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RESEARCH AND DEVELOPMENT TECHNICAL REPORT
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STRATOSPHERIC OZONE DENSITY AS MEASURED BY A CHEMILUMINESCENT SENSOR DURING THE STRATCOM VI-A FLIGHT

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Ozone concentration was measured by the chemiluminescent technique during the STRATCOM VI-A balloon flight flown from Holloman Air Force Base, New Mexico, on 23 September 1975. More than 30 hours of data were collected as the balloon floated at various altitudes in the stratosphere. A diurnal variation in ozone above the ozone peak was observed in the 27 to 40 km region. Wet stratospheric photochemistry is used as a guide to explain the diurnal change in ozone.

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INTRODUCTION

Ozone, a minor constituent of the upper atmosphere, is not distributed uniformly. Its concentration has been measured by rocket-borne [1] as well as balloon-borne sensors [2-5]. These instruments do not stay for long periods in the atmosphere; they are flown with rockets and small radiosonde balloons and hence are not capable of measuring temporal variation in ozone concentration. To observe the effect of solar radiation on the ozone concentration at various altitudes during the day and also during sunset and sunrise, a chemiluminescent sensor was flown with the STRATCOM VI-A payload.

EXPERIMENT

The STRATCOM VI-A balloon was launched on 23 September 1975 at 2300 MST from Holloman Air Force Base near Alamogordo, New Mexico. It reached the float altitude of 38.5 km at 0300 MST on September 24. The balloon floated at this altitude through sunrise at 0530. At 1200 it drifted downward to an altitude of 27.4 km by 1900 MST (sunset occurred at 1828 MST). Shortly after 1900, the balloon started ascending as the ballast was dropped, and reached an altitude of 36 km at 0200 on 25 September. It stayed at this altitude until sunrise at 0456 MST. As the sun heated the balloon, it ascended to an altitude of 39.8 km at 0715 MST. The ozone sensor and some other sensors were turned off at 0500 MST to conserve power for the remaining experiments; therefore, no ozone data were obtained after that time. The flight was terminated at 0900 MST. Figure 1 shows the altitude plotted against time of the flight.

An electrochemical (mast) ozonesonde was also released on 24 September 1975 (1100 MST) from White Sands Missile Range, New Mexico, for comparison purposes.

RESULTS

The solid line on Figure 2 shows the ozone profile as obtained by the chemiluminescent sensor on its first ascent; the dotted line shows electrochemical sonde data. The times shown on the figure indicate the balloon altitude and the corresponding ozone concentration.

Figure 3 shows Figure 2 data and the descent data of ozone concentration along with the time the balloon reached that altitude. Note that between 27 and 38 km a difference in ozone concentration was observed between the nighttime ascent and the afternoon descent.

Figure 4 shows the descent data obtained on the afternoon and evening of 24 September and the ascent data on the night and early morning of 25 September. Figure 5 shows the composite data of the complete flight. Both times the ascent data were obtained during nighttimes and the ozone concentration measured is in good agreement.

The transition through sunrise on 24 September at a constant altitude is shown in Figure 6.

ANALYSIS

During the balloon ascent, up to 25 km, there is good agreement between the chemiluminescent and electrochemical sensors. From 27 to 35 km, the two nighttime ascents are in very good agreement. The descent data in the afternoon shows a marked increase in ozone concentration although it follows the same gradient as ascent.

The diurnal change can possibly be explained by wet photochemistry. During descent, the ozone concentration curve (Figure 4) from noon (point 1) to sunset (point 2) should correspond closely to the undisturbed daytime values since the sensors were descending away from the wake of the balloon.

