

## Recent developments and outstanding problems in the theory of the *D* region

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(Received September 18, 1973.)

The present understanding of the ionization processes, and of the positive and negative ion chemistry of the *D* region is reviewed with particular attention being given to outstanding problems.

Rocket-borne mass spectrometer observations carried out in the past decade have shown that the change in positive ion composition with height (from  $\text{NO}^+$ ,  $\text{O}_2^+$  and metallic ions above to water cluster ions  $\text{H}^+(\text{H}_2\text{O})_n$  below) is a general feature of the *D* region at all latitudes and under all geophysical conditions. Furthermore, these observations indicate that this change occurs over a very small range of heights, between 82 and 86 km under normal conditions and at lower heights during auroral or Polar Cap Absorption conditions. These results are discussed in terms of current ideas concerning the formation of water cluster ions from  $\text{O}_2^+$  and  $\text{NO}^+$  ions.

Mass spectrometer observations by two experimental groups have provided conflicting results concerning the negative ion composition in the *D* region and cannot be used to test theoretical models. Such models have been derived from laboratory measurements, and involve reaction schemes leading from  $\text{O}_2^-$  ions, formed by electron attachment, to ions  $\text{O}_3^-$ ,  $\text{O}_4^-$ ,  $\text{CO}_3^-$ ,  $\text{CO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{NO}_4^-$ . The effect on these models of including recent laboratory measurements of negative ion hydration is considered, and the importance of photodetachment is also mentioned.

### 1. INTRODUCTION

Rocket-borne mass spectrometer observations carried out since 1963, together with improved measurements of electron concentrations, have led to our present knowledge of the ionized components of the *D* region, that part of the ionosphere below about 95 km. At the same time, laboratory investigations of the relevant reactions and numerical studies of ionospheric models have helped to develop an understanding of the ion chemistry involved. Consequently it has been realized that the unique character of the *D* region arises from the presence of chemically active minor neutral constituents and relatively high ambient pressures which permit three-body reactions to occur.

Progress in our understanding of *D*-region processes can be traced in the successive reviews given by Mitra [1968], Thomas [1971] and Sechrist [1972]. The purpose of the present paper is to describe the developments during the last 3 years and to underline

outstanding problems. Emphasis will be given to the production of ionization and to the formation of positive and negative ions. In view of the involvement of certain minor neutral constituents in these processes, our present information on the height distributions of these constituents is first reviewed in section 2. This information has been largely derived from numerical model studies but some experimental data are also available, chiefly from airglow observations. Ideas concerning the production of ionization, described in section 3, have remained unchanged in recent years, the photoionization of nitric oxide by Lyman- $\alpha$  radiation being still considered as the principal source in the middle *D* region. However, recent suggestions of the possible need to reexamine the efficiency of this photoionization process and to consider the photoionization of metastable states of molecular oxygen other than  $\text{O}_2(^1\Delta_g)$  will also be mentioned. Section 4.1 deals with recent mass spectrometer observations of positive ion composition which provide increasing evidence of the disintegration of high-order cluster ions during sampling. The formations of water cluster ions from  $\text{O}_2^+$  and  $\text{NO}^+$  are consid-

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ered separately in sections 4.2 and 4.3. Section 5 describes current theoretical ideas concerning the negative ion chemistry, the implications of recent laboratory measurements relating to negative ion hydration being particularly emphasized. Attention is also drawn to the conflicting results of rocket-borne measurements of negative ion composition by two groups. Finally, in section 6 an attempt is made to summarize the recent developments and to highlight the outstanding problems.

## 2. HEIGHT DISTRIBUTIONS OF RELEVANT MINOR NEUTRAL CONSTITUENTS

**2.1. Nitric oxide.** Measurements of the nitric oxide concentrations in the *D* and *E* regions have been obtained from rocket observations of fluorescence of the NO  $\gamma$ -bands in the dayglow. The observations, after allowing for Rayleigh scattering of sunlight by air molecules and absorption by ozone, yield the column density of NO. Differentiation of the height variation of the column density then provides the height distribution of NO concentration. The results of recent measurements by *Meira* [1971] at Wallops Island, USA, *Tisone* [1973] at Kauai, Hawaii, and *Witt et al.* [1973] at Kiruna, Sweden, are compared with the original measurements of *Barth* [1966] at Wallops Island in Figure 1. All these measurements were derived from observations of the (1-0) band near 2150 Å except those of *Witt et al.* which made use of the (1-4) band near 2550 Å. Although these results refer to various years, seasons, and locations, the concentrations in the middle *D* region agree

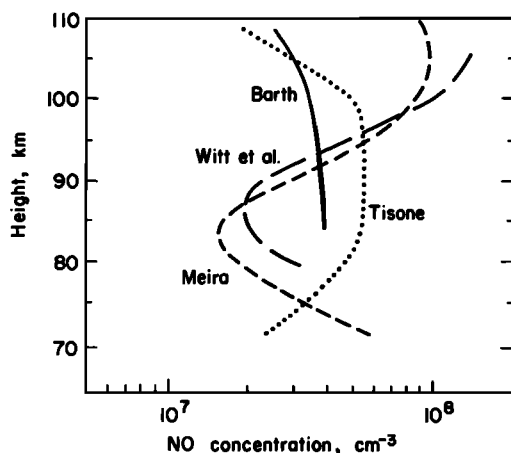


Fig. 1. Height distributions of nitric oxide deduced from rocket observations of the  $\gamma$ -bands of NO in the dayglow by *Barth* [1966], *Meira* [1971], *Tisone* [1973], and *Witt et al.* [1973].

within a factor of 4, all values exceeding  $10^7 \text{ cm}^{-3}$ . It should be emphasized that the greater contribution to the fluorescent emission arises from *E*-region heights and the approach is not ideally suited to *D*-region measurements. However, estimates of NO concentrations in the *D* region deduced from positive ion composition measurements during a Polar Cap Absorption (PCA) event [*Narcisi et al.*, 1972c] have yielded values intermediate between those of *Barth* and *Meira* in Figure 1.

Theoretical models of the NO distribution have been improved by the incorporation of vertical eddy diffusion and by the realization that the most likely process for the production of the molecule is the reaction of  $\text{N}(^2D)$  atoms with  $\text{O}_2$  molecules [*Norton*, 1967; *Norton and Barth*, 1970; *Strobel et al.* 1970; *Strobel*, 1971]. *Brasseur and Nicolet* [1973] have demonstrated that the inclusion of photodissociation leads to a very marked decrease of NO concentrations in the mesosphere. These workers have also shown that the calculated height distributions of NO show pronounced minima at heights between 70 and 80 km; the actual locations and magnitudes of the minima, and concentrations of NO are dependent on the values of eddy diffusion coefficient. For the conditions considered in this study the NO concentrations ranged from about  $5 \times 10^6 \text{ cm}^{-3}$  to  $2 \times 10^7 \text{ cm}^{-3}$  at 80 km.

**2.2. Metastable molecular oxygen and ozone.** Experimental information concerning the height distributions of  $\text{O}_2(^1\Delta_g)$  has been derived from rocket-borne observations of the dayglow emission of the (0-0) band of the infrared atmospheric system  $\text{O}_2(^1\Delta_g - X^3\Sigma_g^-)$  at  $1.27 \mu\text{m}$  [*Evans et al.*, 1968]. From the interpretation of these observations, *Evans et al.* [1968] and *Evans and Llewellyn* [1970] have inferred the existence of a layer of ozone in the height range of 85 to 90 km with maximum concentration of  $1$  to  $3 \times 10^8 \text{ cm}^{-3}$ . Observations of the attenuation of ultraviolet radiations from a rocket with the sun as source near sunset [*Miller and Ryder*, 1973] and from a satellite with stars as sources during nighttime [*Hays et al.*, 1972] have also indicated such a structure in the height distribution of ozone. Previous measurements had been limited to lower heights and showed a gradual decrease in concentration in the lower mesosphere, from about  $10^{10} \text{ cm}^{-3}$  near 60 km to approximately  $10^8 \text{ cm}^{-3}$  near 75 km.

