

Simultaneous Upper Air Composition Measurements by Means of UV Monochromators and Mass Spectrometers

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Molecular oxygen and nitrogen number densities in the altitude range 115–220 km above Sardinia were measured in two sounding rocket experiments (Esro payloads S84 and S90) in February 1972 by a combination of UV monochromators and mass spectrometers. The measured values agree closely with the Cira (1972) values for the 120-km altitude region. At higher altitudes the O₂ profiles measured by UV monochromators indicate deviations from diffusive equilibrium with respect to the N₂ profile measured by the mass spectrometers.

This paper presents final results obtained from two sounding rocket experiments, Esro payloads S84 and S90. The experiments had two independent scientific aims that could be pursued with the same instrumentation on board these payloads. One objective of our investigations was to obtain simultaneous observations of the thermospheric molecular oxygen content by means of two largely independent measuring techniques. These data were to be backed up, as far as possible, by measurements of additional atmospheric constituents, in particular N₂, in order to be able to cross-check the density profiles and scale heights determined for the various constituents. The other objective of the experiments was to collect more detailed and quantitative information on the UV solar spectrum in the Schumann-Runge region, where a considerable uncertainty about the solar fluxes exists. This paper deals with the results obtained from the thermospheric composition measurements; results of the absolute solar flux measurements were discussed in a separate paper by *Ackerman and Simon* [1973].

The two most important techniques for determination of the composition of upper air in the 100- to 200-km altitude region are in situ mass spectrometry and solar EUV and UV absorption measurements. Both methods have their merits and shortcomings, too. Because the shortcomings of the two techniques influence the derived data in different ways, it appears reasonable to try to combine both techniques in one sounding rocket payload in order to allow extensive cross-checks on absolute number densities and relative altitude profiles obtained from the two types of instruments. In fact, *Hall et al.* [1965] argued in favor of such joint measurements of mass spectrometers and EUV monochromators as early as 1965.

Our personal interest in such correlated optical and mass spectrometer experiments was even more alerted by the results of a mass spectrometric investigation of upper air composition in the 150-km altitude region that we performed in December 1966. Unexpectedly high O₂ densities observed in the ion source of the mass spectrometer could only be explained by a considerable degree of recombination of O to O₂ at the ion source walls [*von Zahn and Gross*, 1969]. Such behavior of atomic oxygen had not been noted before in rocket-borne mass spectrometers. It was hoped therefore that

combined mass spectrometer and optical measurements of atmospheric O₂ would allow a distinction between ambient O₂ and molecular oxygen produced inside the ion source of the mass spectrometer by recombination of atomic oxygen.

INSTRUMENTS AND PAYLOAD

Both payloads, Esro S84 and S90, carried identical scientific instrumentation. It consisted of one UV monochromator of the Institut d'Aéronomie Spatiale de Belgique, measuring the absolute solar flux values at the wavelengths 1216, 1450, and 1710 Å; one UV monochromator of the Meteorologisches Institut der Universität München, measuring the absolute solar flux values in the wavelength range 1450–2100 Å; and a mass spectrometer of the Physikalisches Institut der Universität Bonn, measuring absolute number densities of O₂, N₂, and Ar. All three instruments were forward looking and were mounted under the ejectable nose cone of a sun-stabilized Skylark payload, as is shown in Figure 1. The coarse and fine sensors for the two-axis sun stabilization were mounted alongside the instruments (Figure 2) and mounted to the same baseplate as the instruments. Care was taken that after jettisoning of the payload split nose cone and the ion source cap, the mass spectrometer source had a free field of view of 2 π about the forward direction.

The Brussels UV monochromator was essentially an Ebert type spectrometer with a fixed position grating. The image of the entrance slit at three wavelengths was selected by three exit slits uncovered in sequence by means of a sliding shutter. The purpose of this device was to reproduce easily at each scanning sequence of 6 s the same wavelength band passes. The details of the instrument have been described by *Ackerman and Simon* [1973]. The three band pass central wavelengths, 1216, 1450, and 1710 Å, were chosen at values of the oxygen absorption cross section such that absorption measurements would, for a significant period of time, overlap at two wavelengths while the increase or decrease of optical thickness was taking place during the flights. These features give their unique character to the measurement: the oxygen column densities deduced at one wavelength are controlled at another, and the choice of three wavelengths leads to oxygen determinations over a wide range of altitudes. In the case of the S84 flight, measurements have been performed from 90 to 190 km in one shot, to our knowledge for the first time.