The daytime production of ozone is primarily due to the following reactions [6]:

$$O_2 + h\nu\ (< 2424\mathring{A}) \rightarrow O + O \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M\ \text{(twice)} \tag{2}$$

$$\text{Net } 3O_2 \rightarrow 2O_3$$

The destruction reactions of O_3 are as follows:

$$O_3 + h\nu\ (< 3100\mathring{A}) \rightarrow O_2 + O \tag{3}$$

$$O_3 + O \rightarrow O_2 + O_2 \tag{4}$$

$$\text{Net } 2O_3 \rightarrow 3O_2$$

The NO_X destruction reactions:

$$NO_2 + h\nu\ (< 4000\mathring{A}) \rightarrow NO + O \tag{5}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{6}$$

$$NO_2 + O \rightarrow NO + O_2 \tag{7}$$

$$N_2O + O(^1D) \rightarrow 2NO \tag{8}$$

The HO_X destruction reactions:

$$H_2O + O(^1D) \rightarrow 2HO \qquad (9)$$

$$CH_4 + O(^1D) \rightarrow CH_3 + HO \qquad (10)$$

$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (11)$$

The net gain in ozone is the difference between the destruction and the production reactions.

The sunset transition occurred from sunset at 1828 MST to 2004 MST (point 2 to point 3). During the transition, the balloon slowed down until it reached its lowest altitude and then slowly started ascending. In reference to the ozone chemistry, during the sunset transition, UV sunset first occurs at the shortest wavelengths. Consequently, the ozone production by Equations (1), (2), and (5) is no longer active. However, all the remaining destruction reactions of O_3 by NO_X and HO_X remain. At the sensor location, the destruction reactions of O_3 were probably enhanced due to the presence of water vapor. However, this enhanced destruction of O_3 in the vicinity of the ozone sensor is not very apparent because the balloon was descending into air with a higher concentration of ozone.

As the night progressed from point 3 to point 4, the ascending cold balloon and payload package acted as sinks of water vapor, and the balloon temperature was essentially that of the air temperature. Hence the disturbance by the balloon and payload should be minimal, and the measured values of ozone by the sensors should correspond to the nighttime equilibrium values of the undisturbed atmosphere. Consequently, a comparison of the ozone measurements of the daytime descent (point 1 to point 2) and the nighttime ascent (point 3 to point 4) shown in Figure 4 shows a diurnal change in the ozone above the ozone peak.

The nighttime decrease in the ozone profile may be explained by the absence of the daytime production and destruction reactions, the nighttime equilibrium of O_3 being primarily established by Equations (2) and (4) since NO and HO are essentially depleted. Another possible explanation could be the subsidence of the O_3 layer. However, this explanation is unlikely because of the meteorological conditions existing at that time.

During twilight, as the scattered light increased (Figure 6), ozone concentration slowly decreased from its nighttime equilibrium. At twilight, as the sky receives scattered UV in the region between 3100Å and 4000Å, ozone is destroyed by NO_X reactions. This destruction of ozone may have caused the ozone concentration decrease. At sunrise when energies of wavelengths less than $\lambda < 3100Å$ start arriving at the balloon and payload platform, causing water vapor to be released from the platform, the destructive reactions of HO_X plus NO_X accelerate the reduction of ozone [7]. Additional ozone is produced as the wavelength radiation less than 2424Å becomes available at the platform altitude [Equation (1)] and the formation of ozone exceeds its destruction. This increase is shown by the change in slope in Figure 6 at about 0600 MST.

Model calculations for sunrise transition [8] were made for 25, 30, 35, and 40 km altitudes and are plotted in Figure 6. The changes in ozone concentration during that transition period for 25 and 30 km indicate a slight decrease until sunrise and then a slight increase. For 35 km the trend is opposite, i.e., an increase during the night and then a decrease. The 40 km calculation shows the same trend as for 35 km, but the amplitude is large. An additional calculation made for 40 km altitude which included large amounts of water vapor (10^3 times the normal) is also plotted on the same figure. The effect of large amounts of water vapor in the model is quite significant.

The diurnal variation in ozone concentration as observed between 27 and 40 km (Figure 4) is consistent with the model calculation made with additional water. Thus it is apparent that the ozone sensor was measuring ozone in the wake of the balloon during both ascents, while during descent the measurements were not in the wake of the balloon. The sunrise effect, however, could not be explained on the model calculation and may be a clue to significant processes not yet included in these models.