**2.3. Atomic oxygen, water vapor, hydroxyl, hydroperoxyl, and atomic hydrogen.** For these constituents ( $\text{O}(^3P)$ ,  $\text{H}_2\text{O}$ ,  $\text{OH}$ ,  $\text{HO}_2$ , and  $\text{H}$ ) the ex-

perimental information is either very limited or non-existent. However, they have attracted considerable attention in photochemical models of a hydrogen-oxygen atmosphere in which account has been taken of vertical transport by eddy diffusion. In recent developments of these theoretical models attention has been drawn to a possible reduction in solar flux intensities in the wavelength range 1300 to 1800 Å from the values of *Detwiler et al.* [1961] adopted previously [*Hinteregger*, 1970], and the need to include predissociation of  $O_2$  by the Schumann-Runge bands [*Hudson et al.*, 1969; *Hudson and Mahle*, 1972].

Recent results for  $O(^3P)$  and  $H_2O$  as derived for middle latitudes by *Shimazaki and Laird* [1972] for summer conditions and *Thomas and Bowman* [1972] for equinox periods, are shown in Figures 2 and 3. Both studies took account of predissociation by the Schumann-Runge bands but that of *Shimazaki and Laird* made use of the solar flux intensities for 1400 to 1800 Å measured by *Detwiler et al.* [1961] while *Thomas and Bowman* [1972] used fluxes reduced by factors of 1.5 to 3 depending on wavelength. The greater photodissociation rates for  $O_2$  resulting in the study of *Shimazaki and Laird* contribute to the greater  $O(^3P)$  concentrations in Figure 2. However, the difference in  $H_2O$  concentrations adopted at low heights and in eddy diffusion

coefficients complicates a comparison between the two theoretical height distributions. The experimental results also included in Figure 2 were derived from rocket-borne measurements of the oxidation of silver-strip sensors by *Henderson* [1971] and of 5577 Å ( $O^1D - O^1S$ ) emission in the dayglow by *Dandekar and Turtle* [1971].

Estimates of  $H_2O$  concentrations deduced from measurements are included in Figure 3 with the theoretical height distributions. These estimates have been derived by *Narcisi and Swider* [1973; also, personal communication, 1973] from an interpretation of positive ion composition measurements during a PCA event at Churchill, Canada. Although no direct comparison of these deduced concentrations with the computed results for middle latitudes is justified, the more rapid decrease in concentration at heights above 82 km, implying small values of eddy diffusion coefficient, might also be relevant to middle latitude conditions.

No direct measurements of OH,  $HO_2$ , or H concentrations are available for middle *D*-region heights. Rocket-borne observations of fluorescence in the  $OH(A^2\Sigma - X^2\Pi)$  band at 3064 Å in the dayglow by *Anderson* [1971a, b] have indicated OH concentrations of  $5.5 \times 10^6 \text{ cm}^{-3}$  and  $3.5 \times 10^6 \text{ cm}^{-3}$  at heights of 60 and 70 km, respectively, in agreement with the calculated results of *Thomas and Bowman*

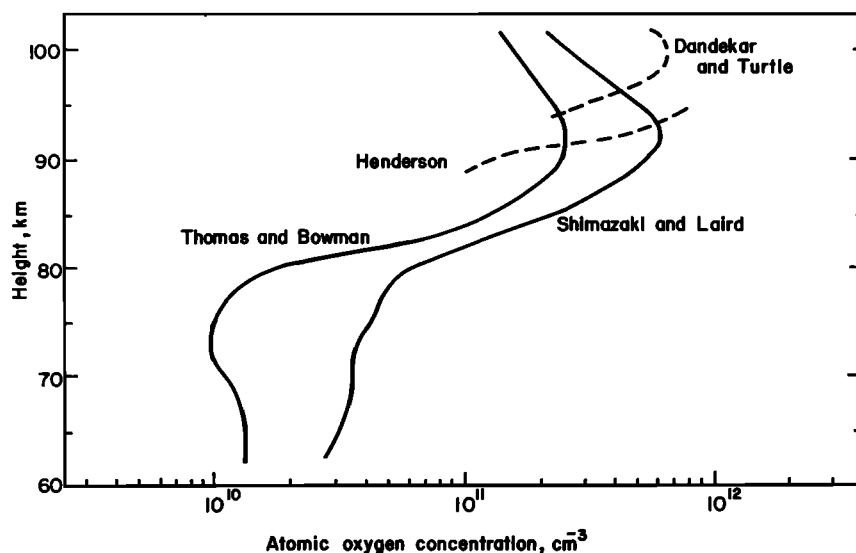


Fig. 2. Height distributions of  $O(^3P)$  concentrations in daytime. The full curves represent the theoretical results of *Shimazaki and Laird* [1972] and *Thomas and Bowman* [1972]; the broken curves have been deduced from rocket-borne observations of the oxidation of silver-strip sensors by *Henderson* [1971] and of 5577 Å emission in the dayglow by *Dandekar and Turtle* [1971].

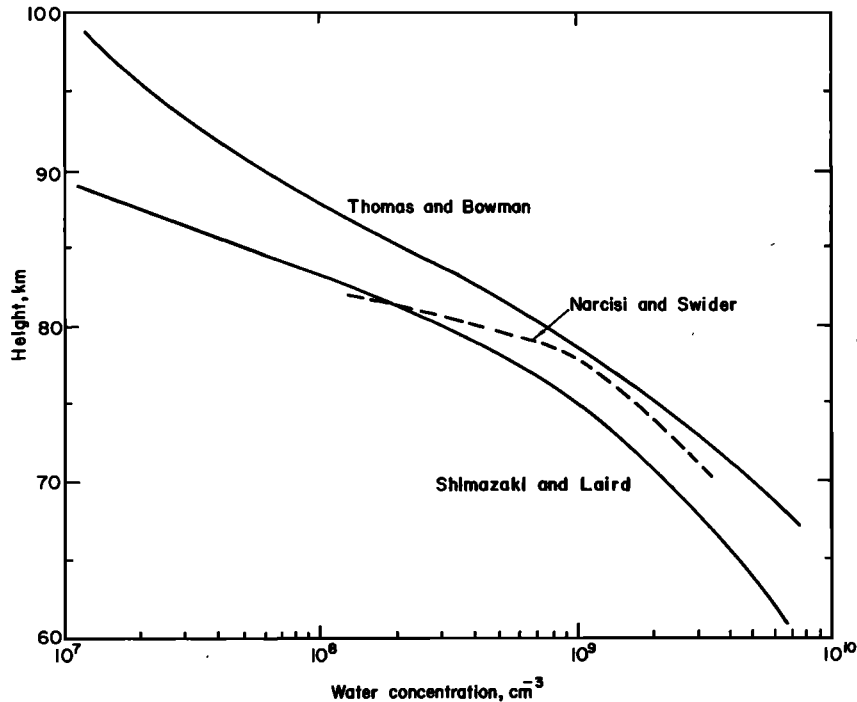


Fig. 3. Height distributions of water vapor concentration. The full curves represent the theoretical results of *Shimazaki and Laird* [1972] and *Thomas and Bowman* [1972]; the broken curves have been deduced by *Narcisi and Swider* [1973, also personal communication, 1973] from positive ion composition measurements during a PCA event.

[1972]. The only estimate of H concentrations in the *D* region has been by *Evans and Llewellyn* [1973] from an analysis of rocket observations of hydroxyl and infrared atmospheric bands in the airglow at Churchill, Canada. However, their proposed concentrations of  $3 \times 10^7 \text{ cm}^{-3}$  at heights between 80 and 90 km are substantially smaller than are indicated by theoretical treatments.

