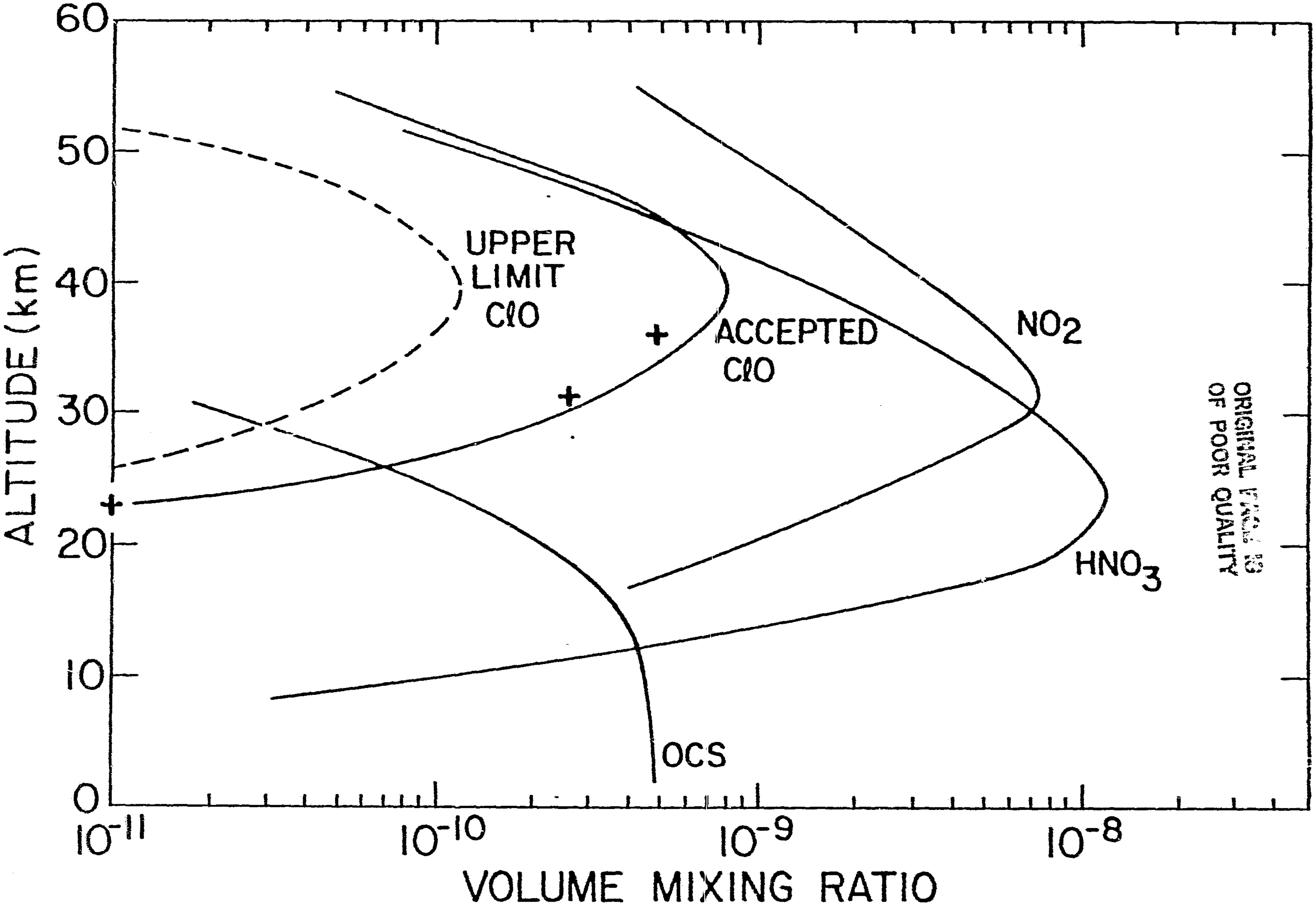
P(12) 14CO2 (856.51545 cm-1)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