Ion composition measurements in the lower ionosphere during the November 1966 and March 1970 solar eclipses

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Abstract—Positive ion composition measurements in the D- and lower E-regions were performed on three rocket flights during the November 1966 solar eclipse program conducted at Cassino, Brazil. Progressing into totality, the E-region results showed that NO^+ and O_2^+ decreased in concentration while the ratio NO^+/O_2^+ increased. Long-lived meteoric atomic-ions appeared to be unaffected within the short period of the eclipse. A meteoric ion layer that was submerged prior to totality, became prominent as the molecular ions decayed and produced a sporadic E-layer at 105 km near totality. The D-region results provided evidence for the existence of a fast process for the conversion of NO^+ to water cluster ions. The decrease in water cluster ion concentration at totality was probably less than a factor of four in the vicinity of 80 km. Negative ion composition measurements were obtained over Wallops Island, Virginia between 70 and 111 km close to totality of the 7 March 1970 solar eclipse. Heavy negative cluster ions were predominant below 92 km and were restricted to below this altitude. Between 90 and 98 km, and only on rocket descent, there were relatively large concentrations of ions with masses near 16, 32, 46 and 62 amu, probably O^-, O_2^-, NO_2^- and NO_3^-. Such large concentrations were not measured in earlier flights in the undisturbed ionosphere and cannot be explained with presently known processes.

Introduction

A solar eclipse presents a unique opportunity to investigate the many physical and chemical processes which determine the behaviour of the D- and lower E-regions of the ionosphere. Positive and negative ion reactions, electron attachment and detachment processes and ion–ion mutual neutralization reactions, can all be studied by analysis of the response of the lower ionosphere to the rapidly varying solar ionization during a solar eclipse. With this objective, simultaneous measurements of the variations in solar radiation, positive and negative ion species and electron concentration were conducted in coordinated rocket and ground based programs. The ion composition results and the attendant aeronomical implications, especially concerning the ion chemistry, are the subject of this paper.

Positive ion composition measurements in the D- and lower E-regions were performed on three Nike-Hydac rocket flights from Cassino, Brazil during the November 1966 solar eclipse program. Negative ion composition measurements were obtained from a single Nike-Iroquois rocket flight from Wallops Island, Virginia during the 7 March 1970 solar eclipse. Table 1 presents the rocket launch times, apogees and corresponding eclipse conditions. The eclipse data shown are for 90 km on upleg for D-4, and for the entire trajectory above 70 km for D-11 and AO7.902-5.

Experimental Method

The cryopumped positive ion mass spectrometer has been described elsewhere (Narcisi and Bailey, 1965; Bailey and Narcisi, 1966). The three instruments flown from Brazil were programmed to scan the 10–64 amu mass range in 1·85 sec

Table 1

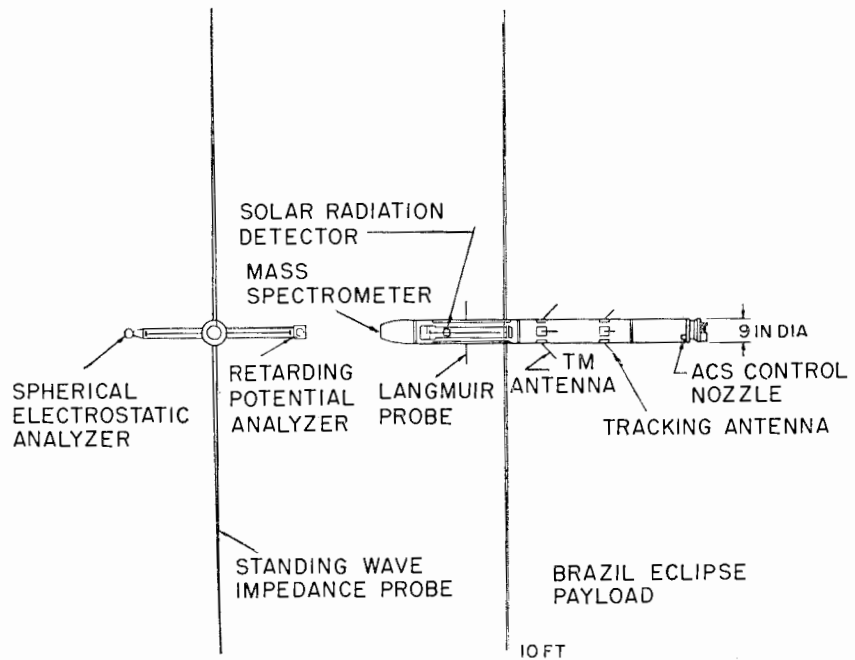| Rocket	Launch time (GMT) Date	Eclipse conditions	Apogee (km)
Positive ion measurements, Cassino, Brazil			
Certification	1355:21 5 November 1966		106·2
D-4	1354 12 November 1966	80% (Obscuration)	107·0
D-11	1408:37 12 November 1966	Totality	95·2
Negative ion measurements, Wallops Island, Virginia			
AO7.902-5	1839:30 7 March 1970	99·2–96·5% (Obscuration after totality)	110·9