### 3. SOURCES OF IONIZATION

**3.1. Daytime rates.** Figure 4 represents the ion pair production rates for solar zenith angles near  $60^\circ$  during solar minimum conditions. The results for 2 to 8 Å, soft X ray, EUV, and Lyman- $\beta$  radiations have been calculated by *Bourdeau et al.* [1966]; those for the photoionization of  $\text{O}_2(^1\Delta_g)$  by radiations of wavelength 1027 to 1118 Å have been provided by *Huffman et al.* [1971], the values being reduced from those suggested originally by *Hunten and McElroy* [1968] when allowance was made for absorption by atmospheric  $\text{CO}_2$ ; those for the photoionization of NO by Lyman- $\alpha$  radiation have been deduced from the NO distribution of *Meira* [1971]

and a radiation flux of  $4.3 \text{ erg cm}^{-2} \text{ sec}^{-1}$ ; and those for galactic cosmic rays relate to  $50^\circ$  geomagnetic latitude and have been taken from *Webber* [1962]. It is evident that with concentrations as large as those shown in Figure 1, the photoionization of NO by Lyman- $\alpha$  radiation represents the main source of ionization in the middle *D* region under solar minimum conditions; the contribution of 2 to 8 Å is expected to increase substantially, perhaps by three orders of magnitude, at solar maximum.

It will be seen in section 4.2.2 that the relatively large rates of production of  $\text{NO}^+$  in the middle *D* region represent a major problem. *Donahue* [1972] has speculated that perhaps the laboratory measurements of the cross section for photoionization of NO by Lyman- $\alpha$  radiation are not directly applicable to *D*-region conditions, or alternatively that the detailed variation of cross section with wavelength might show low values over the 1-Å width of the Lyman- $\alpha$  line.

**3.2. Nighttime rates.** The photoionization of NO by Lyman- $\alpha$  radiation in the nightglow has been shown to be a likely source of ionization in the

nighttime *D* region [Ogawa and Tohmatsu, 1966], and the ionizing effects of precipitating high energy particles have also been considered to be important [Tulinov et al., 1969; Potemra and Zmuda, 1970]. Possible contributions of galactic X-ray sources to the nighttime *D* region have also been examined following reports of changes in propagation characteristics associated with the transit of sources such as Scorpius XR-1. The ion pair production rates corresponding to each of these ionization mechanisms are represented in Figure 5. The results for the ionization of NO by scattered Lyman- $\alpha$  radiation is based on the NO distribution of Meira [1971] and a radiation flux of  $2.0 \times 10^{-3}$  erg cm $^{-2}$  sec $^{-1}$  ster $^{-1}$  [Donahue, 1964; Tinsley, 1969]. The curve for high energy particles has been taken from Gough and Collin [1973] and has been derived from rocket-borne measurements of fluxes of electrons of energy greater than 40 keV at S. Uist, Scotland, during a magnetically quiet night. The rates for 0.2 to 40 Å X rays from Scorpius XR-1 represent the results of calculations by Poppoff and Whitten [1969], and those for cosmic rays again refer to solar minimum condi-

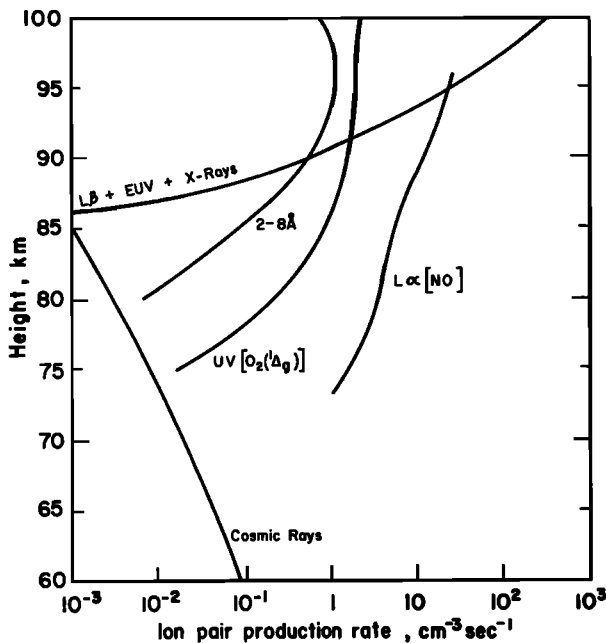


Fig. 4. Ionization rates in the quiet daytime *D* region for solar minimum conditions and solar zenith angles near 60°. The results for 2 to 8 Å, soft X rays, Lyman- $\beta$ , and EUV are from Bourdeau et al. [1966]; the rates for the ionization of O $_2$ ( $^1\Delta_g$ ) are from Huffman et al. [1971]; the rates for galactic cosmic rays are from Webber [1962]; the rates for nitric oxide are based on the height distribution of Meira [1971] and a Lyman- $\alpha$  flux of 4.3 erg cm $^{-2}$  sec $^{-1}$ .

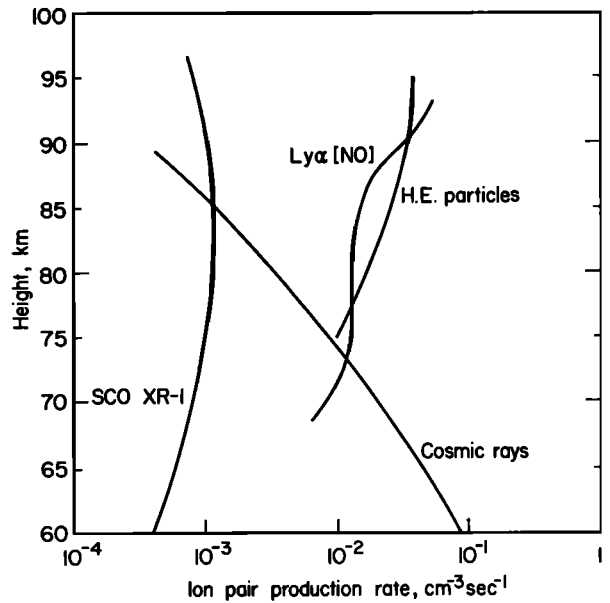


Fig. 5. Ionization rates in the quiet nighttime *D* region. The rates for 0.2 to 40 Å X rays from Scorpius XR-1 have been calculated by Poppoff and Whitten [1969]; the rates for high energy particles are from Gough and Collin [1973]; the rates for galactic cosmic rays are from Webber [1962]; the rates for nitric oxide are based on the height distribution of Meira [1971] and a Lyman- $\alpha$  flux of  $2.0 \times 10^{-3}$  erg cm $^{-2}$  sec $^{-1}$  ster $^{-1}$ .

tions at 50° geomagnetic latitude and are from Webber [1962].

It is to be noted that the Lyman- $\alpha$  and particle fluxes used in the derivation of the appropriate curves in Figure 5 represents relatively low values. Nevertheless, these two sources clearly provide the greatest contribution to the nighttime *D* region. Previous estimates, for example by Potemra and Zmuda [1970], have made use of substantially larger Lyman- $\alpha$  and particle fluxes. It is expected that the latter will be dependent on the level of magnetic activity. In view of the uncertainty in NO concentrations and the variability in both scattered Lyman- $\alpha$  and precipitating particle fluxes, it is not possible to estimate the relative importance of these two sources of ionization at nighttime.

#### 4. POSITIVE ION COMPOSITION

4.1. *Mass spectrometer observations.* Positive ion composition measurements in the *D* region have been made over a range of latitudes and a variety of geophysical conditions [Narcisi and Bailey, 1965; Narcisi, 1967; Narcisi et al., 1972a, b; Goldberg and Blumle, 1970; Goldberg and Aikin, 1971, 1973;

*Krankowsky et al.*, 1972; *Zbinden et al.*, 1973]. In all cases rocket-borne mass spectrometers have been employed with either cryogenically cooled pumps or titanium getter pumps.