CONCLUSIONS

A diurnal change in the ozone concentration was observed in the region between 27 and 40 km during this balloon flight. These observations are consistent with the model calculations made with additional water vapor and indicate that the balloon was outgassing throughout most of the flight.

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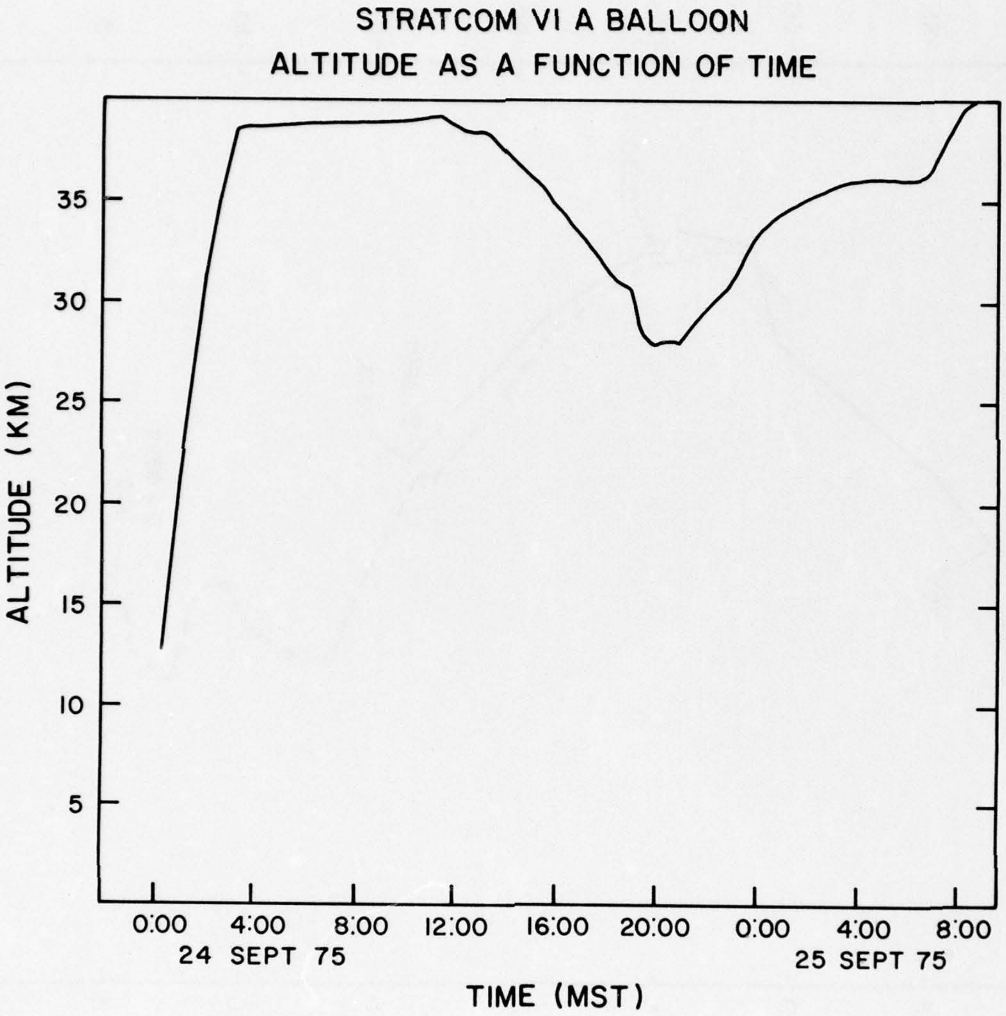

Figure 1. Balloon altitude as a function of time.

