Reports

Atomic Chlorine and the Chlorine Monoxide Radical in the Stratosphere: Three in situ Observations

Abstract. *Three simultaneous observations of atomic chlorine (Cl) and the chlorine monoxide radical (ClO) are reported which encompass the altitude interval between 25 and 45 kilometers. Together, Cl and ClO form a gas-phase catalytic cycle potentially capable of depleting stratospheric ozone. Observed Cl and ClO densities, although variable, imply that chlorine compounds constitute an important part of the stratospheric ozone budget. The results are compared with recent models of stratospheric photochemistry which have been used as a basis for predicting ozone depletion resulting from fluorocarbon release.*

Chlorine-containing compounds are now known to be an important component of stratospheric photochemistry. In 1974 a number of research groups identified atomic chlorine and chlorine monoxide as potentially important agents in the catalytic destruction of ozone and discussed the effect of various chlorine sources on the global ozone budget (*1*, *2*). That work was preceded by the development of hypotheses describing the photochemical structure of the stratosphere which included the oxides of hydrogen and nitrogen and identified ozone as the sole atmospheric constituent capable of screening the earth's surface from harmful near-ultraviolet solar radiation (*3*).

For the near future the greatest potential threat to ozone appears to be that suggested by Molina and Rowland (*2*), who first associated the ubiquitous presence of chlorofluoromethanes in the troposphere, reported by Lovelock *et al.* (*4*), with gas-phase catalytic destruction of ozone in the stratosphere. This destruction follows the photolytic release of free chlorine from the parent molecules, principally $CFCl_3$ and CF_2Cl_2, in the middle and upper stratosphere, which results from exposure to solar ultraviolet radiation. The most probable fate of the chlorine atom thus formed is reaction with ozone

$$Cl + O_3 \xrightarrow{k_1} ClO + O_2 \qquad (1)$$

forming the chlorine monoxide radical, which then reacts principally either with atomic oxygen

$$ClO + O \xrightarrow{k_2} Cl + O_2 \qquad (2)$$

or with nitric oxide

$$ClO + NO \xrightarrow{k_3} Cl + NO_2 \qquad (3)$$

to reform atomic chlorine. Reactions 1 to 3 are rapid bimolecular reactions, which have been studied extensively in the laboratory (*5*) and are now well understood. The first two constitute a catalytic chain in which an oxygen atom recombines with an ozone molecule, reforming the O_2 bond and enhancing the rate of ozone destruction.

To quantitatively evaluate the importance of chlorine in the global ozone budget, it is necessary to determine the concentrations of Cl and ClO as a function of altitude throughout the region in which atmospheric ozone is controlled by local photochemistry (25 to 45 km). As an initial step toward this end, we report here the results of three in situ experiments in which we determined simultaneously the concentrations of Cl and ClO in the stratosphere over the altitude range of interest. A discussion of the resonance