The ion composition revealed by such measurements is illustrated in Figure 6 which shows the results obtained at a solar zenith angle of  $20^\circ$  during November 1966 at Cassino, Brazil [*Narcisi et al.*, 1972a]. It is seen that  $O_2^+$  and  $NO^+$  represent the major ions above about 82 km, a broad layer of  $Mg^+$  and  $Fe^+$  ions occurs with a peak near 93 km, and at heights below 82 km the water cluster ion  $H^+(H_2O)_2$  dominates the composition, with  $H_3O^+$  and  $H^+(H_2O)_3$  also being observed.

The broad layer of metal ions near 93 km seems to be a permanent feature of the lower ionosphere. In addition to  $Fe^+$  and  $Mg^+$  ions,  $Na^+$ ,  $Al^+$ ,  $K^+$ ,  $Ca^+$ ,  $Cr^+$ ,  $Co^+$ ,  $Ni^+$ , and  $FeO^+$  have been reported, the relative concentrations of these ions being reasonably consistent with the relative abundance of the elements in chondrite meteorites which strike the Earth.

The rapid decrease with height of the water cluster ion concentrations near 82 km in Figure 6 is characteristic of normal daytime conditions. However, this transition height between water cluster ions and  $O_2^+$  and  $NO^+$  ions is raised to about 86 km during twilight or nighttime, and occurs at heights below 80 km dur-

ing conditions of auroral activity [*Krankowsky et al.*, 1972] and during a PCA event [*Narcisi et al.*, 1972b]. It has been suggested by *Reid* [1970], *Sechrist* [1970], and others that the change of electron loss rate associated with the change in ion species gives rise to the steep gradient of ionization which is commonly observed between 80 and 90 km under normal conditions.

The majority of mass spectrometer observations have shown  $H^+(H_2O)_2$  to be the predominant ion below the transition height, with significant concentrations of  $H_3O^+$ ,  $H^+(H_2O)_3$ , and  $NO^+ \cdot H_2O$  also being present. There is, however, some doubt whether the lower order cluster ions  $H_3O^+$  and  $H^+(H_2O)_2$  are representative of ambient conditions. Fragmentation of weakly bound ions can occur through thermodynamic break-up at the shock layer because of increased temperatures, or through collisions resulting from the draw-in electric fields [*Narcisi and Roth*, 1970]. Evidence has been provided by *Goldberg and Aikin* [1971] and *Krankowsky et al.* [1972] that large cluster ions tend to be observed with lower velocity rockets and also during the reduced shock conditions on the downleg of the trajectory than during the upleg ram conditions. In addition, *Johannessen and Krankowsky* [1972] found that the concentrations of higher-order cluster ions  $H^+$

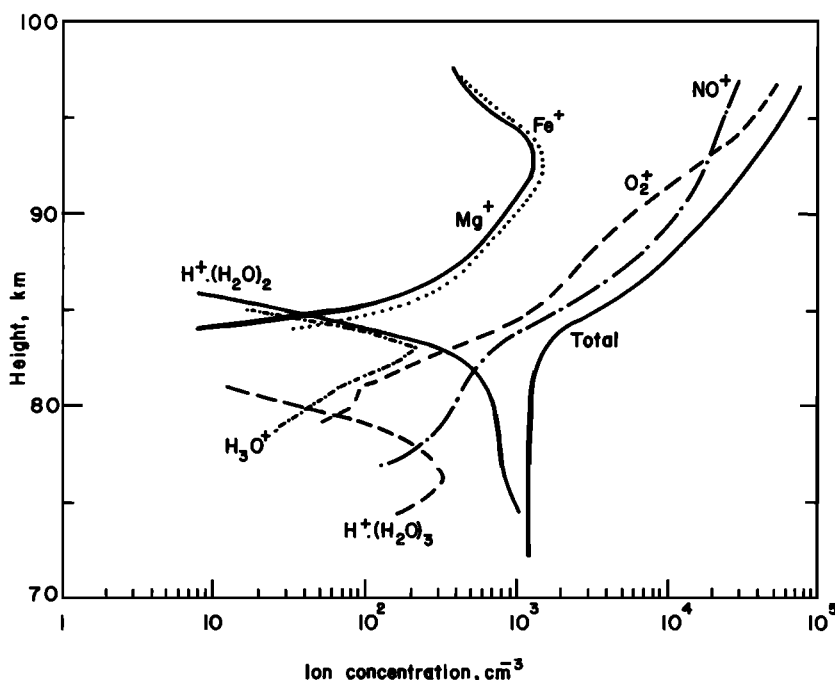
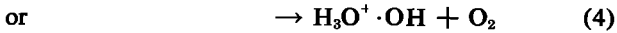
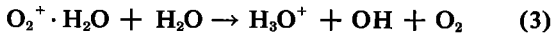
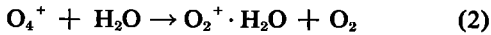
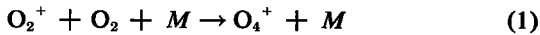


Fig. 6. Rocket-borne mass spectrometer observations of the positive ion composition for a solar zenith angle of  $20^\circ$  at Cassino, Brazil [*Narcisi et al.*, 1972a].

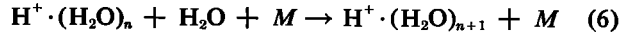
$(\text{H}_2\text{O})_4$ ,  $\text{H}^+(\text{H}_2\text{O})_5$ ,  $\text{H}^+(\text{H}_2\text{O})_6$  were enhanced in the cold high latitude summer mesosphere. More recently, *Arnold et al.* [1973] have examined the effects of using a reduced but changeable draw-in electric field. With reduced field and improvements in mass spectrometer design these workers found that the major ion below 85 km had a mass of  $73^+$  corresponding to  $\text{H}^+(\text{H}_2\text{O})_4$ , and ions of mass  $55^+$  ( $\text{H}^+(\text{H}_2\text{O})_3$  and  $37^+$  ( $\text{H}^+(\text{H}_2\text{O})_2$ ) were next in importance. The ion of mass  $48^+$ , corresponding to  $\text{NO}^+\cdot\text{H}_2\text{O}$  and recorded in previous measurements, was also observed and new ions of masses corresponding to  $\text{NO}^+\cdot\text{CO}_2$ ,  $\text{NO}^+\cdot\text{N}_2$  and  $\text{O}_2^+\cdot\text{CO}_2$  were found above 85 km. These latter ions and also  $\text{NO}^+(\text{H}_2\text{O})_2$  observed by *Johannessen and Krankowsky* [1972] are of particular interest in connection with current ideas concerning the formation of water cluster ions (see section 4.2.2).

#### 4.2. Formation of water cluster ions, $\text{H}^+(\text{H}_2\text{O})_n$ .

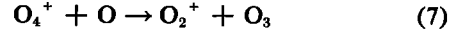
4.2.1. *With  $\text{O}_2^+$  as precursor ion.* A reaction scheme for the formation of water cluster ions originating with  $\text{O}_2^+$  was proposed by *Fehsenfeld and Ferguson* [1969], *Ferguson and Fehsenfeld* [1969], and *Good et al.* [1970b]. It involved the three-body formation of  $\text{O}_4^+$  and subsequent two-body reactions to form  $\text{H}_3\text{O}^+$  and  $\text{H}^+(\text{H}_2\text{O})_2$  ions:



Successive three-body reactions were considered to lead to the higher-order ions:



*Ferguson* [1971] later drew attention to the importance of the reaction



He pointed out that the rapid increase in the rate of this reaction associated with the growth of atomic oxygen concentration above 80 km, Figure 2, could account for the sudden decrease of water cluster ions with increase of height near 82 to 86 km.