Fig. 1. Brazil solar eclipse payload showing the position of the mass spectrometer and the other instrumentation.

and to measure the total ion current for masses larger than 49 amu for the subsequent 0·15 sec. The position of the mass spectrometer in the Nike-Hydac payload is shown in Fig. 1. In addition to the mass spectrometer, the payloads contained a retarding potential analyzer, an impedance probe, a Langmuir probe, a spherical ion trap, a solar X-ray detector and a Lyman-α detector. All of the payloads had an attitude control system (ACS) which utilized jets of high pressure nitrogen gas. The ACS was programmed to maintain the payload near zero angle of attack over its trajectory after separation from the rocket motor at 60 km. A vacuum cap seal was

ejected with the nose cone on vehicle ascent, exposing the 0·030-in. diameter mass spectrometer sampling orifice.

The negative ion mass spectrometer has been described briefly by NARCISI *et al.* (1971). It differs from the positive ion instrument mainly in that it employs a pulse counting ion detection system. This instrument, cylindrical Langmuir probes, a gyro aspect system, radar beacon and FM/FM telemetry comprised the Nike Iroquois payload launched from Wallops Island. The negative ion instrument was programmed to sweep the mass range 14–170 amu in 1·5 sec followed by a measurement of all ions greater than 150 amu in 0·15 sec.

DATA AND ANALYSIS

(a) *Positive ions*

The major positive ion species measured were $19^+(H_3O^+)$, $24^+(Mg^+)$, $30^+(NO^+)$, $32^+(O_2^+)$, $37^+(H_5O_2^+)$, $48^+(NO^+ \cdot H_2O)$, $55^+(H_7O_3^+)$ and $56(Fe^+)$. In addition to the isotopes of $Mg^+(25^+$ and $26^+)$, $Fe^+(54^+)$ and $^{16}O\ ^{18}O^+(34^+)$ several other minor constituents such as sodium, aluminum, nickel, calcium and molecular nitrogen ions were also detected. This paper, however, will only be concerned with the altitude distributions of the major postive ions.

The data were first plotted in terms of the ion current measured at the mass peak height versus altitude. The altitude error is believed to be less than about 1 km. Some of the ion current profiles exhibited severe modulations. Owing to a lack of reliable aspect data, no attempt was made to normalize the measured current profiles for the particular instrument sensitivity, vehicle speed and vehicle aspect by the method outlined by NARCISI (1971). Instead the current variations were smoothed out by eye. The reasons for the current modulation and magnitudes of the uncertainties introduced by smoothing for each flight follow.

The certification round developed severe coning because the payload failed to separate from the Hydac motor, rendering the ACS ineffective. Only the ascent data are considered. The greatest modulations were in the 30 and 32 amu ion currents above 93 km; the smooth curves drawn for these constituents deviate a maximum of approximately a factor of 2 from the measured values. For all other constituents (and below 93 km for 30 and 32) the smoothed current profiles are generally within 30 per cent of the measured values.