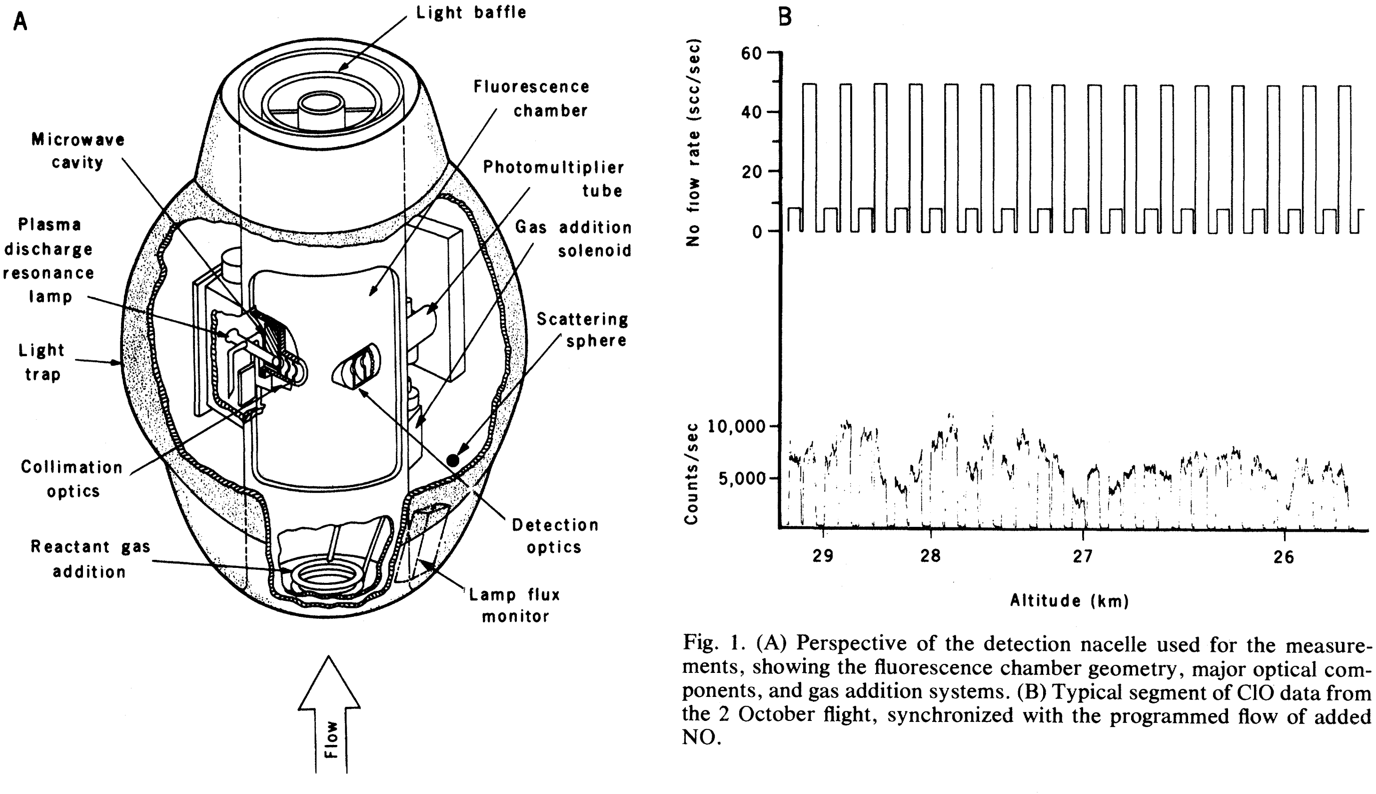


Fig. 1. (A) Perspective of the detection nacelle used for the measurements, showing the fluorescence chamber geometry, major optical components, and gas addition systems. (B) Typical segment of ClO data from the 2 October flight, synchronized with the programmed flow of added NO.

fluorescence detection technique used for this study, which was employed previously to determine the stratospheric concentrations of atomic oxygen and hydroxyl, appears elsewhere (*6*), so only brief mention of the experimental method is given here.