The overall scheme based on  $\text{O}_2^+$  as precursor is illustrated in Figure 7. This refers to a height of 80 km, a distinction being drawn between very fast reactions, corresponding to ion lifetimes less than 2 sec and represented by heavy lines; reasonably fast reactions, corresponding to lifetimes of 2 to 100 sec and represented by thin lines; and slow reactions, corresponding to longer lifetimes and represented by broken lines. The ion lifetimes were derived using rate coefficient data of *Ferguson et al.* [1965], *Good et al.* [1970a, b], *Fehsenfeld et al.* [1971a] and *Fehsenfeld and Ferguson* [1972], and the neutral concentrations shown in Table 1 with  $\text{O}_2$  and  $\text{N}_2$  as the third body,  $M$ .

*Ferguson and Fehsenfeld* [1969] made use of the  $\text{O}_2(^1\Delta_g)$  photoionization rates proposed by *Hunten and McElroy* [1968] in applying this reaction scheme to reproduce the water cluster ion measurements of *Narcisi and Bailey* [1965]. However, when account is taken of the reduced production rates of *Huffman et al.* [1971] the supply of  $\text{O}_2^+$  ions is too small to produce significant water cluster ion concentrations,

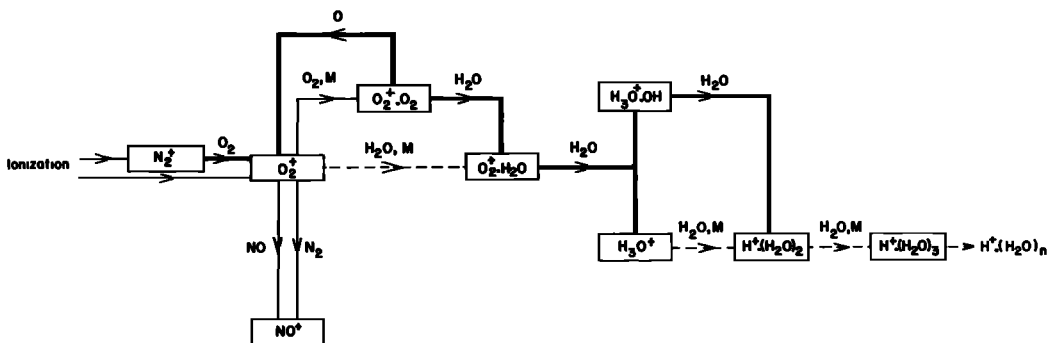


Fig. 7. Schematic representation of positive ion reactions leading to the formation of water cluster ions from  $\text{O}_2^+$  ions, according to the model of *Ferguson and Fehsenfeld* [1969], *Good et al.* [1970b], and *Ferguson* [1971]. Changes corresponding to ion lifetimes of less than 2 sec, 2 to 100 sec, and greater than 100 sec are represented by heavy lines, thin lines, and broken lines, respectively.

Height (km)	O (cm <sup>-3</sup> )	O <sub>2</sub> (cm <sup>-3</sup> )	O <sub>3</sub> (cm <sup>-3</sup> )	CO <sub>2</sub> (cm <sup>-3</sup> )	N <sub>2</sub> (cm <sup>-3</sup> )	H <sub>2</sub> O (cm <sup>-3</sup> )
80	$5.0 \times 10^{10}$	$8.7 \times 10^{13}$		$1.3 \times 10^{11}$	$3.3 \times 10^{14}$	$6.0 \times 10^8$
65	$2.0 \times 10^{10}$ Day $1.0 \times 10^4$ Night	$7.3 \times 10^{14}$	$5.0 \times 10^9$ Day $2.0 \times 10^{10}$ Night	$1.0 \times 10^{12}$	$2.7 \times 10^{15}$	$6.0 \times 10^9$

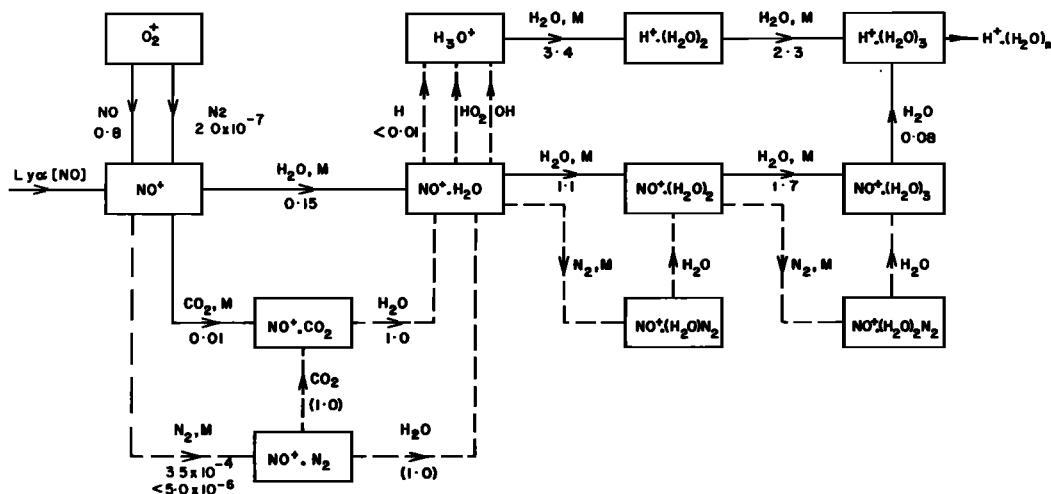


Fig. 8. Schematic representation of positive ion reactions leading to the formation of water cluster ions from  $\text{NO}^+$  ions, according to the model of *Fehsenfeld and Ferguson* [1969] extended by *Dunkin et al.* [1971], *Heimerl and Vanderhoff* [1971], *Niles et al.* [1972], and J. M. Heimerl (personal communication, 1972). The full lines represent reactions for which rate coefficients are established and broken lines are used for those reactions for which rate coefficients are not established or are unavailable.



switching reaction with  $\text{H}_2\text{O}$ :



No measurements of the rate coefficient of reaction (9) are available but the measurements of Dunkin *et al.* have indicated that it is very fast, Ferguson [1971] suggesting that it is about  $10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ . Based on the molecular concentrations given in Table 1 with  $\text{O}_2$  and  $\text{N}_2$  as the third body,  $M$ , the lifetime of  $\text{NO}^+$  ions at 80 km is estimated to be  $2 \times 10^3 \text{ sec}$  for reaction (8) compared with  $3 \times 10^4 \text{ sec}$  for the direct three-body hydration. In view of the relatively large dissociative recombination coefficient of water cluster ions [Leu *et al.*, 1973], a still more rapid hydration of  $\text{NO}^+$  is required than that represented by reactions (8) and (9), in order to reproduce the relative concentrations of  $\text{NO}^+$  and water cluster ions observed [Donahue, 1972]. Such a process, in which  $\text{N}_2$  replaces  $\text{CO}_2$  in reactions (8) and (9), has been proposed by Heimerl and Vanderhoff [1971], and Niles *et al.* [1972]:



The rate coefficient for reaction (10) found by Heimerl *et al.* [1972],  $3.5 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1}$ , is substantially larger than the upper limit of  $5.0 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$  reported by Dunkin *et al.* [1971]. The higher value corresponds to a lifetime of  $\text{NO}^+$  at 80 km of 20 sec whereas the lower value yields a lifetime comparable with or longer than that found for reaction (8). No measurement of the rate coefficient of reaction (11) is available but the similar reaction involving  $\text{NO}^+ \cdot \text{NO}$  and  $\text{H}_2\text{O}$  has a coefficient of  $1.4 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$  [Puckett and Teague, 1971].