The D-4 payload also did not separate from the Hydac motor and the vehicle behaved poorly. The best measurements were obtained near apogee on upleg and throughout descent. The descent measurements are treated here. The current modulations in the 30 and 32 amu ion currents above 90 km were sinusoidal in nature, not in phase nor of the same period, and with maximum amplitude excursions of a factor of three about mean value curves. These mean value curves were used as the 30 and 32 amu ion current profiles. The smoothed curves for the other constituents are generally within 40 per cent of the measurements.

The D-11 payload separated from the rocket motor and was stabilized by the ACS so that the current modulations were not as serious as in the previous two rockets. The current profiles were obtained by smoothing a superposition of the ascent and descent measurements such that the smoothed profiles were within ±50 per cent of the ascent and descent measurements.

These 'smoothed' ion currents were converted to ion concentrations in the following manner. The ion currents for all species at a given altitude were summed, $\sum_i I_i$, and normalized to a total ion concentration, N, at the same altitude. The currents for the various species were then converted to ion concentrations, N_i, by setting $N_i = NI_i/\sum_i I_i$. This procedure weights all ion masses equally and the error introduced by this assumption is generally small compared to the assigned errors here. The ion concentration profiles were determined from the measurements of the standing wave impedance probe (electron concentration), Langmuir probe (electron concentration) and the retarding potential analyzer (positive ion concentration) on the same vehicle. These results were kindly supplied by J. C. Ulwick of AFCRL. The retarding potential analyzer provided positive ion concentrations down to 86 km while the other probes provided electron density measurements as low as 64 km. Accurate positive ion concentrations are difficult to obtain between 70 and 90 km (Sayers, 1970), so these were estimated from the measurements available. For the certification round, the positive ion concentration was measured between 86 and 106 km and below 86 km it was set equal to the electron concentration, except below 76 km where the positive ion concentration was arbitrarily increased to yield about equal concentrations of negative ions and electrons near 72 km. Error limits in the resulting profile are believed to be about 20 per cent above 90 km and about a factor of 2 from 80 to 72 km. Positive ion concentrations were available above 87 km from the D-4 and D-11 measurements. The concentrations below 87 km were estimated using the mass spectrometer ion currents, instrument sensitivities and vehicle speeds. The low altitude portions of these profiles are probably correct to within a factor of 3 while above 90 km they are correct to about 20 per cent. The certification and D-11 profiles are generally in excellent agreement with the measurements of Mechtly et al. (1969), performed from the same location, and those of Kane (1970) for the 20 May 1966 annular eclipse over Greece.

The results of this analysis for the three Brazil flights are shown in Figs. 2–4. Further notes of caution are required in regard to these profiles. The ion currents measured below about 80 km were attenuated, more so with decreasing altitude, by collisional loss within the instruments. This resulted from the slow pump recovery following the high pressure burst when the nose cone was ejected at a lower than planned altitude (all of the rockets failed to achieve the predicted apogee). The measured relative composition is thus affected by the ion collisional cross-sections. Additional complications are incurred by mechanisms which act to break up the water cluster ions such as shock layer thermodynamic decomposition and/or electric-field-induced collisional fragmentation (see Narcisi and Roth, 1970). Because the larger water cluster ions are more weakly bound, it is possible to detach water molecules from them by gas collisions either in the shock-heated gas or after the ion gains the detachment energy in the sampling electric field. These ions are not lost but are measured as lower hydrate ions. For these reasons the results below about 86–82 km shown in Figs. 2–4 are subject to considerable uncertainties.