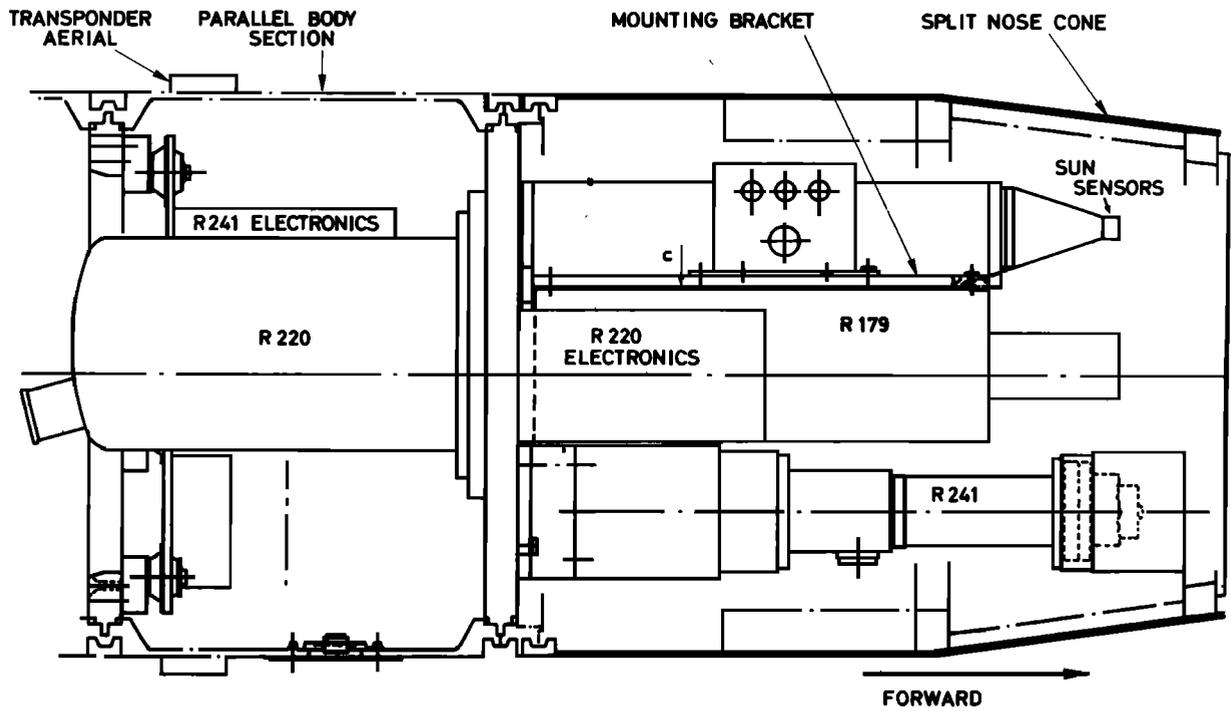


Fig. 1. Cross section of the instrument bay in Esro payloads S84 and S90 showing the Brussels UV monochromator (R220), the Munich UV monochromator (R179), the Bonn mass spectrometer (R241), and the sun sensors all mounted to a common platform under the ejectable nose cone. The mass spectrometer is shown with the ejectable ion source cap still attached to the instrument.

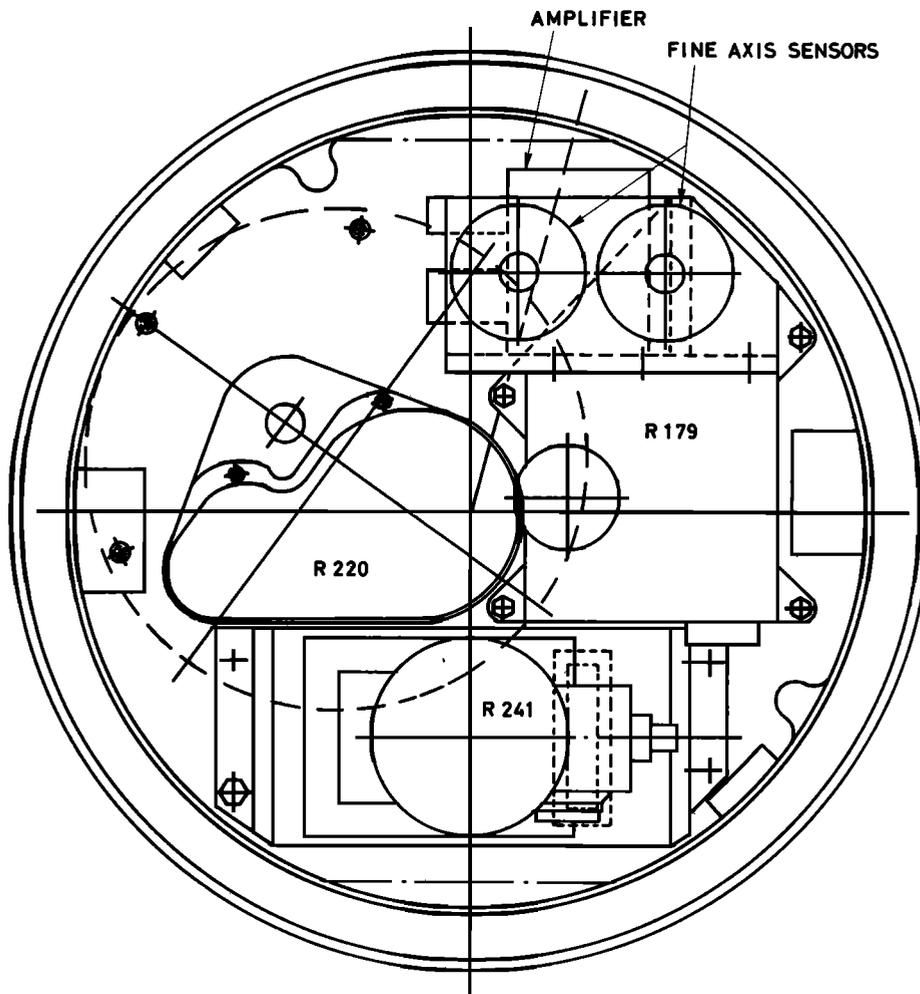


Fig. 2. Front view of the instrument bay. All three instruments were mounted with the center line of their field of view parallel to the axis of the sun sensors.