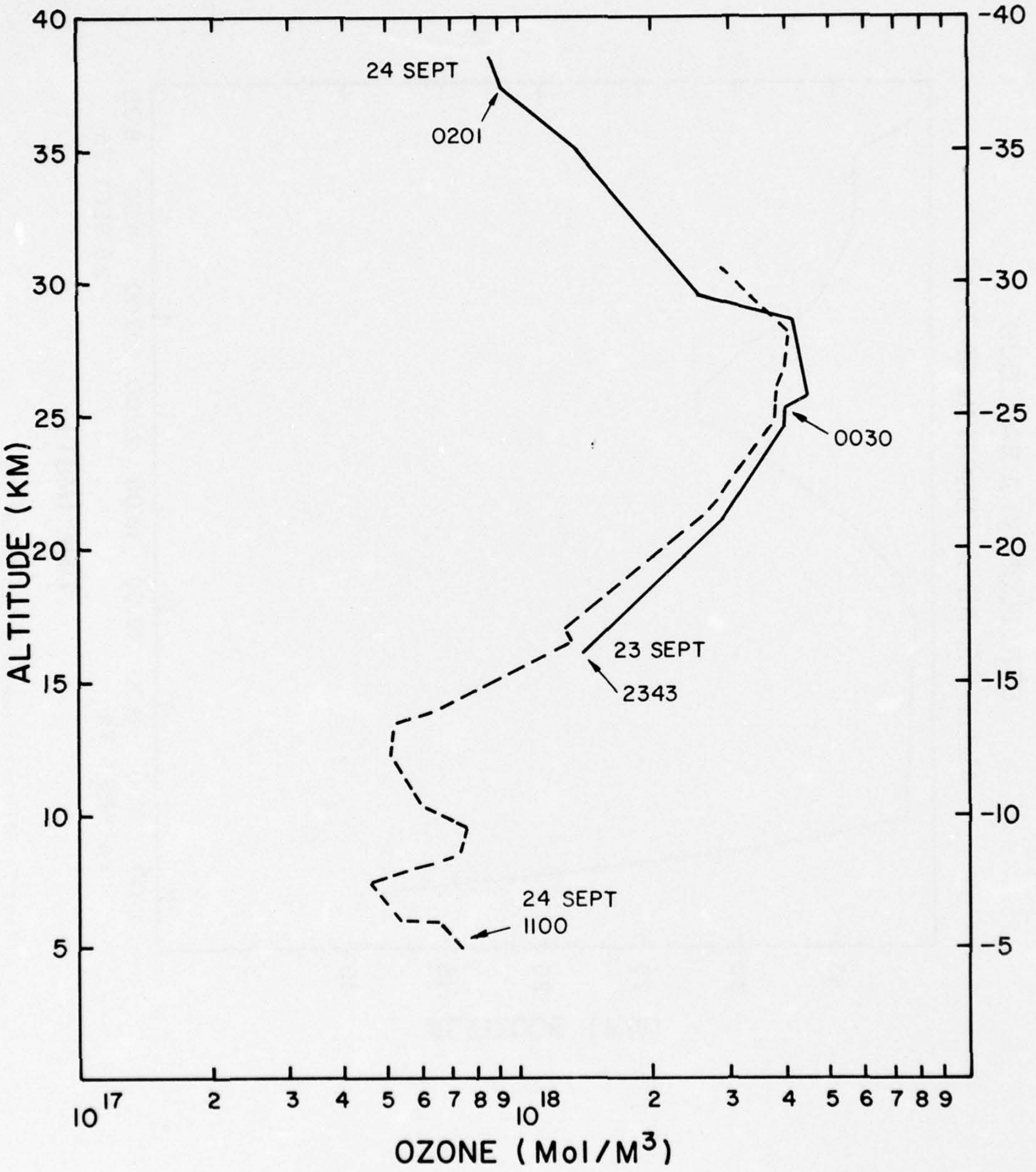

Figure 2. Ozone concentration measured by the chemiluminescent sensor as the balloon ascended through troposphere and stratosphere (solid line). Electrochemical (mast) ozonesonde profile (dotted line) is also shown.