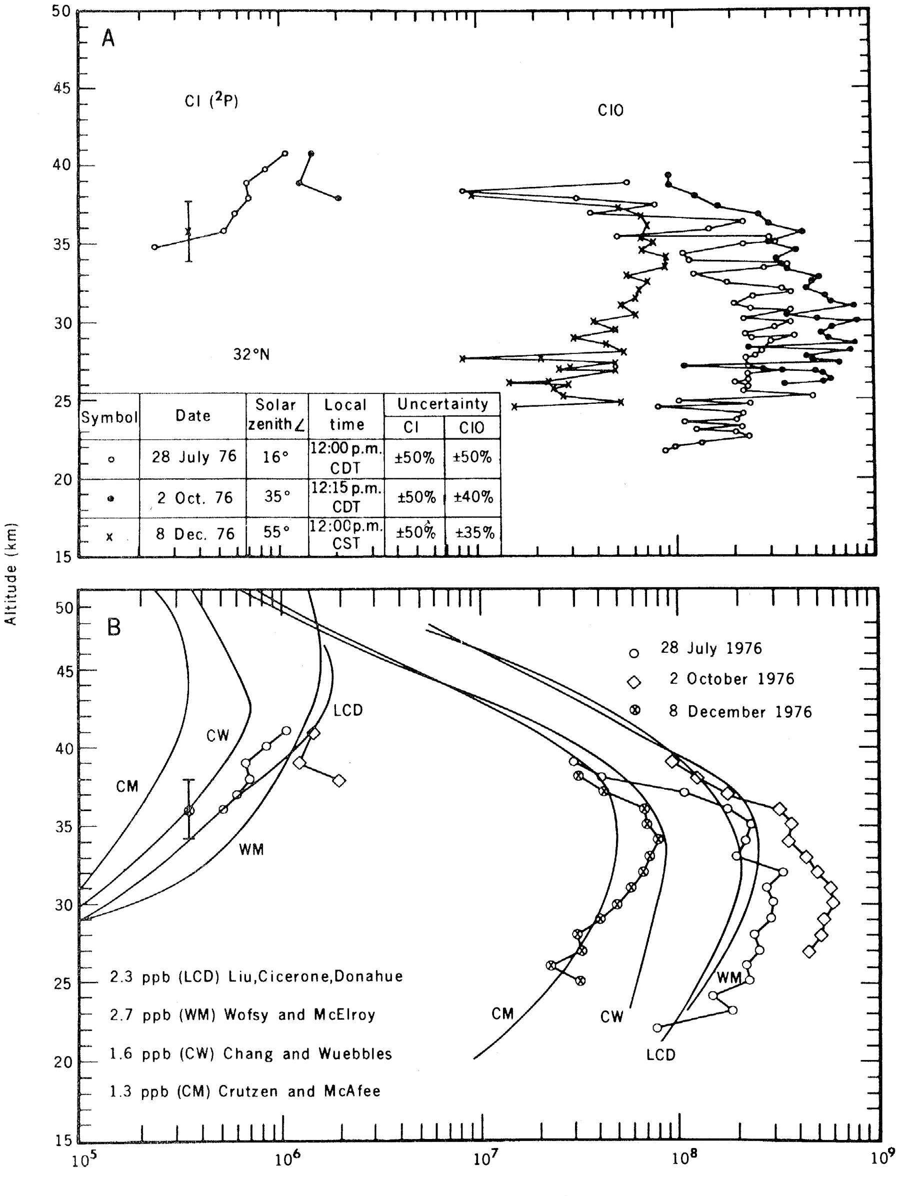
In general, atoms and diatomic molecules have allowed transitions between bound electronic states separated in energy by 3 to 15 ev, corresponding to the vacuum and near ultraviolet spectral regions. Their resonance absorption and subsequent spontaneous isotropic reemission of photons provide a mechanism for detecting their presence in the gas phase at concentrations extending down to a part per trillion. To detect a particular atom or molecule, a beam of photons resonant in energy with a selected transition of that species is passed through the sample gas, and photons resonantly scattered from the beam are counted by a photomultiplier tube–pulse detection system. The number of photons resonantly scattered from the beam per unit time, in the absence of reabsorption, is proportional to the concentration of scattering centers within the beam.

For in situ sampling of atoms and free radicals in the stratosphere, the photon beam, formed by collimating the output from a low-pressure (~ 2 torr) plasma discharge lamp, and the observation direction of the photon detector are arranged so that they are mutually perpendicular to a high-velocity (~ 100 m/sec) flow of stratospheric air. The flow of the air sample, which passes through the interior of a hollow, aerodynamically shaped pod or nacelle (Fig. 1A), is created by lowering the device through the atmosphere on a stabilized parachute dropped from a balloon near the stratopause (44 km).