Ferguson [1971] has suggested that the ion  $\text{NO}^+ \cdot \text{N}_2$  is too weakly bound to be significant for  $\text{NO}^+$  loss but Niles *et al.* [1972] have proposed that a switching reaction with  $\text{CO}_2$  can yield the more stable ion  $\text{NO}^+ \cdot \text{CO}_2$ :

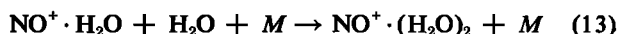


Again no value of the rate coefficient of this reaction is available but Niles *et al.* have stated that it is expected to be rapid.

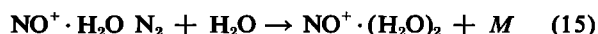
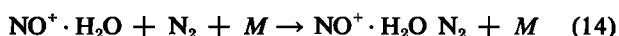
As mentioned in section 4.1, the observation of ions of mass consistent with  $\text{NO}^+ \cdot \text{N}_2$  and  $\text{NO}^+ \cdot \text{CO}_2$  provides some support for these ideas.

According to the model proposed by Fehsenfeld

and Ferguson [1969], further hydration of  $\text{NO}^+ \cdot \text{H}_2\text{O}$  occurs by the direct three-body process:

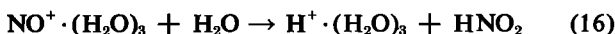


J. M. Heimerl (personal communication, 1972) has suggested, however, that the intermediate formation of a cluster ion with  $\text{N}_2$  and subsequent switching with water occurs more rapidly:



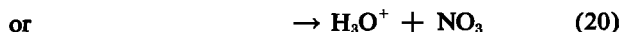
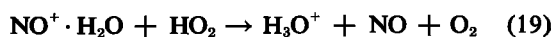
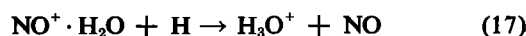
The rate coefficient for reaction (14) is not known but it is found that for the molecular concentrations shown in Table 1, loss of  $\text{NO}^+ \cdot \text{H}_2\text{O}$  by reaction (14) is more rapid than the direct three-body hydration provided the rate coefficient is greater than  $2.1 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$ . Obviously a similar result would apply to the conversion of  $\text{NO}^+ \cdot (\text{H}_2\text{O})_2$  to  $\text{NO}^+ \cdot (\text{H}_2\text{O})_3$ .

According to the model outlined by Fehsenfeld and Ferguson [1969], the production of water cluster ions begins with the reaction:



It can be seen that with the inclusion of the reactions involving clustering to  $\text{N}_2$  and subsequent switching with  $\text{H}_2\text{O}$  the scheme is capable of a fairly rapid production of  $\text{H}^+ \cdot (\text{H}_2\text{O})_3$ .

Reference has already been made to the possibility that ions  $\text{H}_3\text{O}^+$  and  $\text{H}^+ \cdot (\text{H}_2\text{O})_2$  observed during rocket measurements might represent the products of fragmentation of  $\text{H}^+ \cdot (\text{H}_2\text{O})_3$  and larger cluster ions. However, Burke [1970] has suggested that  $\text{H}_3\text{O}^+$  could be formed from  $\text{NO}^+ \cdot \text{H}_2\text{O}$  by a reaction with H atoms, and Niles *et al.* [1972] and J. M. Heimerl (personal communication, 1972) have drawn attention to the possible importance of corresponding reactions involving OH and  $\text{HO}_2$  radicals:



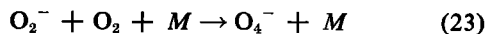
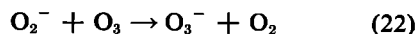
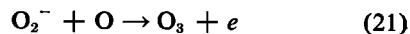
Ferguson [1971] has reported an upper limit of  $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$  for the rate coefficient of reaction (17). It is then found that for the molecular concentrations shown in Table 1, reaction (17) competes with the direct further hydration of  $\text{NO}^+ \cdot \text{H}_2\text{O}$  at 80 km only if the H concentration exceeds  $3 \times 10^7$

$\text{cm}^{-3}$ . No information is available concerning the rate coefficients of reactions (18), (19), and (20). It is known that reaction (18) is exothermic but because of the uncertainties in bond energies of  $\text{HO}_2$  and  $\text{NO}_3$  no statement is possible about the exothermicity of reactions (19) and (20). Concentrations of  $10^6 \text{ cm}^{-3}$  are reasonable for OH and  $\text{HO}_2$  at 80 km [Thomas and Bowman, 1972; Shimazaki and Laird, 1972]. With these values the rate of coefficient of reaction (18), (19), or (20) needs to be about  $3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  in order for the reaction to compete with direct hydration of  $\text{NO}^+ \cdot \text{H}_2\text{O}$  at 80 km. It is to be noted that these limits on the H concentration and on the rate coefficients of (18), (19), and (20) will be increased if the rate coefficient of the postulated reaction (14) is greater than the previously discussed value of  $2.1 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$ . For instance, for a value of  $10^{-32} \text{ cm}^6 \text{ sec}^{-1}$  for this rate coefficient, the specific rate for reaction (17), (18), (19), or (20) would need to be greater than  $10^{-8} \text{ sec}^{-1}$  for it to be competitive. This value would imply either an H-atom concentration at 80 km greater than  $10^8 \text{ cm}^{-3}$  or a rate coefficient for reaction (18), (19), or (20) in excess of  $10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ .

## 5. NEGATIVE ION CHEMISTRY

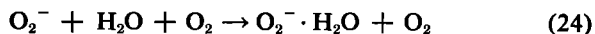
Mass spectrometer measurements of negative ion composition in the D region have been carried out by only two groups and unfortunately the two sets of measurements have produced conflicting results [Narcisi et al., 1971, 1972a; Arnold et al., 1971]. Consequently our present understanding of the negative ion chemistry has been derived largely from laboratory measurements. On the basis of work by Fehsen-

feld et al. [1967, 1969], it is believed that the  $\text{O}_2^-$  ions formed by the rapid three-body attachment of electrons to  $\text{O}_2$  molecules [Chanin et al., 1959] can undergo reactions:



The ions  $\text{O}_3^-$  and  $\text{O}_4^-$  can then be involved in a sequence of reactions which leads initially to  $\text{CO}_3^-$  and  $\text{CO}_4^-$ , and finally to  $\text{NO}_2^-$  and  $\text{NO}_3^-$  [Fehsenfeld and Ferguson, 1968; Fehsenfeld et al., 1969]. The  $\text{NO}_3^-$  is believed to terminate the chain. Negative ion models based on these and related laboratory measurements have been devised by Reid [1970], Arnold and Krankowsky [1971], Turco and Sechrist [1972b], and Thomas et al. [1973]. That of Thomas et al. is represented in Figure 9; the dotted lines refer to possible photodetachment processes.

A major limitation of these negative ion schemes has been the absence of information concerning the hydration of long-lived ions, such hydration being expected from laboratory measurements. The following represent the results of some relevant measurements, in units of  $\text{cm}^6 \text{ sec}^{-1}$ , carried out in recent years:



$$3.0 \times 10^{-28} \text{ [Pack and Phelps, 1971]}$$

$$1.6 \times 10^{-28} \text{ [Payzant and Kebarle, 1972]}$$

$$2.2 \times 10^{-28} \text{ [Fehsenfeld and Ferguson, 1974]}$$

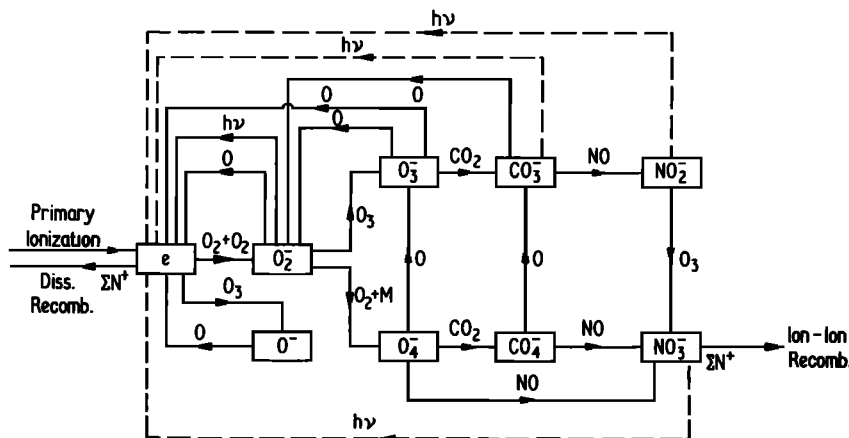
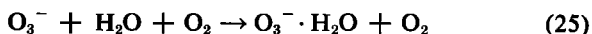
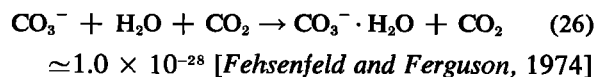