Above 90 km, although the total ion concentrations are believed to be quite accurate, an error of ± 50 per cent is assigned to the concentrations of the individual constituents for the above reasons.
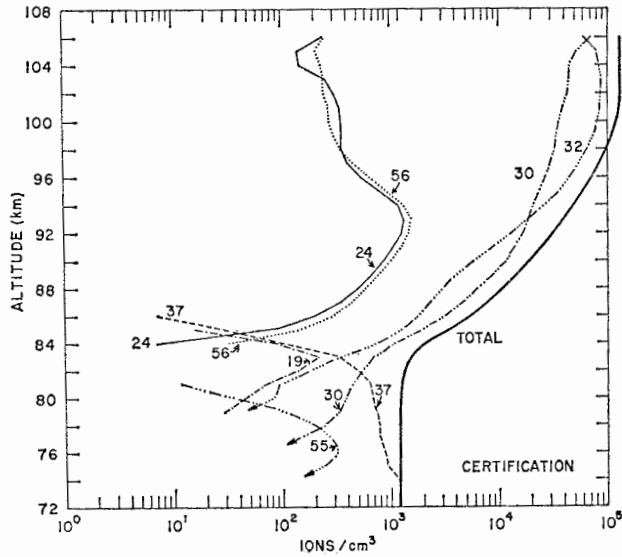
Fig. 2. Major positive ions in the *D*- and *E*-regions for a full sun at about 20°
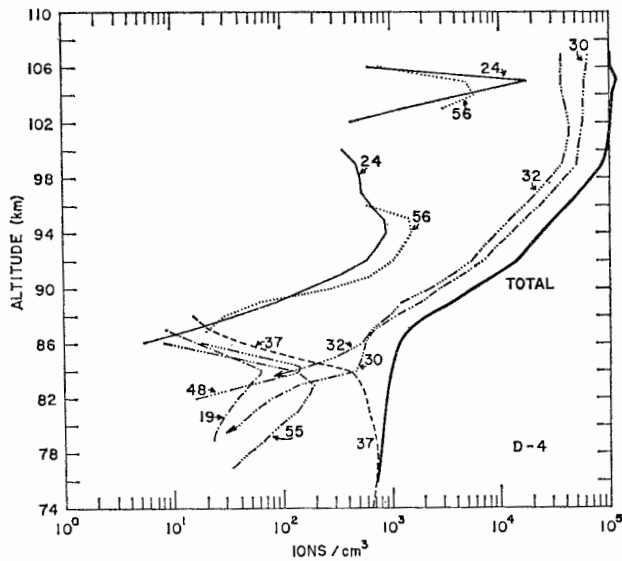solar zenith angle.

Fig. 3. Major positive ions in the *D*- and *E*-regions. The rocket was rising at 90 km
when the Sun was 80 per cent obscured.

(b) *Negative ion measurements*

The negative ion measurements are plotted directly as measured in Fig. 5 in terms
of the mass peak heights in ion counts per second versus altitude for ascent and de-
scent. Straight-line segments are used to connect adjacent data points for each
species. Because of several difficulties, discussed by NARCISI *et al.* (1971), no attempt
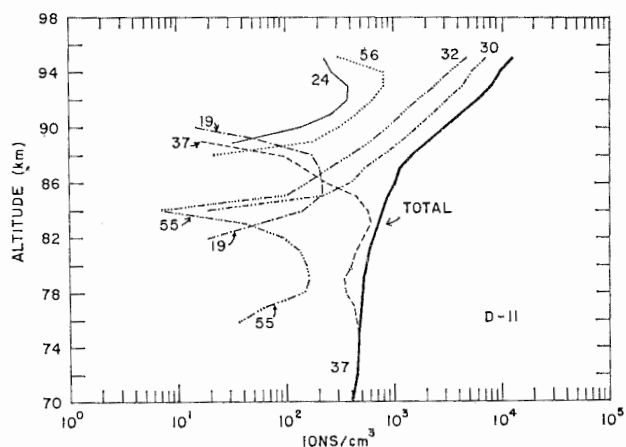was made to determine accurate negative ion concentrations.

Fig. 4. Major positive ions in the D- and E-regions at totality. At the trajectory altitudes of 70 km (ascent), 95 km (apogee) and 70 km (descent), the elapsed times after second contact were about 40 sec, 80 sec and 115 sec, respectively.