For the detection of atomic chlorine, the $^2D_{5/2}$–$^2P_{3/2}$ resonance transition at 1189 Å was selected, because at that wavelength absorption by molecular oxygen is negligible within the detection chamber of the instrument at stratospheric pressures. Ethane, added at predetermined intervals to the instrument throat during descent, was used to eliminate Cl atoms from the flow and thus establish the background count rate in the absence of fluorescence by Cl atoms.

The spectroscopy of ClO has been the subject of considerable study in recent years (*7*), and although the molecule has an allowed transition from the $X^2\Pi$ ground state to the $A^2\Pi$ excited state in a convenient spectral region (2700 to 3000 Å), the *A* state predissociates, eliminating direct molecular resonance fluorescence as a useful stratospheric measurement technique. However, when NO is added to the instrument throat the rapid bimolecular reaction between NO and ClO (reaction 3) takes place; this provides a convenient means for converting ClO to Cl, which is then detected by resonance fluorescence at 1189 Å. Although in principle a single instrument could be used to detect both Cl and ClO if C_2H_6 and NO are alternately added, in practice two separate detection nacelles are used, mounted approximately 1 m apart on a common support frame suspended below the parachute. Absolute calibration is accomplished by installing the detection chamber of each flight instrument in a laboratory vacuum facility, which is capable of producing a known Cl concentration in a high-velocity flow over the pressure regime encountered during the atmospheric measurement.

Three simultaneous observations of Cl and ClO have been made; the first on 28 July 1976 at 12:00 noon Central daylight time (CDT) (local solar zenith angle, χ = 16°), the second on 2 October 1976 at 12:15 p.m. CDT (χ = 30°), and the third on 8 December 1976 at 12:00 noon Central standard time (χ = 55°). In all cases a 4.2×10^5 m^3 helium balloon, launched at dawn from Palestine, Texas, 32°N, bore the experimental package to an altitude of ~ 43 km. After activation and stabilization of the instruments, the measurement phase was begun by severing from the balloon the stabilized parachute, which controlled both the velocity and the angle of attack of



Symbol	Date	Solar zenith∠	Local time	Uncertainty	
				Cl	ClO
○	28 July 76	16°	12:00 p.m. CDT	±50%	±50%
●	2 Oct. 76	35°	12:15 p.m. CDT	±50%	±40%
x	8 Dec. 76	55°	12:00 p.m. CST	±50%	±35%

Fig. 2. (A) Concentration profiles of Cl(^2P) and ClO simultaneously determined on 28 July, 2 October, and 8 December 1976, showing considerable local structure as well as a significant decrease in concentration in December. (B) Comparison of predicted and observed Cl and ClO concentrations in the stratosphere.

the experimental package during descent.

Figure 1B shows a 4-km frame of ClO data with 0.08-second time resolution from the 2 October flight, synchronized with the programmed flow of added NO. In addition to demonstrating the structure in the data, Fig. 1B shows that the detector count rate is independent of NO at flow rates between 8 and 50 standard cubic centimeters (scc) per second; the two flows were chosen to verify complete conversion of ClO to Cl, while avoiding Cl depletion by the reaction

$$Cl + NO + M \rightarrow NOCl + M$$

where M is a third body.

Figure 2A gives the Cl and ClO densities determined on the three flights, showing (i) marked local structure in each of the ClO profiles, the Cl densities being too small to provide spatial detail, and (ii) significant variation in the average concentrations of Cl and ClO observed in the July, October, and December experiments. Experimental uncertainties for the measurements are listed in Fig. 2A and are based primarily on uncertainties in (i) absolute calibration in the laboratory (±20 percent), (ii) convolution of the lamp resonance line and the atomic absorption cross section as a function of lamp body temperature (±20 percent), and (iii) absolute flux measurements during flight (±10 percent). The instruments were calibrated before and after each flight and the hardware, interference filters, and key optical components were identical for all flights.