Fig. 9. Schematic representation of negative ion changes during daytime, according to the model of Thomas et al. [1973].

$$2.1 \times 10^{-28} \text{ [Pack and Phelps, 1971]}$$

$$2.7 \times 10^{-28} \text{ [Fehsenfeld and Ferguson, 1974]}$$



$$8.4 \times 10^{-29} \text{ [Payzant et al., 1972]}$$

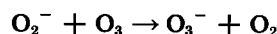
$$1.6 \times 10^{-28} \text{ [Fehsenfeld and Ferguson, 1974]}$$



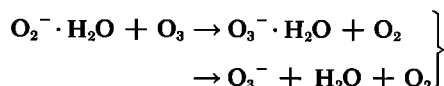
$$7.5 \times 10^{-29} \text{ [Payzant et al., 1972]}$$

The loss of  $\text{O}_2^-$ ,  $\text{O}_3^-$ ,  $\text{CO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  ions arising from these reactions can be compared with that expected for each from reactions already incorporated in negative ion models. Such a comparison has been made for a height of 65 km on the assumption that the rate coefficients shown for reactions (24) through (28) all apply with  $\text{O}_2$  and  $\text{N}_2$  as the third body; use was made of the reactions and rate coefficients listed by Thomas et al. [1973] and the concentrations of neutral constituents shown in Table 1. It is found that for  $\text{O}_2^-$ ,  $\text{O}_3^-$ , and  $\text{NO}_2^-$  the losses by hydration are considerably slower than those by the other reactions for these ions shown in Figure 9. For  $\text{CO}_3^-$  ions, loss by reaction (26) is slow compared with that resulting from the reaction with O atoms in daytime. In the absence of significant O atom concentration at 65 km during nighttime, the major loss of  $\text{CO}_3^-$  is expected to be from the reaction with NO; it is found that hydration is competitive as a loss for this ion only if the NO concentration is less than about  $10^8 \text{ cm}^{-3}$ . For  $\text{NO}_3^-$  ions, recombination with positive ions, and photodetachment in daytime, has been considered as the main loss process in negative ion models. The estimated specific loss rate by hydration at 65 km,  $1.5 \times 10^{-3} \text{ sec}^{-1}$ , is substantially larger than that from recombination, based on a positive ion concentration of  $10^8 \text{ cm}^{-3}$  and a recombination rate coefficient of  $10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ . However, during daytime hydration of  $\text{NO}_3^-$  will only be important if the photodetachment coefficient is smaller than  $10^{-3} \text{ sec}^{-1}$ .

These considerations would imply that current negative ion reaction schemes will not be affected seriously when account is taken of the hydration reactions (24) through (28). Furthermore, Fehsenfeld and Ferguson [1974] have demonstrated that many of the negative ion reactions are not altered by hydration of the negative ion involved. For example, in the reactions of  $\text{O}_2^-$  and  $\text{O}_2^- \cdot \text{H}_2\text{O}$  with  $\text{O}_3$ :



$$3.0 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \text{ [Fehsenfeld et al., 1967]}$$



$$3.1 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \text{ [Fehsenfeld and Ferguson, 1974]}$$

Similar agreement was found in the corresponding reactions of  $\text{O}_3^-$  and  $\text{O}_3^- \cdot \text{H}_2\text{O}$  with  $\text{CO}_2$ , and  $\text{CO}_3^-$  and  $\text{CO}_3^- \cdot \text{H}_2\text{O}$  with NO and  $\text{NO}_2$ .

The importance of the photodetachment of electrons from negative ions represents the second major uncertainty in negative ion models. Measurements of the electron affinities of  $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{O}_3^-$ , and  $\text{CO}_4^-$  have been reviewed by Phelps [1969], and values of 2.38 and 3.9 eV have been recently reported for  $\text{NO}_2^-$  [Dunkin et al., 1972] and  $\text{NO}_3^-$  [Ferguson et al., 1972]. Experimental values of photodetachment coefficients are available for  $\text{O}^-$  [Branscomb et al., 1958],  $\text{O}_2^-$  [Woo et al., 1969], and  $\text{O}_3^-$  [Byerly and Beaty, 1971; Burt, 1972a], although the two values for  $\text{O}_3^-$  differ by more than a factor of six. Values of electron affinities and photodetachment rates have also been reported for  $\text{CO}_3^-$  and  $\text{CO}_3^- \cdot \text{H}_2\text{O}$  by Burt [1972b] but these values have been questioned recently by Ferguson et al. [1973]. No experimental data on photodetachment coefficients are available for  $\text{NO}_2^-$  and  $\text{NO}_3^-$  but estimates have been made for theoretical model studies [Kamiyama, 1970; Turco and Sechrist, 1972a]. In such studies Turco and Sechrist [1972b] have examined the importance of photodetachment of electrons from various ions in a detailed study of sunrise changes in the D region, and Thomas et al. [1973] have suggested that photodetachment of electrons from major negative ions, such as  $\text{NO}_3^-$ , is necessary to reproduce the electron concentrations below 70 km in daytime.

Mass spectrometer observations carried out under quiet conditions during nighttime at Churchill [Narcisi et al., 1971] and near totality of a solar eclipse at Wallops Island during March 1970 [Narcisi et al., 1972a] showed evidence of hydrated ions; masses consistent with  $\text{NO}_3^- \cdot (\text{H}_2\text{O})_n$ , with possible admixtures of  $\text{CO}_3^- \cdot (\text{H}_2\text{O})_n$ , where  $n = 0$  through 5, were observed. These observations are illustrated in Figure 10 which shows the results obtained on the upleg of the rocket flight during the eclipse. This also shows a layer of cluster ions of masses in excess of  $150^-$  observed near 88 km. A similar layer of ions of masses in excess of  $54^-$  was also observed during

the nighttime measurements [Narcisi *et al.*, 1971]. Narcisi *et al.* [1972a] have drawn attention to large decreases in electron concentrations observed near 87 km during both the eclipse and during nighttime. Since such large decreases are not apparent in the positive ion results, electron attachment to form negative ions is indicated. They have pointed out that in view of the relatively low pressures existing at 87 to 88 km, the large cluster ions cannot be explained on the basis of presently known vapor phase reactions. Instead, they suggest the possible importance of conglomerates in the negative ion chemistry at these heights.

Ions consistent with  $\text{NO}_3^-(\text{H}_2\text{O})_n$  were also found below 85 km during daytime and nighttime during a PCA event in November 1969 [Narcisi *et al.*, 1972d]. As mentioned previously, the daytime presence of such ions is relevant to the question of the rate of photodetachment from  $\text{NO}_3^-$  ions. A striking result of these daytime measurements was the predominance of  $\text{O}_2^-$  ions between 72 and 94 km; at night  $\text{O}^-$  was the major ion between 74 and 94 km with  $\text{O}_2^-$  also being present below 80 km. As pointed out by Narcisi [1972], the observations of these ions above 80 km are difficult to understand in view of the expected rapid associative detachment by O atoms.