The various ion species have been tentatively identified as $16^-(O^-)$, $32^-(O_2^-)$, $35^-(Cl^-)$, $46^-(NO_2^-)$ and 62^- through 152^- as $NO_3^- (H_2O)_n$, $n = 0–5$, with some possible admixture of $CO_3^-(H_2O)_n$, $n = 0–5$. The same problems exist in the measurement of the large negative water cluster ions as in the measurement of large positive ion clusters. A 40-V ion draw-in potential was utilized on this flight. When a 20-V draw-in potential is applied, the mass 152 concentration becomes greater than that of mass 134, instead of the opposite which is seen in Fig. 5. Presumably the larger cluster loses a water molecule upon collision more easily in the stronger electric field (see NARCISI *et al.*, 1971). The downleg decrease in the layer of negative ions centered about 87·5 km is probably due to increasing pressure in the quadrupole on descent. Figure 5 indicates that the heavy ions (>150 amu) are much more abundant than the lighter mass ions. However, because of difficulties experienced in the laboratory in calibrating the total ion mode for the measurement of ions heavier than 150 amu, the actual relative abundance is not certain.

DISCUSSION

(a) *E-region*

The major ions in the E-region are generally NO^+ and O_2^+, as shown in Figs. 2–4. Some N_2^+ was measured near apogee of the certification and D-4 payloads but the N_2^+ concentrations were quite small in comparison to those of NO^+ and O_2^+. A diurnal model of the E-region has been developed for these species that incorporates both ion-chemical and ion-transport processes and which agrees quite well with the ionospheric measurements, considering the accuracies of these measurements and the laboratory measured rate constants (KENESHEA *et al.