Figure 2B shows a comparison between the data of Fig. 2A averaged over 1-km intervals and four theoretical predictions of the Cl and ClO densities (*8*) for summer midday conditions at 30°N, corresponding to the maximum predicted Cl and ClO concentrations for the geographic position of the measurement. The chlorine mixing ratio, defined as the total number of chlorine atoms, bound and free, per unit volume divided by the total atmospheric number density, is indicated for each model and represents the opinion of the respective author.

Three points, apparent from inspection of Fig. 2, deserve emphasis. First, the Cl and ClO concentrations observed in the July and October flights were equal to or greater than those predicted by any of the four models (which were selected to encompass the full range of predicted chlorine radical concentrations). Together with the results of laboratory studies of the rate constants for reactions 1 to 3 and measurements of atomic oxygen and ozone in the stratosphere (*9*), this demonstrates that chlorine compounds can, under certain conditions, contribute an important component to the photochemical budget of stratospheric ozone. Second, a marked decrease in both Cl and ClO is apparent in the December data. The observed change cannot be explained by a simple photochemical dependence on solar zenith angle (*10*) but may be related to large-scale atmospheric circulation. Third, there is approximate agreement between the observed and predicted Cl/ClO ratios. This suggests that reactions 1 to 3, which are the chlorine reactions believed to be involved directly in the homogeneous gas-phase catalytic destruction of ozone, constitute the dominant reaction sequence that establishes a photochemical steady state between Cl and ClO in the stratosphere.

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11. H. J. Grassl, R. E. Shetter, J. C. Maurer, and B. P. Elero of the Space Physics Research Laboratory, University of Michigan, made major contributions to the construction, calibration, and flight of these experiments. Many helpful discussions with S. C. Liu, R. J. Cicerone, and T. M. Donahue took place during the course of this work. J. Stanley, J. Martin, B. Baker, W. Gibson, J. Neeley, and other members of NASA Johnson Space Center supplied field operation and telemetry support. All flights took place from the National Scientific Balloon Facility (with support from the National Science Foundation), Palestine, Texas, under the direction of R. Kubara and staff. The research was supported by the NASA Upper Atmospheric Research Office under contract NAS9-14609.

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Uranus: The Rings Are Black

Abstract. *An upper limit of 0.05 is established for the geometric albedo of the newly discovered rings of Uranus. In view of this very low albedo, the particles of the rings cannot be ice-covered as are those of rings A and B of Saturn.*

The recent discovery of at least five rings about Uranus (*1*) during the occultation of star SAO 158687 raises the question of possible earlier observations of the rings. During the 1972 and 1974 oppositions of Uranus, I photographed Uranus and its environs (*2*), using an 888-nm interference filter and a Varo image-intensifying tube in the method suggested by Kuiper (*3*) for recording possible faint inner satellites of the major planets. No new satellites were found on these plates to the limit of magnitude 17 at Roche's limit of 2.4 radii of Uranus. The region inside of Roche's limit (where the ring system lies) was overexposed in all of the 1-hour plates taken in the search for new satellites. One plate (Fig. 1) had an exposure of 5 minutes and shows the satellites Ariel, Umbriel, Titania, and Oberon. It shows only a possible trace of the ring system.

Four of the five rings (α, β, γ, and δ) have widths of 14 km (approximate width of each ring) in their plane and individually would not have been photographed even if they reflected all of the incident sunlight. The outermost, ring ϵ, is of variable width, but the average of the widths given by all four groups of observers (*1*) was 100 km in its plane. The attenuation of the star's light was nearly complete (60 to 90 percent) for ring ϵ but only about 20 to 40 percent for rings α, β, γ, and δ. In my photograph the maximum separation from ring α to ring ϵ would have been 0.5 arc sec at their ansae, less than the seeing disk. I will con-