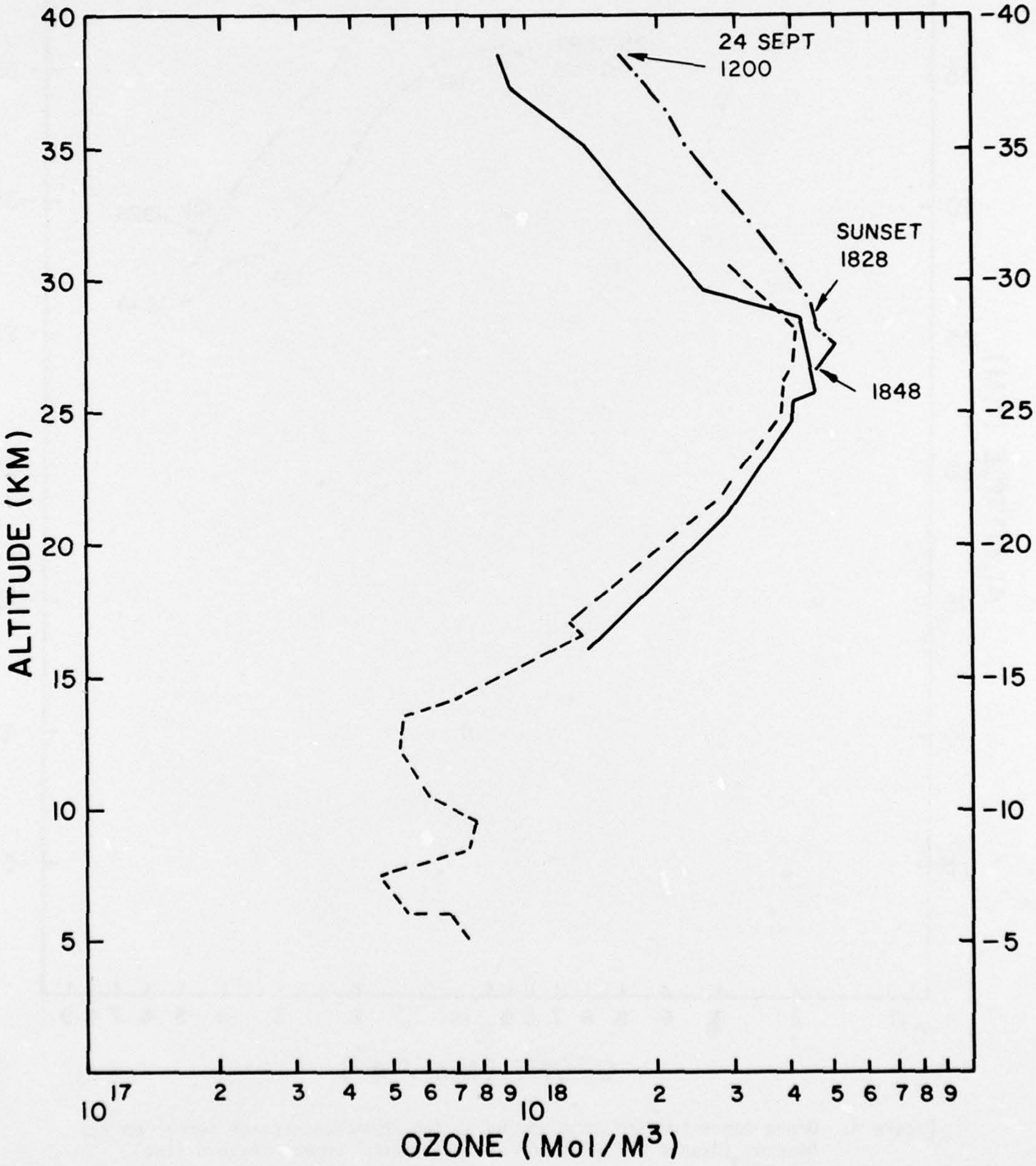

Figure 3. Same as Figure 2 plus ozone concentration measured by chemiluminescent sensor as the balloon descended in the afternoon of 24 September 1975 (dashed dotted line).