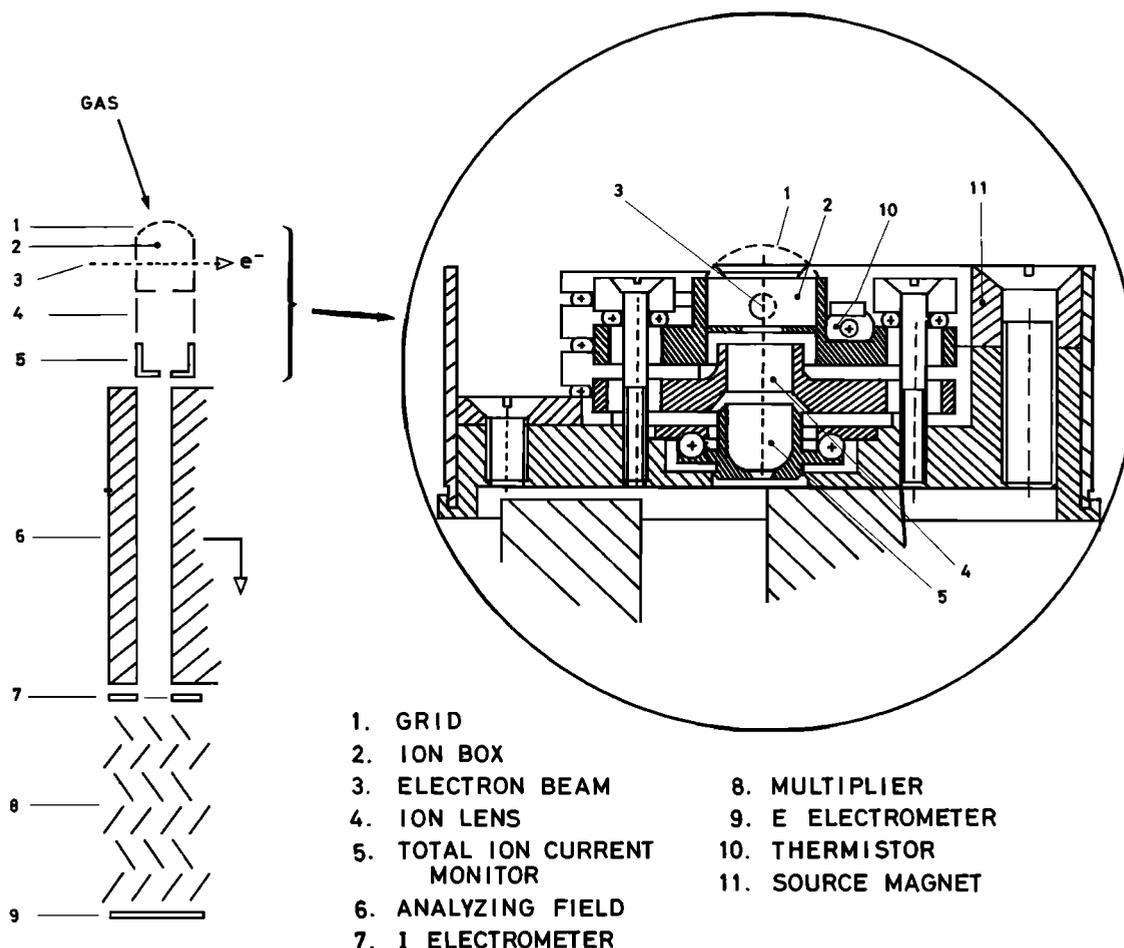


Fig. 3. Schematic of the detector layout and cross section of the mass spectrometer ion source. The electron beam (3) is focused by a small magnet (11). The temperature of the ion box walls (2) is measured by means of a thermistor (10).

The Munich two-channel UV spectrometer was designed to measure directly the difference in intensity of radiation with 2100 and 1550 Å (upleg of flight) and with 2100 and 1450 Å (downleg of flight). Because final results from this instrument are not available yet, additional details of this experiment need not be discussed here.

The Bonn mass spectrometer employs a semiopen electron impact ion source, a monopole spectrometer as an analyzing field, a threefold ion detection system, and a multiplier operated in an analog mode. The instrument was an improved version of the spectrometer described by *Bitterberg et al.* [1970] and included the following new features:

1. The ion box, ion lens, and total ion current monitor (see Figure 3) were made from pure gold in order to evaluate the influence of this material on the general performance of the ion source.
2. For evaluation of the design of a future satellite experiment this ion source carried two redundant filaments.
3. The instrument employed a threefold ion detection system (see Figure 3). The ions generated in the ion source are partly focused to the entrance orifice of the analyzing field and partly collected by the total ion current monitor feeding the input of a linear electrometer (T electrometer). The T electrometer readings are thus related to the total ion flux leaving the ion source and a direct measure of the neutral particle density. Behind the analyzing field the ion current passes through a grid system, which collects about 50% of the ion current and feeds another linear electrometer (I electrometer). The remain-

ing ions enter the multiplier, become converted to electrons, and are amplified. The electron collector feeds a logarithmic electrometer (E electrometer) with a range of 5 decades. The use we made of these three independent collectors will be outlined along with the data reduction procedure.