*, 1970; KENESHEA and MACLEOD, 1970; NARCISI, 1971). Thus, it is believed that if the proper ionization source function can be obtained as a function of the eclipse status, then the E-region response can be derived with good accuracy. This computation will be performed by others in the future. Some cursory observations are made here.
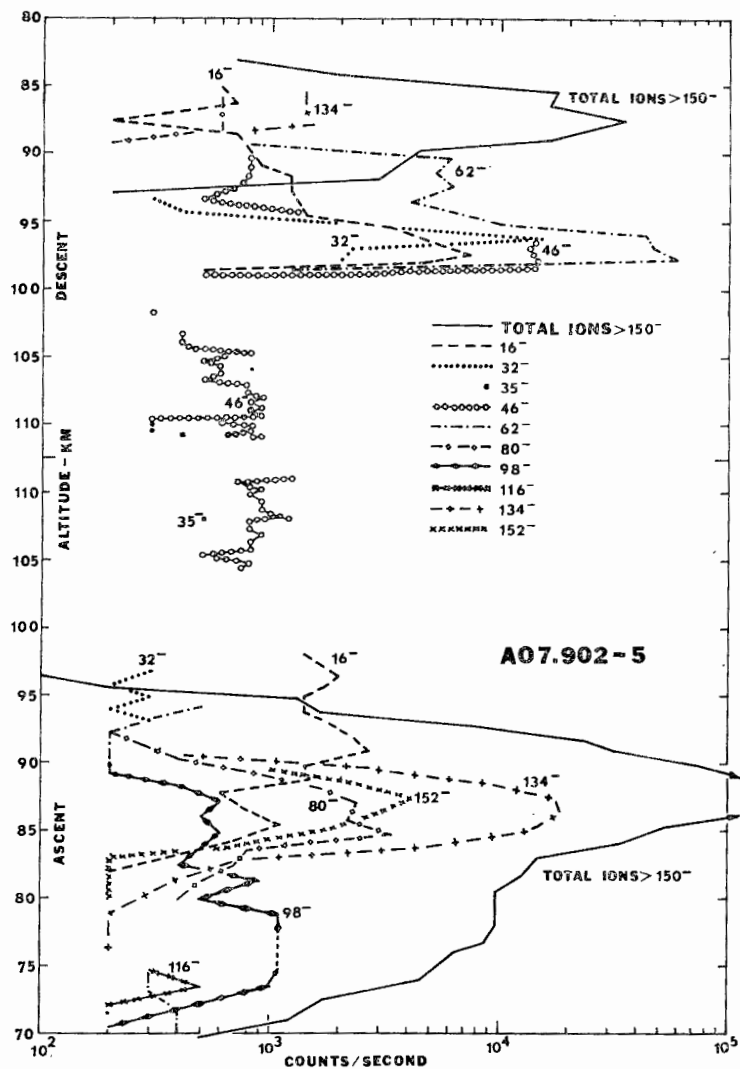
Fig. 5. Negative ion composition measurements shortly following totality. The solar obscuration was 99·1–99·2 per cent in the 70–111 km upleg region and 97·8–96·6 per cent in the 111–82 km downleg region. The vehicle angle of attack was between 0 and 12° from 70–90 km on upleg and decreased uniformly from 32 to 6° on descent from 100–82 km.
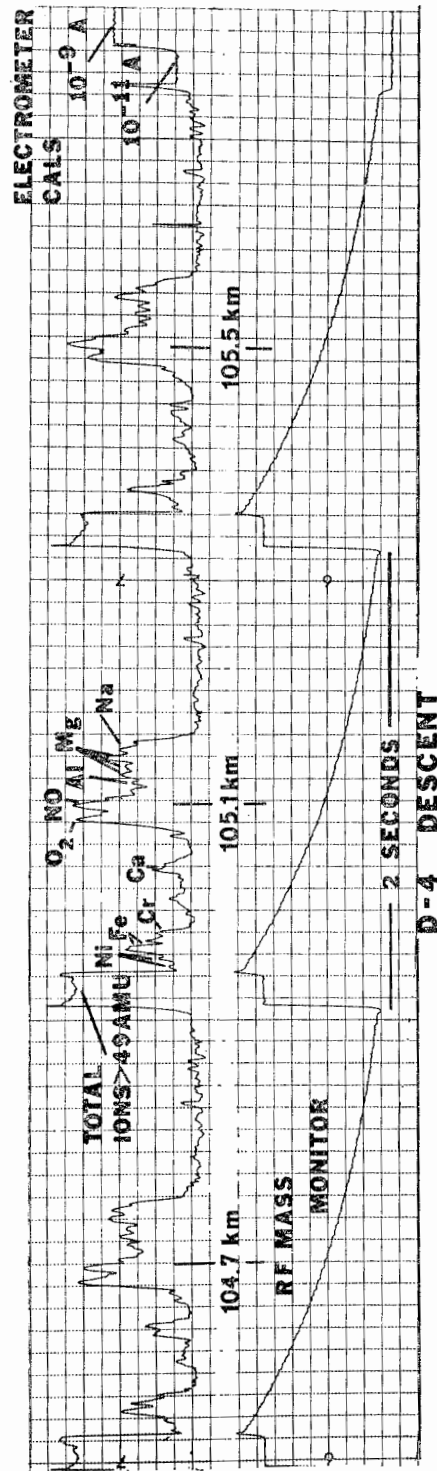
The results in Figs. 2–4 show that the NO^+/O_2^+ ratio increases with progression into totality. Although this can be questioned, considering the extreme errors placed on the results, it is nevertheless entirely expected. Using MEIRA's (1971) neutral nitric oxide values (3–10×10^7 cm^{-3} at 90–110 km), it can easily be shown that the charge transfer reaction $O_2^+ + NO \rightarrow NO^+ + O_2$ at 6×10^{-10} cm^3 sec^{-1} (FEHSEN-FELD et al., 1970) proceeds at a faster rate than electron recombination, $O_2^+ + e \rightarrow O + O$ at 2×10^{-7} $(300/T)$ cm^3 sec^{-1} (BIONDI, 1968). Even though NO^+ recombines

with electrons at about twice the $O_2{}^+$ electron recombination rate, the charge transfer compensates for this and thus effectively increases the $NO^+/O_2{}^+$ ratio.