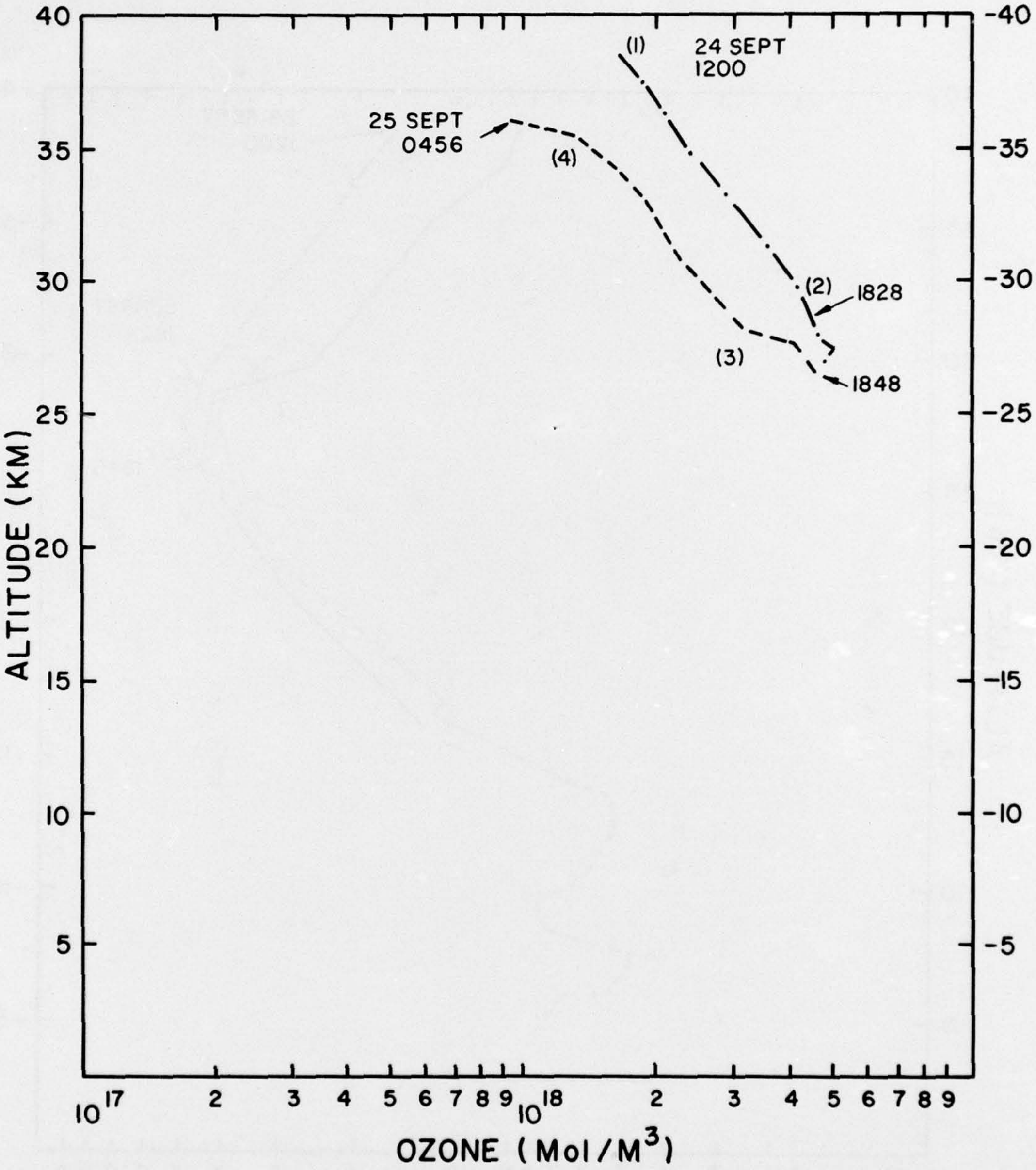

Figure 4. Ozone concentration as measured by the chemiluminescent sensor on its descent (dashed dotted line) and the second ascent (dashed line).