4. Because the spectrometer axis was parallel to the optical axis of the payload (thus allowing a two-axis stabilization

TABLE 1. Flight Parameters of Esro Payloads S84 and S90 Launched From Salto di Quirra, Sardinia, on February 28, 1972

| Parameter | S84 | S90 |
|--|--------|---------|
| Geographic coordinates | 9°11'E | 39°36'N |
| Local time of launch, CET | 0654 | 1047 |
| Solar zenith angle at apogee, deg | 89.8 | 52.8 |
| Apogee, km | 242 | 251 |
| Azimuth of trajectory, degrees from north | 51 | 130 |
| $F_{10.7}^*$ (1 day before launch) | 143.0 | 143.0 |
| $F_{10.7}^*$ (average for Dec. 1971 to April 1972) | 124.5 | 124.5 |
| Kp (6 hours before launch) | 3- | 3- |
| $T_{\text{exosphere}}$, K (Cira, 1972) | 913 | 1012 |
| Mass spectrometer | | |
| Ejection of ion source cap, km | 108 | 119 |
| Electron energy in ion source, eV | 68 | 80 |

* F values are in $10^{-22} \text{ W m}^{-2} \text{ Hz}^{-1}$ at 10.7-cm wavelength.

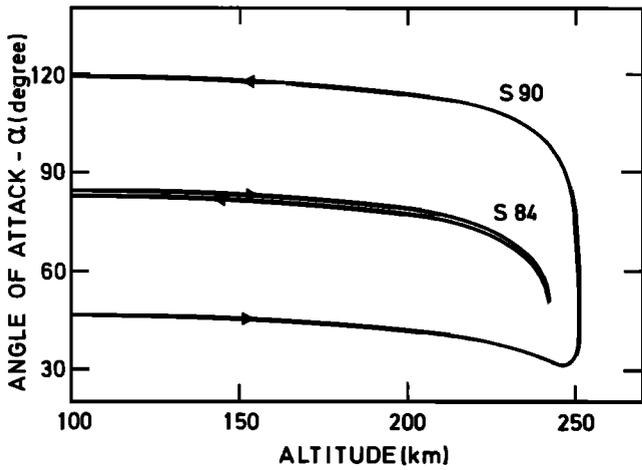
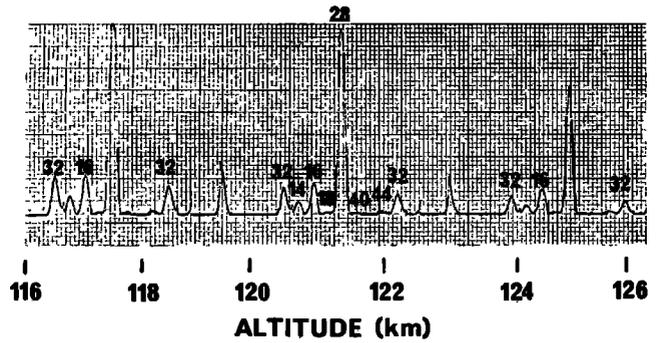


Fig. 4. Angle of attack α (angle between payload axis and velocity vector) versus altitude. Because the sun was close to the local horizon during flight S84, the α upleg and downleg profiles fall almost on top of each other.

system only), the ion source and analyzing field were directly facing into the sun. It was therefore a recognized danger that solar UV could enter the multiplier and cause an increased multiplier background current. Therefore the multiplier was mounted off axis from the analyzing field, and additional baffles and shields were placed inside the spectrometer to block the direct access of UV light to the multiplier.

A mobile pump stand provided us with the capability to per-



During the S84 flight the sun was very close to the local horizon. For the UV monochromators this meant a large optical path length of solar radiation through the atmosphere; thus the ranges of useful absorption measurements at the three preset wavelengths were shifted to comparatively high altitudes. For the mass spectrometer this change provided two advantages. First, after sun acquisition the payload maintained a horizontal attitude; as a result, the mass spectrometer was able to take data on the upleg and downleg of the flight. Second, owing to this near horizontal attitude the angle of attack was almost the same for data points collected at a given altitude on the upleg and downleg. Figure 4 illustrates the history of the angle of attack throughout the flight above 100-km altitude.

Figure 5 indicates the quality of spectra obtained from the I electrometer of the mass spectrometer. The example is taken from the downleg data of S84, showing clearly an ion current ratio $I(16^+)/I(32^+) > 1$ at 116 km. Although this paper does not deal directly with the in situ measurement of atomic oxygen, we wish, however, to point out here that the large angle of attack of S84 at 116 km prevented any ambient oxygen atoms from crossing the electron beam of the ion source without first hitting an ion source surface. Thus the entire 16^+ peak must originate from O atoms that have had at least one wall collision before ionization.