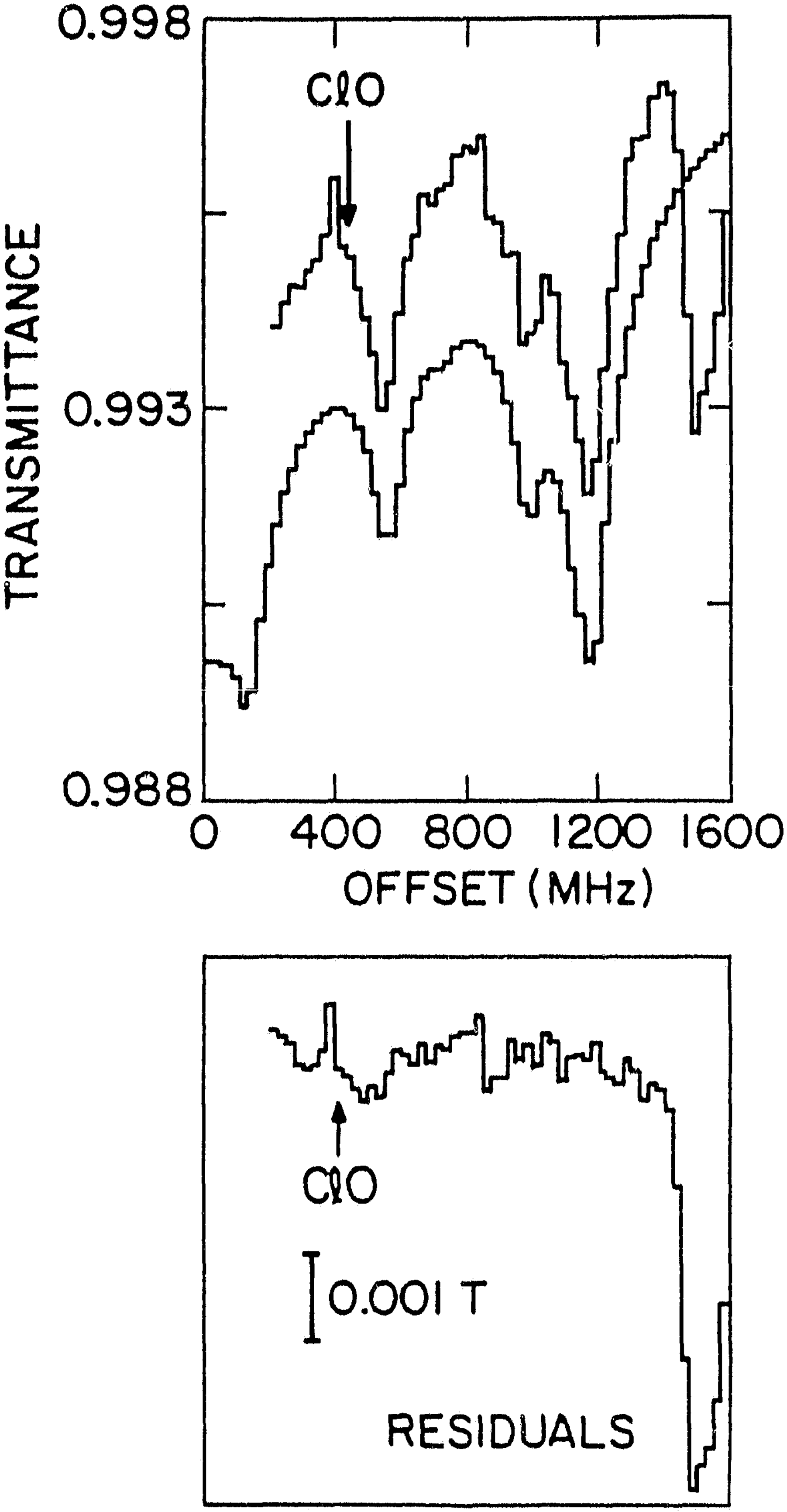
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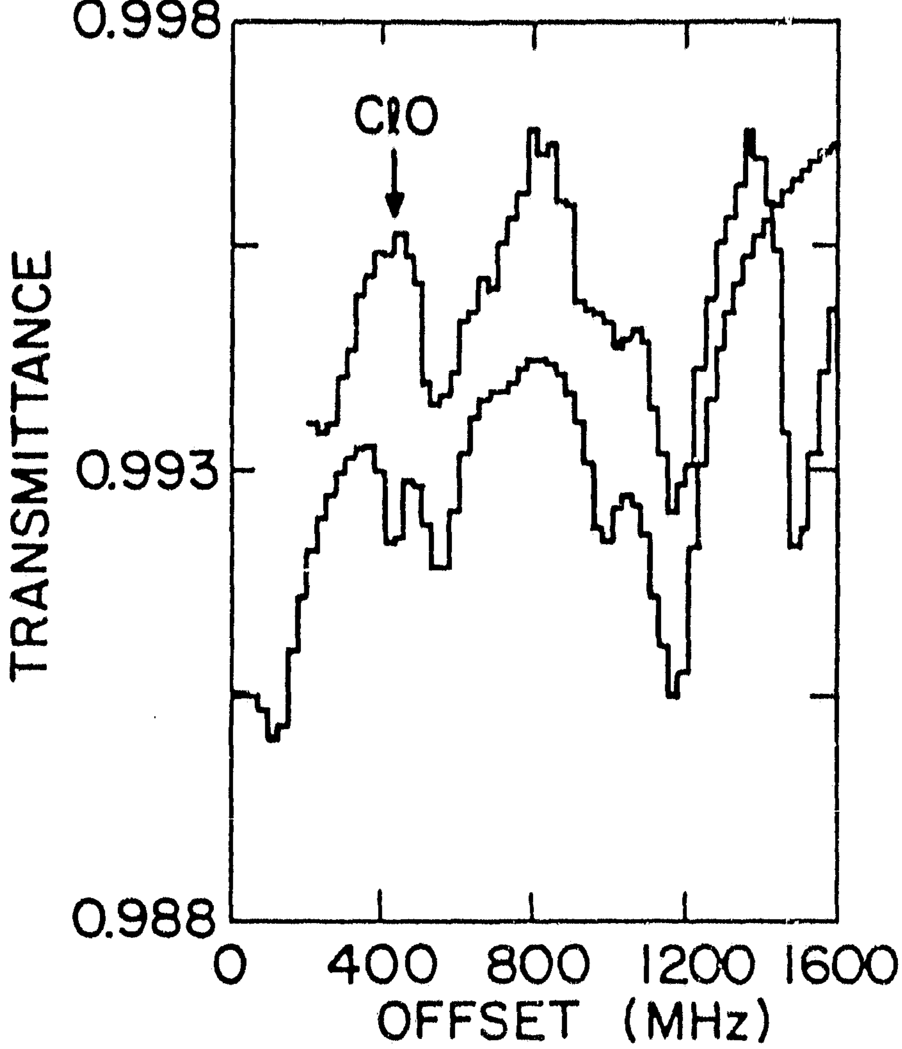