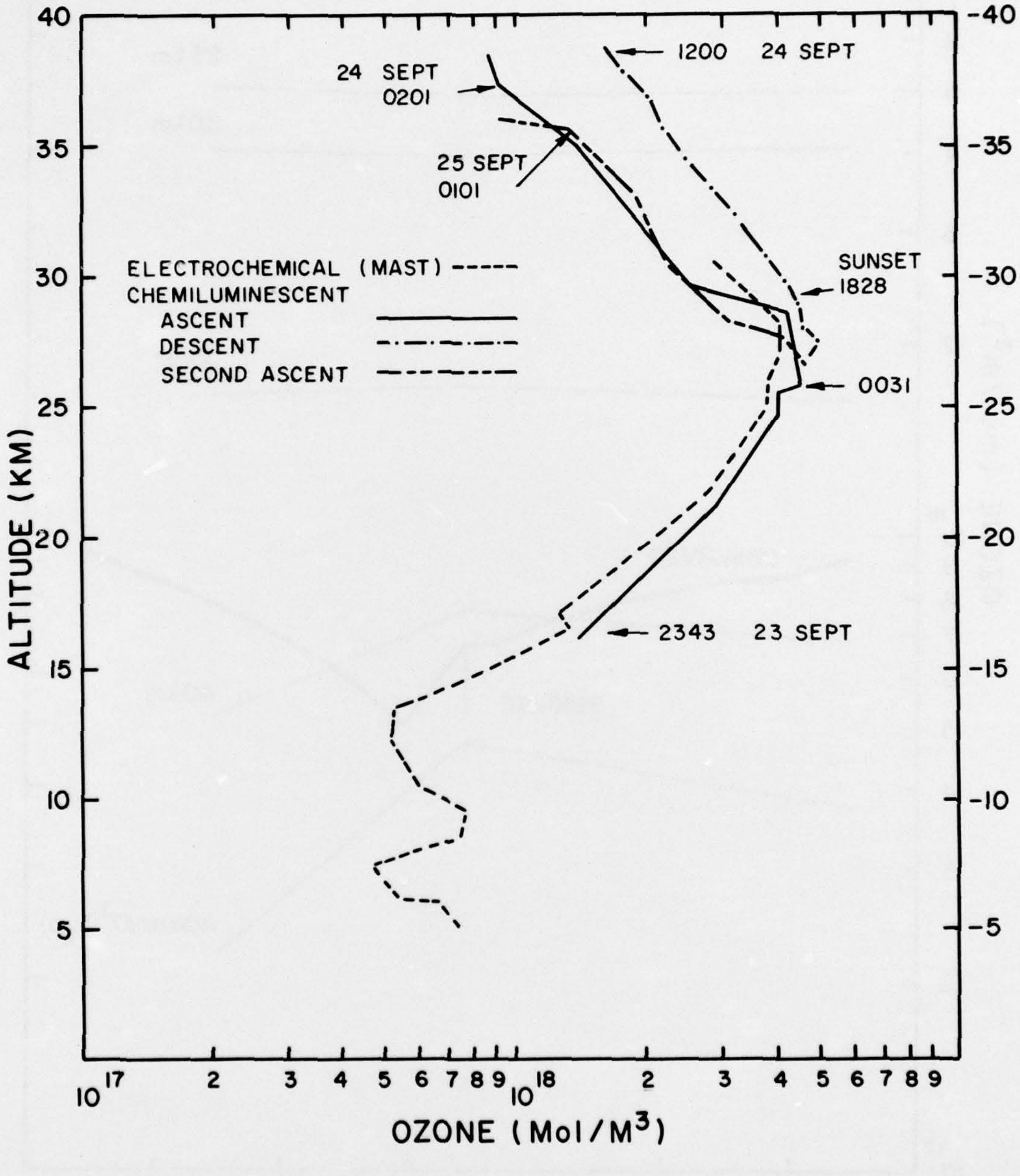

Figure 5. Composite profiles of ozone concentration as measured by the chemiluminescent sensor on STRATCOM VI-A flight. Electrochemical profile is also shown.