Unfortunately, our attempts to prevent solar UV light from reaching the multiplier of the mass spectrometer proved ineffective. Upon jettisoning of the ion source caps for both payloads, a large but steady background current appeared on the E electrometer channels, which rendered them essentially worthless. Thus all the data presented below are taken from the T and I electrometers. Owing to their lower sensitivity the N_2 data only reach up to 220 km, and the O_2 data, to 165 km.

DATA REDUCTION

The monochromator appeared not to have been fully outgassed during the ascent. The photon flux measurements were only considered after stabilization of the signals observed in the absence of absorption. This occurred at about 230-km altitude while the rockets were still ascending. On the downleg the signals decayed in sequence, first at 1450 Å, then at 1710 Å, and eventually at 1216 Å. Using the intensity I_0 (when there was no atmospheric absorption) and the intensities I (when absorption was taking place), Beer's law $I = I_0 \exp(-\sigma n_t)$ was applied to determine the total number of oxygen molecules n_t along the optical path. At 1450 and 1710 Å the values of absorption cross sections σ were taken from Ackerman [1971]. They were weighted by taking into account the instrumental band passes and the relative variation of solar intensity with wavelength [Detwiler et al., 1961]. At 1216 Å the Lyman α line shape and the variation of O_2 absorption cross section over its width were taken into account following the procedure of Hall [1972].

The total number of molecules were then plotted versus altitude, and the tangents to the curves yielded scale height values. These were combined with the solar zenith angle and with the earth geometrical parameters taken from Swider [1964] to determine number densities versus altitude. A new generation of scale heights was determined from these values and reintroduced in the computation. The iteration was stopped after reaching equilibrium. The number densities so deduced are represented in Figure 6 by smooth curves drawn through the data points for the two flights. The curves are re-

produced in Figure 7 for the sake of comparison with other data obtained by means of optical techniques. (It should be emphasized that the derivation of the O_2 number densities from the UV data does not require any assumption about the vertical distribution of this constituent.)

In the case of the mass spectrometers the data reduction involved the following standard steps. First, measured ion currents were converted into ion source densities through application of laboratory calibration data on the sensitivity (which is equal to the ratio of ion current output over ion source number density) of the spectrometer for N_2 and O_2 . Second, ion source densities were converted to ambient number densities through application of the ram effect correction by assuming negligible adsorption and chemical reactions of the constituents at the ion source walls [Hedin et al., 1964].

The following details within our data reduction procedure appear noteworthy:

1. We had to make a choice between various calibration curves available, in particular, for the N_2 sensitivity of the spectrometer. The T and I electrometers both had independent calibration data obtained at the laboratory and at the launch site. For both spectrometers we decided to keep unaltered the calibration data obtained for the T electrometer at the launch site. The other calibration data were adjusted so as to conform with this primary calibration curve; the ratio of N_2 over O_2 sensitivities at the I electrometer was thus maintained.

2. At altitudes below 130 km the nitrogen number den-

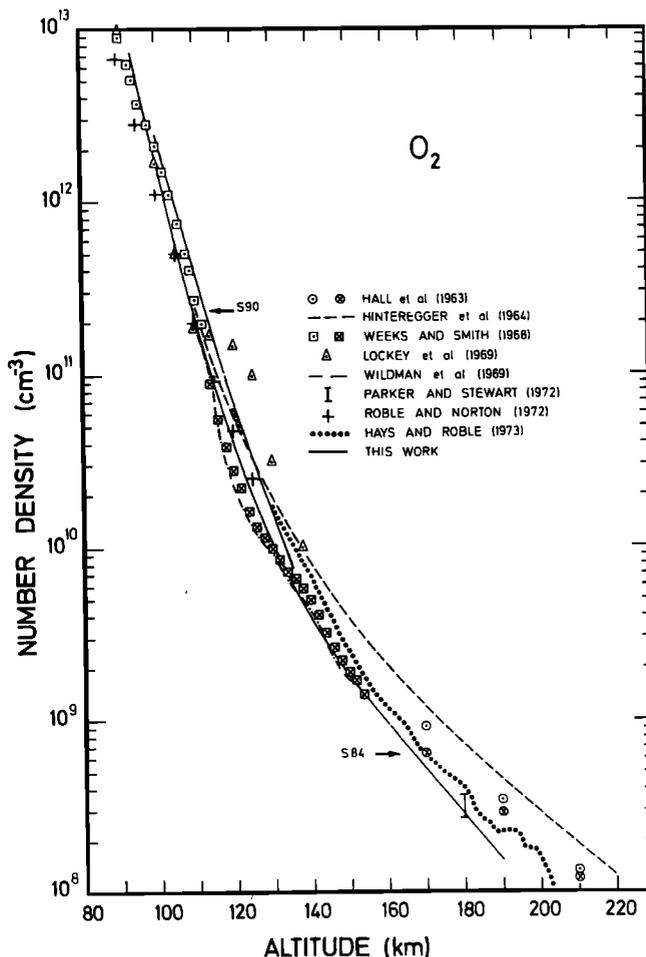


Fig. 7. The O_2 number densities versus altitude from UV absorption data.