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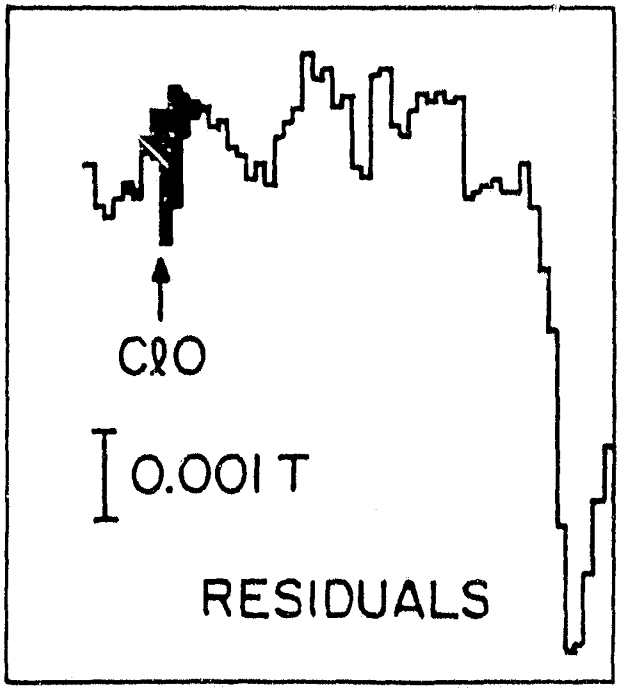
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