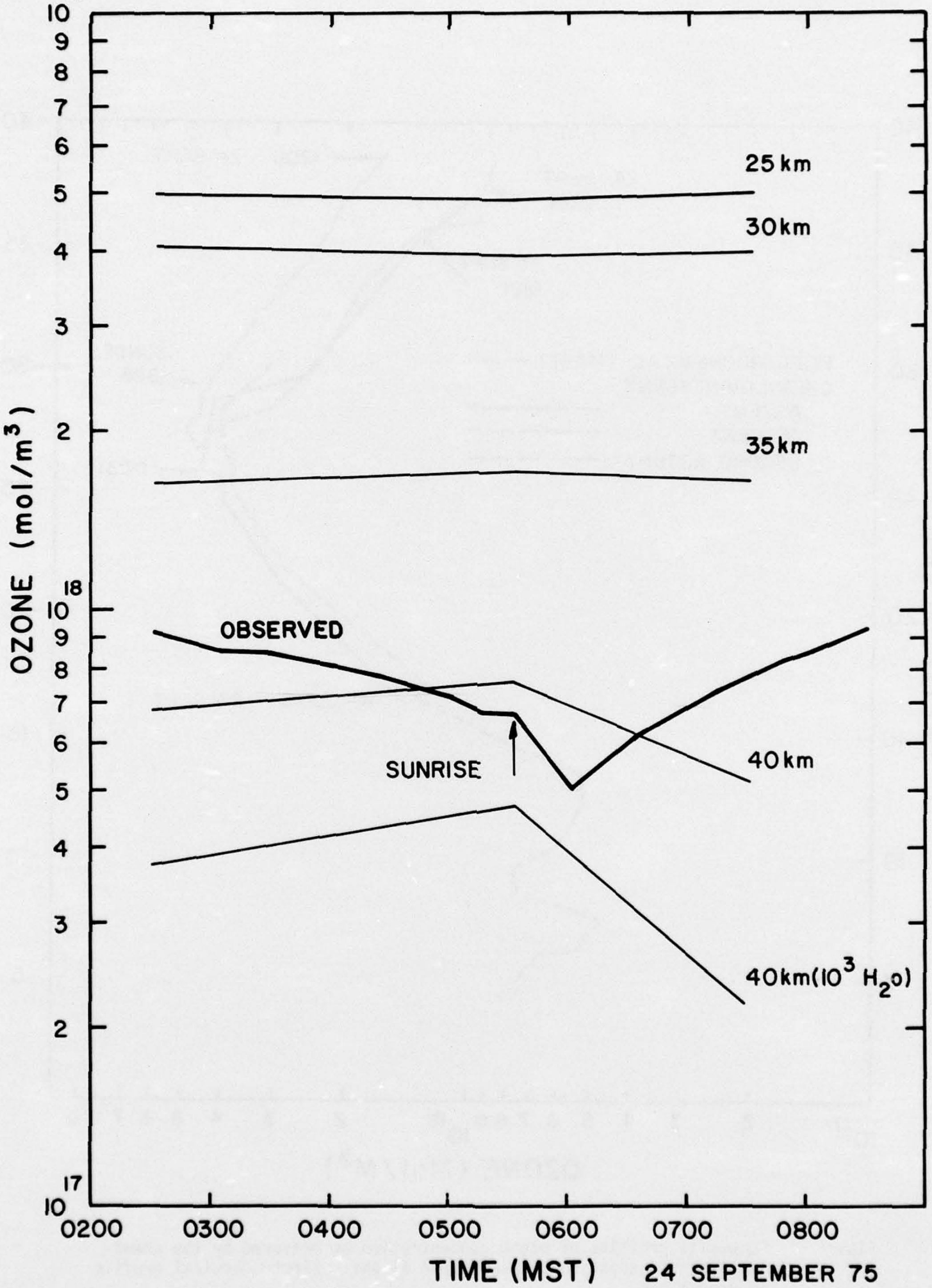

Figure 6. Sunrise effect as observed by the chemiluminescent sensor. The balloon was floating at a constant altitude of 38.6 km. Model calculation for 25, 30, 35, and 40 km are also plotted. An additional profile at 40 km contained 10^3 times the normal water vapor in the calculation.

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