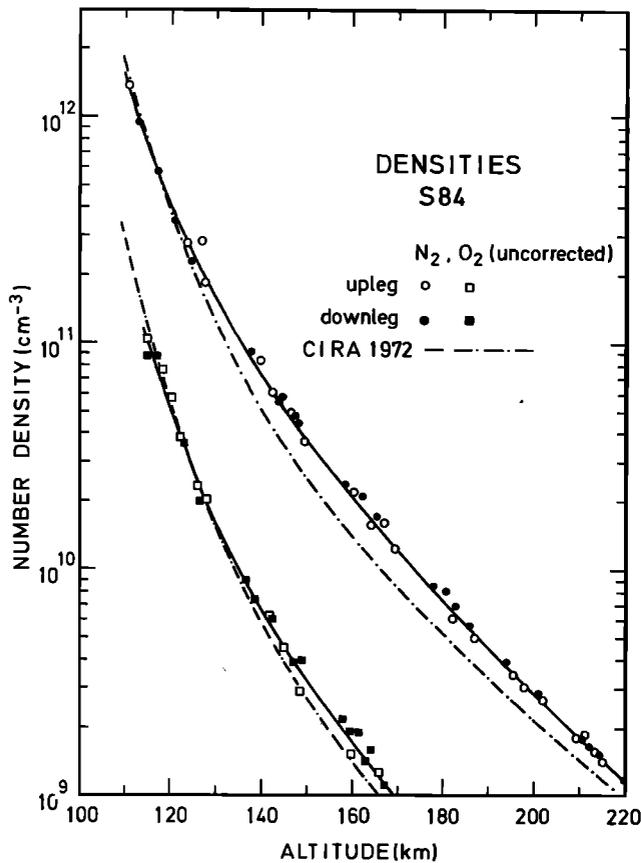


Fig. 8. The O_2 and N_2 number densities measured by the mass spectrometer during flight S84.

sities were calculated from the mass 14 peaks, whose height is more linear with ion source density than the mass 28 peaks.

3. For the S90 data a background correction was applied to the high-altitude N_2 data that brought the number densities down by 10% at 200 km. This correction was suggested by the observation of a noticeable mass 28 background on the downleg of the flight when the spectrometer was actually looking into the wake of the payload.

Further details of the analysis procedure for the mass spectrometer data are given by *Laux and von Zahn* [1974]. The number densities for O_2 and N_2 so deduced from the mass spectrometer are shown in Figure 8 (for S84) and Figure 9 (for S90).

DISCUSSION

We are quite satisfied with the agreement between the independent data obtained from the three wavelengths (Figure 6) in the case of the UV monochromator and the agreement between N_2 and O_2 densities obtained from the S84 upleg and downleg part of the flight (Figure 8) in the case of the mass spectrometer. We further note that at low altitudes (115 km for S84, 130 km for S90) the intercomparison of the absolute O_2 number densities derived from the two different instruments yields quite good results (see Table 2). Last, but not least, a comparison with previous experiments (Figure 7) and a model atmosphere (Figures 8 and 9) indicates a fair degree of conformity with possible geophysical variability in the state of the lower thermosphere, accounting for the observed minor deviations.

A closer look, however, reveals a feature that deserves more consideration. Although the $n(O_2)$ densities derived from the

two different techniques at low altitudes agree, it is evident that the gradients of the altitude profiles are different. This fact is more clearly shown in Figure 10 in which the two data sets are compared directly for the flight that gave the largest altitude coverage. The difference amounts to a factor 1.7 at 160 km, which we consider outside our calibration errors. The question then becomes, Which O_2 profile comes closer to the real atmospheric conditions? For the UV extinction measurement, raising the O_2 values in the 150-km region would require the assumption of lower absorption cross sections at both 1450 and 1710 Å. It appears, however, rather unlikely that the cross sections used so far are so much in error as to account for the whole observed variance. On the other hand, lowering the mass spectrometer O_2 values could be justified by assuming that in fact additional O_2 was produced inside the ion source by recombination of O into O_2 . Using the appropriate Cirra (1972) O densities and taking into account the different ram factors for O and O_2 , one can calculate that about 10% of all incoming O atoms would have to recombine to O_2 at the ion source walls to explain the difference between the mass spectrometer observations and the UV measurements. Although we do not wish to exclude this possibility, we have to note the following. The O_2 profile measured by the mass spectrometer comes closer to being in diffusive equilibrium with the simultaneously measured N_2 profile than the UV absorption data. This comparison is indicated in Figure 10 by the calculated O_2 profile with $n(O_2) = 9.75 \times 10^{10} \text{ cm}^{-3}$ at 115-km altitude, which is in perfect diffusive equilibrium with the measured N_2 distribution. If we correct the measured O_2 profile for possible contributions of