It needs to be emphasized that the negative ion composition measurements carried out by Arnold *et al.* [1971] during nighttime under weak auroral conditions showed no evidence of hydrated  $\text{NO}_3^-$  ions. Instead,  $\text{CO}_3^-$  was the dominant ion present and significant concentrations of  $\text{HCO}_3^-$  and  $\text{NO}_3^-$  were also observed from 71 to 80 km. In general, the heavy cluster ions recorded were completely different from those reported by Narcisi *et al.* [1971, 1972a, d]. In addition large concentrations of Cl<sup>-</sup> ions, of isotopic mass 35<sup>-</sup> and 37<sup>-</sup>, were measured below 80 km and masses consistent with  $\text{O}_2^-(\text{H}_2\text{O})_2$  and  $\text{CO}_3^-\cdot\text{H}_2\text{O}$  were also observed as trace constituents. Further in-situ measurements are essential in order to establish the negative ion composition for comparison with existing theoretical models, and to indicate possible lines for further laboratory investigations.

## 6. SUMMARY AND OUTLINE OF OUTSTANDING PROBLEMS

Although there have been significant advances in theoretical models of the D region during recent years, it cannot be claimed that there has been a

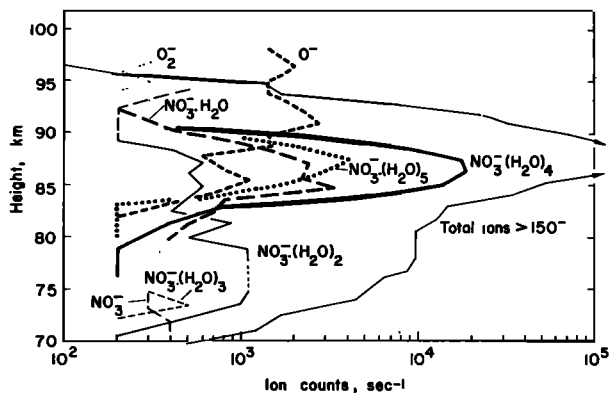


Fig. 10. Rocket-borne mass spectrometer observations of the negative ion composition near totality of a solar eclipse at Wallops Island during March 1970 [Narcisi *et al.* 1972a]. Note the hydrated ions  $\text{NO}_3^-(\text{H}_2\text{O})_n$  and the layer of heavy ions near 88 km.

substantial improvement in our understanding of the processes operating. Considerable effort has been made to study theoretically the height distributions of minor neutral constituents and some experimental information has also become available. Improved measurements of positive ion composition have been carried out and these together with recent laboratory studies relate particularly to the question of the formation of water cluster ions,  $\text{H}^+(\text{H}_2\text{O})_n$ , from  $\text{NO}^+$ . Negative ion composition measurements have been achieved by two groups but some of the results cannot be understood on the basis of current theoretical models of negative ion chemistry. It will be convenient to summarize some of the major developments during this three-year period and to draw attention to particular problems still outstanding:

(a) Important improvements have been made in theoretical models of minor constituents such as NO,  $\text{O}(^3P)$ , and  $\text{H}_2\text{O}$ ; the height variation of eddy diffusion coefficient continues to be a major uncertainty in such models.

(b) Observations of the  $\gamma$ -bands of NO in the dayglow are not particularly well suited to the measurements of NO concentrations in the mesosphere, but recent observations at different latitudes and the previous results of Barth [1966] all show agreement to within a factor of 4. All measurements show concentrations in excess of  $10^7 \text{ cm}^{-3}$ . The confirmation of such concentrations by an independent technique represents an urgent need.

(c) The major change in views concerning sources of ionization in daytime has been the realization that part of the ultraviolet radiation capable of ionizing

$O_2(^1\Delta_g)$  molecules in the mesosphere is absorbed by  $CO_2$  at greater heights. The ionization of NO by solar Lyman- $\alpha$  radiation represents the major source of ionization in the middle *D* region during daytime, especially under solar minimum conditions. At nighttime, ionization is produced primarily by Lyman- $\alpha$  in the nightglow and the precipitation of particles but the relative importance of these two sources is difficult to assess.

(d) Rocket-borne mass spectrometer observations have shown that the transition from  $O_2^+$  and  $NO^+$  to water cluster ions,  $H^+(H_2O)_n$ , occurs at 82 km during daytime and at 86 km during twilight or nighttime under normal conditions, and at lower heights during disturbed conditions at high latitudes. Recent improved measurements have indicated the greater importance of high-order cluster ions, and increased attention is being given to the possibility that the ions  $H_3O^+$  and  $H^+(H_2O)_2$  observed might result from fragmentation during sampling. The establishment of the true ambient positive ion composition is an essential prelude to future progress in theoretical studies.

(e) Theoretical models have shown that as a result of the reduction in photoionization rate of  $O_2(^1\Delta_g)$ , the reaction scheme for the production of water cluster ions from  $O_2^+$  ions is unable to account for the measurements made under normal conditions, especially at the lower heights. However, it offers a satisfactory explanation of the observations during disturbed conditions at high latitudes.

(f) The need for a reaction scheme for the production of water cluster ions from  $NO^+$  ions has represented one of the principal *D*-region problems. A major requirement is the rapid conversion of  $NO^+$  to  $NO^+ \cdot H_2O$ . The initial clustering to  $N_2$ , reaction (10), followed by reactions with  $CO_2$  and  $H_2O$ , reactions (12) and (9), could provide such a conversion. However, the available measurements of the rate coefficient of reaction (10) differ by about two orders of magnitude. Analogous changes, as represented by reactions (14) and (15), have been postulated for the rapid formation of higher hydrates of  $NO^+$ . The identification of ions  $NO^+ \cdot N_2$ ,  $NO^+ \cdot CO_2$ , and  $NO^+ \cdot (H_2O)_2$  in recent mass spectrometer measurements provides some support for this type of reaction scheme, but the establishment of rate coefficients for reactions (9), (10), (11), (12), (14), and (15) is essential for a quantitative study. Reactions (17), (18), (19), and (20) have been proposed for the formation of  $H_3O^+$  from  $NO^+ \cdot H_2O$  but the possible

importance of such reactions will depend on the competing loss processes for this hydrated ion.

(g) Negative ion models have been devised on the basis of laboratory measurements. Later measurements have indicated that the hydration of  $O_2^-$ ,  $O_3^-$ ,  $CO_3^-$ , and  $NO_2^-$  will not alter the models significantly. Recent model studies have demonstrated the importance of the photodetachment of electrons from ions such as  $NO_3^-$  during sunrise and daytime. Although values of electron affinities have been recently reported for  $NO_2^-$  and  $NO_3^-$ , no information is available on the photodetachment coefficients for these and certain other relevant ions.

(h) Mass spectrometer measurements of negative ion composition have confirmed certain predictions based on laboratory studies but also pose major problems: the observations by two groups have produced conflicting results concerning the major species present; evidence has been found for a layer of heavy ions situated near 88 km, such ions being inexplicable by presently known vapor phase reactions; the observations of  $O^-$  and  $O_2^-$  as predominant ions in the middle and upper *D* region during nighttime and daytime, respectively, in a PCA event cannot be understood in view of the expected rapid associative detachment of electrons from these ions by oxygen atoms. Further observations are essential to establish the ambient negative ion composition, to identify necessary laboratory investigations, and to form a basis for more realistic theoretical models.

*Acknowledgments.* The author is indebted to the following people for allowing him to quote their work prior to publication: R. S. Narcisi and W. Swider concerning the height distribution of  $H_2O$ ; F. Arnold, K. H. Marien, and D. Krankowsky concerning positive ion composition measurements; E. E. Ferguson, F. C. Fehsenfeld, and A. V. Phelps concerning negative ion laboratory measurements; and J. M. Heimerl concerning the further hydration of  $NO^+ \cdot H_2O$ .

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