Meteoric atomic-ions are always found in the E-region as shown in Figs. 2–4. The omnipresent main meteoric layer centered near 93 km contains, in addition to iron and magnesium, smaller quantities of sodium, aluminum, calcium, nickel and other metal ions. In Figs. 2–4, it is seen that while the meteoric layer near 93 km hardly changes in the certification and D-4 measurements, it shows about a factor of 2 decrease at totality on D-11, although this change may not be significant within the quoted errors. Because of the long-lived nature of these atomic ions above 90 km, little change is expected during the short period of the eclipse except possibly some small transport variations. The stability of the meteoric ions during the eclipse is exemplified by the submerged meteoric ion layer measured on D-4 near 105 km. This layer, measured on both ascent and descent, also contained sodium, aluminum, calcium, chromium and nickel ions (Fig. 6) and barely produced a noticeable protrusion on the total ion profile at the time of the D-4 flight. However, although at totality the D-11 apogee was below the altitude of this layer, MECHTLY *et al.* (1969) found a sporadic E-layer, essentially at the same altitude, on a rocket launched during totality about 16 min after D-4. The sporadic E-layer consisted of a spike extending 50 per cent above the background electron concentration profile. Note that the magnitude of the D-4 layer of about 2×10^4 ions cm^{-3} is enough to produce the 50 per cent spike above the background concentration of 4×10^4 ions cm^{-3} measured by Mechtly *et al.* On a rocket launched after totality (80 per cent solar obscuration), ULWICK (AFCRL, private communication) found about a 20 per cent protrusion above background on the total ion profile at this altitude. Thus the sporadic E-layer was probably formed when the NO^+ and $O_2{}^+$ concentrations decayed to values comparable to the meteoric ion concentrations.

(b) *D-region*

The present difficulty in the chemistry of the quiescent D-region is the requirement for a fast process which can convert NO^+ to water cluster ions in the 70–86 km region. NO^+ is by far the major ion produced during quiet periods in this altitude range but it is not observed as the major ion in the mass spectrometer measurements (NARCISI and ROTH, 1970). Although there are many uncertainties associated with the D-region measurements, it seems clear that water cluster ions dominate. Evidence for such a fast conversion process is indicated in the eclipse measurements by the rapid disappearance and decay of NO^+ in the 78–86 km region while the water cluster ions actually increased between 83 and 90 km at totality (Figs. 2–4). The rapidity of this unknown process may be appreciated by comparing the D-4 measurements, during which this process already appears to be proceeding, to the D-11 measurements. The time difference between D-4 descent and D-11 ascent is about 12·5 min in which time NO^+ at 84 km, for example, decays from about 500 cm^{-3} to about 20 cm^{-3}. Because atomic oxygen short-circuits the $O_2{}^+$ water cluster production mechanism determined by FEHSENFELD and FERGUSON (1969) and GOOD *et al.* (1970) between 80 and 86 km, $O_2{}^+$ is lost mainly by charge transfer with NO, forming NO^+, and by electron recombination. Based on only a few existing measurements at the time, NARCISI (1967) pointed out that the $H_5O_2{}^+$ concentration decreases

Fig. 6. D-4 flight mass spectra showing the meteoric species contained in the submerged ion layer near 105 km.

abruptly near 82 km in the daytime near local noon but at night this cut-off occurs at about 86 km. Since then additional measurements confirmed these earlier observations and showed that during twilight conditions (88–99° solar zenith angles) the conditions are similar to the nighttime case (Narcisi, 1971). In the eclipse the daytime to twilight/nighttime transition occurs in a very short time. The implication seems to be that since this NO^+ conversion reaction is so fast it may involve a constituent that is not present in sunlight but which increases rapidly in darkness in the 82–86 km region. Since fast vapor phase reactions have been extensively sought, and none found to date (Narcisi and Roth, 1970), the possibility exists that conglomerates in the cold mesopause region are responsible. Hunt (1969) suggested the presence of invisible water conglomerates $(H_2O)_n$, with sizes up to 10^{-5} cm in diameter along with various possible methods of ionization to form water cluster ions. A fast reaction of NO^+ with these conglomerates may be the possible conversion process. In sunlight the conglomerates may be diminished by photodissociation but these may reform rapidly in darkness.