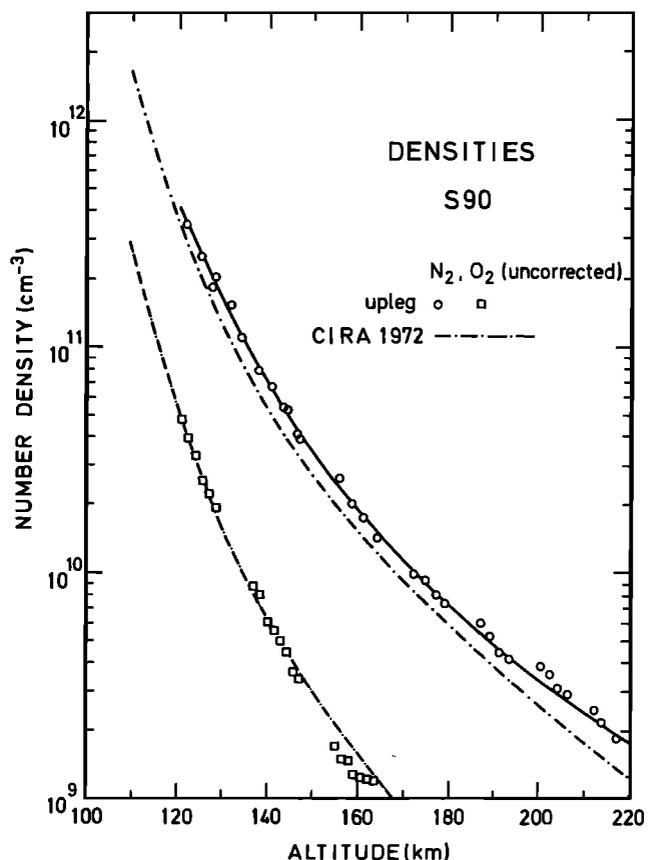


Fig. 9. The O_2 and N_2 number densities measured by the mass spectrometer during flight S90.

TABLE 2. Measured O₂ and N₂ Number Densities

| Altitude, km | S84 | | | S90 | | |
|-----------------|------------------------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|
| | UVM $n(\text{O}_2)$ | MS $n(\text{O}_2)$ | MS $n(\text{N}_2)$ | UVM $n(\text{O}_2)$ | MS $n(\text{O}_2)$ | MS $n(\text{N}_2)$ |
| 115 | 9.50×10^{10} | 9.75×10^{10} | 7.20×10^{11} | | | |
| 120 | 4.30×10^{10} | 4.9×10^{10} | 4.00×10^{11} | 7.30×10^{10} | | |
| 125 | 2.10×10^{10} | 2.74×10^{10} | 2.45×10^{11} | 3.30×10^{10} | 2.8×10^{10} | 2.6×10^{11} |
| 130 | 1.10×10^{10} | 1.65×10^{10} | 1.57×10^{11} | 1.60×10^{10} | 1.6×10^{10} | 1.65×10^{11} |
| 135 | 6.40×10^9 | 1.04×10^{10} | 1.05×10^{11} | 8.10×10^9 | 9.7×10^9 | 1.05×10^{11} |
| 140 | 4.10×10^9 | 6.93×10^9 | 7.2×10^{10} | | 6.2×10^9 | 7.0×10^{10} |
| 145 | 2.70×10^9 | 4.75×10^9 | 5.1×10^{10} | | 4.15×10^9 | 4.85×10^{10} |
| 150 | 1.90×10^9 | 3.33×10^9 | 3.7×10^{10} | | 2.78×10^9 | 3.4×10^{10} |
| 155 | 1.35×10^9 | 2.38×10^9 | 2.76×10^{10} | | 1.9×10^9 | 2.5×10^{10} |
| 160 | 1.00×10^9 | 1.72×10^9 | 2.08×10^{10} | | 1.35×10^9 | 1.9×10^{10} |
| 165 | 7.40×10^8 | 1.26×10^9 | 1.58×10^{10} | | | 1.46×10^{10} |
| 170 | 5.40×10^8 | | 1.22×10^{10} | | | 1.15×10^{10} |
| 180 | 2.80×10^8 | | 7.35×10^9 | | | 7.3×10^9 |
| 190 | 1.4×10^8 | | 4.55×10^9 | | | 4.8×10^9 |
| 200 | | | 2.89×10^9 | | | 3.33×10^9 |
| 210 | | | 1.85×10^9 | | | 2.4×10^9 |
| 220 | | | 1.19×10^9 | | | 1.77×10^9 |

Densities are in per cubic centimeter. UVM stands for ultraviolet monochromator, and MS stands for mass spectrometer.

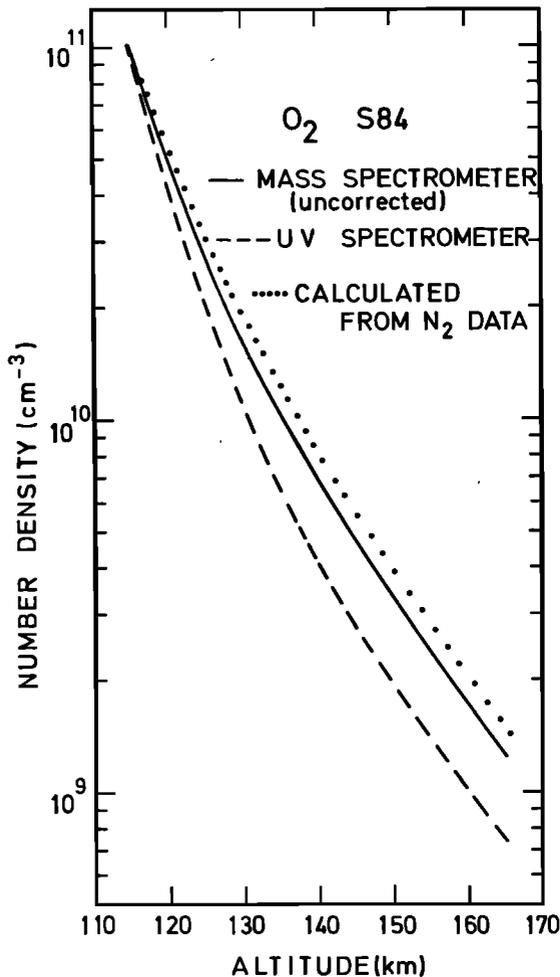


Fig. 10. Comparison of final UV monochromator data and mass spectrometer data (uncorrected for possible recombination of ambient O into O₂) on O₂ number densities obtained from flight S84. The dotted line indicates a theoretical O₂ profile that matches the 115-km altitude data of the mass spectrometer and follows higher up a distribution that is in diffusive equilibrium with the N₂ profile measured simultaneously.

the recombination of O to O₂, it would move to lower values and thus further away from the diffusive equilibrium profile.

In summary, we conclude that owing to the quantitatively unknown recombination effects of O, the mass spectrometrically measured O₂ profile can only be considered as an upper bound to the genuine ambient O₂ distribution. On the other hand, we place considerable faith in the O₂ profiles measured by the UV monochromators and the N₂ profiles of the mass spectrometers. These profiles, however, can not be reconciled with the prevalence of diffusive equilibrium conditions. The deviation from the equilibrium conditions to the O₂ distribution implies upward flow of O₂. This direction is in general accordance with the idea that photodissociation of O₂ and dissociative recombination of O₂⁺ throughout the thermosphere must lead to an upward transport of O₂ and a corresponding downward transport of O.

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REFERENCES

- Ackerman, M., Ultraviolet solar radiation related to mesospheric processes, in *Mesospheric Models and Related Experiments*, edited by G. Fiocco, D. Reidel, Dordrecht, Netherlands, 1971.
- Ackerman, M., and P. Simon, Rocket measurement of solar fluxes at 1216 Å, 1450 Å and 1710 Å, *Solar Phys.*, 30, 345, 1973.
- Bitterberg, W., K. Bruchhausen, D. Offermann, and U. von Zahn, Lower thermosphere composition and density above Sardinia in October 1967, *J. Geophys. Res.*, 75, 5528, 1970.
- Detwiler, C. R., D. L. Garrett, J. D. Purcell, and R. Tousey, The intensity distribution in the ultraviolet solar spectrum, *Ann. Geophys.*, 17, 263, 1961.
- Hall, J. E., Atmospheric pressure, density and scale height calculated from H Lyman- α absorption allowing for the variation in cross-section with wavelength, *J. Atmos. Terr. Phys.*, 34, 1337, 1972.
- Hall, L. A., W. Schweizer, and H. E. Hinteregger, Diurnal variation of the atmosphere around 190 kilometers derived from solar extreme ultraviolet absorption measurements, *J. Geophys. Res.*, 68, 6413, 1963.

- Hall, L. A., W. Schweizer, and H. E. Hinteregger, Improved extreme ultraviolet absorption measurements in the upper atmosphere, *J. Geophys. Res.*, **70**, 105, 1965.
- Hays, P. B., and R. G. Roble, Stellar occultation measurements of molecular oxygen in the lower thermosphere, *Planet. Space Sci.*, **21**, 339, 1973.
- Hedin, A. E., C. P. Avery, and C. D. Tschetter, An analysis of spin modulation effects on data obtained with a rocket-borne mass spectrometer, *J. Geophys. Res.*, **69**, 4637, 1964.
- Hinteregger, H. E., L. A. Hall, and G. Schmidtke, Solar XUV radiation and neutral particle distribution in July 1963 thermosphere, *Space Res.*, **5**, 1175, 1964.
- Laux, U., and U. von Zahn, *Forschungsbericht BMFT WF 74-XX*, Bundesministerium für Forschung und Technol., Bonn, in press, 1974.
- Lockey, G. W. A., B. H. Horton, and B. Rofe, Satellite measurement of upper atmospheric molecular oxygen densities, *Nature*, **223**, 387, 1969.
- Parker, A. E., and K. H. Stewart, Measurements of molecular oxygen in the thermosphere, *J. Atmos. Terr. Phys.*, **34**, 1223, 1972.
- Roble, R. G., and R. B. Norton, Thermospheric molecular oxygen from solar extreme ultraviolet occultation measurements, *J. Geophys. Res.*, **77**, 3524, 1972.
- Swider, W., The determination of the optical depth at large solar zenith distances, *Planet. Space Sci.*, **12**, 761, 1964.
- Weeks, L. H., and L. G. Smith, Molecular oxygen concentrations in the upper atmosphere by absorption spectroscopy, *J. Geophys. Res.*, **73**, 4835, 1968.
- Wildman, P. J. L., M. J. Kerley, and M. S. Shaw, Molecular oxygen measurements from 100 to 150 km at Woomera, Australia, *J. Atmos. Terr. Phys.*, **31**, 981, 1969.
- von Zahn, U., and J. Gross, Mass spectrometric investigation of the thermosphere at high latitudes, *J. Geophys. Res.*, **74**, 4055, 1969.

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