(c) Negative ions

Additional evidence in support of the presence of conglomerates are the negative ion measurements in the D-region. These reveal very large negative ion clusters up to 90–92 km. The total ions greater than 150 amu profile may indicate still larger ion masses (recall earlier limitations discussed concerning the relative abundance of these heavy ions). Such large clusters are unexplainable by presently known vapor phase reactions and again it appears likely that conglomerates may be playing an important role in the negative ion chemistry. Ulwick (AFCRL, private communication) found that both during the eclipse at totality and at night, the electron density shows a very large decrease near 87 km which does not appear in the positive ion profiles. This indicates an increasing negative ion concentration which occurs near the maximum of the large negative ion cluster layer.

Mechtly et al. (1969) show a decrease of 300 to 100 electrons cm^{-3} at 82 km after 2 min in totality. If these and Ulwick's measurements are correct, a fast electron attachment process is required other than the classical three-body electron attachment to O_2 which does not appear to provide a fast enough electron removal rate. O_2^- shows no particular enhancement below 90 km in either the ascent or descent data (Fig. 5).

As shown in Fig. 5 the large count rates for 16^-, 32^-, 46^-, and 62^- between 99 and 90 km were measured on downleg but not on upleg. Such large abundances of ions have not been measured in this altitude range in seven other negative ion flights. The downleg region was in darkness (97–97·5 per cent solar obscuration) about 3·5 min longer than the upleg region (99·2 per cent solar obscuration). However, there are no known processes by which large amounts of such ions could be produced at the fast rate required to balance the known large loss rates due to ion–ion mutual neutralization reactions and associative detachment reactions with atomic oxygen (Peterson et al., 1971; Fehsenfeld et al., 1967).

The ions $35^-(Cl^-)$ and $46^-(NO_2^-)$ above 100 km are probably contaminants.

Rocket measurements of negative ion composition have just begun in earnest over the last 2 yr and a number of experimental difficulties exist (Narcisi et al.,

1971). In addition there is a considerable lack of knowledge concerning the negative ion chemistry. Therefore, a great amount of rocket experimentation and laboratory work is required before definitive conclusions can be made regarding the negative ion processes occurring in the D-region.

CONCLUSIONS

Although the ion composition measurements were insufficiently accurate for rigorous quantitative evaluations of ionospheric processes, the following qualitative observations were evident.

Taking into account the accuracy of the results, the upper limit of the decrease in positive ion concentrations about 80 km from full sun to totality was less than a factor of 4. The decay in the positive ion concentrations below 88 km was much less than the accompanying decrease in electron concentrations, implying the formation of negative ions by electron attachment. If these measurements are correct, three body attachment to O_2 alone cannot satisfactorily explain the observed electron loss. The unexplainable layer of large negative cluster ions observed near 88 km suggests the possibility of other attachment processes. The D-region results provide strong evidence for the existence of a fast ionospheric reaction which converts NO^+ to water cluster ions, but the actual reaction cannot be determined from the measurements. Since known gas phase reactions cannot resolve either the electron or the ion processes, fast reactions with hypothesized mesospheric conglomerates were suggested as an alternative, but this requires future confirmation.

In spite of inaccuracies, the E-region results exhibited the expected behavior of the molecular ions during the eclipse. Generally, both NO^+ and O_2^+ concentrations decayed while the NO^+/O_2^+ ratio increased with solar obscuration. In contrast to the rapidly decaying molecular ions, the long lifetimes of the meteoric ions were apparent by the constancy of the submerged meteoric ion layer during the short period of the eclipse, which protruded to form a sporadic E-layer at totality.

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