Topics in Current Chemistry

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Editors: S. Veprek and M. Venugopalan

This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for "Topics in Current Chemistry" in English.

Preface

During the past ten years significant developments have taken place in the field of plasma chemistry. Progress of research, or the lack of it in certain areas, was discussed at a number of Gordon conferences, and at four international symposia, several round tables and topical meetings sponsored by IUPAC. The editors of *Topics in Current Chemistry* have therefore undertaken to bring the advances into perspective by issuing volumes which are subtitled *Plasma Chemistry*. The volumes will deal with topics which are the main concern of many researchers. Such topics include elementary processes in low pressure plasmas, plasma-material interactions, plasma polymerization and thermal plasma processing. Because of the ever increasing importance of energy and environmental problems the editors have found it only fit to begin the series with a chapter on elementary plasma reactions of environmental interest.

Among the significant developments mention may be made of the realization that electron-impact induced excitation of vibrational states and subsequent v-v climbing is the most important dissociation process in many gases under conditions obtained in low pressure plasmas. A successful recent application of the low pressure plasma is in the preparation of materials with extreme requirements of purity, homogeneity and radial profile of refractive index, all of which are necessary in the manufacture of optical wave guides. Plasma etching and polymerization technologies are rapidly emerging and elementary processes occuring at solid surfaces immersed in plasmas are receiving considerable attention. Investigations of plasma-material interactions have contributed to a better understanding of the impurity release and have led to suggestions for future control of impurities in magnetically confined thermonuclear machines for nuclear fusion research. Thermal plasmas have been applied in ceramics, powder technology and extractive metallurgy; in the production of solar grade silicon, in nitric oxide synthesis, and in the gasification and desulfurization of coal.

It is hoped that the volumes will appeal to a broad spectrum of readers and will promote further research in the field of plasma chemistry.

The editors acknowledge the help and cooperation of Dr. F. L. Boschke and his staff at Springer-Verlag. They are grateful to the various authors for their timely contributions and to their colleagues and families for encouragement during the preparation of the volumes.

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S. Vepřek

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Elementary Plasma Reactions
of Environmental Interest

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1 Introduction

The atmosphere, which extends to many thousands of kilometres from the Earth's surface before it merges with the very tenuous interplanetary gas, is immersed in a radiation field mainly generated by the sun but which includes galactic cosmic ray components. Energetic short wavelength components of the radiation field ensure that the atmosphere is at least partially ionized at all times, the degree of ionization varying by many orders of magnitude throughout the atmosphere. The production of very reactive ions, electrons and neutral radicals initiates an extremely complex gas-phase chemistry which can modify greatly the composition of the atmosphere, thus generating the perceived atmospheric environment.

In the upper reaches of the atmosphere, more specifically in the magnetosphere and upper ionosphere, the degree of ionization is relatively high, the charged particles are electrons and positive ions only and the gas pressure is very low. The plasma properties of these regions are very evident and they have received considerable attention from physicists over the last few decades principally those concerned with radiowave propagation[1]. The chemistry of these regions is relatively simple and reasonably well understood, being described by just a few binary reaction processes (Sect. 3.2.2 and 4). Descending through the atmosphere into the middle and lower ionosphere, through the stratosphere and troposphere, the gas pressure increases approximately exponentially with decreasing altitude. Negative ions ultimately replace electrons as the negatively charged species and thus a positive ion/negative ion plasma exists in which the charged particle/neutral particle ratio is very small because of the high pressure which obtains but in which the absolute charged particle density still is appreciable (Sect. 2.2). Thus the chemistry becomes much more complex. Ternary reactions, the rate coefficients of which are known to be very sensitive to temperature, become very important. Also the presence of a large number of different neutral molecular species variously generated (biogenetically, man-made pollutants, etc.) which are efficiently photolysed by solar radiation, ensure that a rich ion and a parallel neutral chemistry will be continuously occurring, the latter dominating the chemical evolution in the stratosphere and the troposphere. Nevertheless, the presence of significant concentrations of charged particles coupled with their greater reactivity will have a significant influence on chemical evolution in the medium. It is with the elementary charged particle reactions which are occurring continuously in the environmental plasma that this review is concerned.

Progress towards an understanding of ionospheric ion chemistry has resulted from in-situ determinations of ion composition using balloon-, rocket- and satellite-borne mass spectrometers coupled with the development and exploitation of laboratory experiments to determine reaction rate coefficients, ion products, etc. Progress has been much slower with respect to stratospheric and tropospheric chemistry, not least due to the difficulties inherent in mass spectrometer sampling of these relatively high pressure regions. However, significant advances have been made recently both in in-situ sampling techniques and in the acquisition of relevant laboratory data.

In order that the discussion of the individual reaction processes, which combined to describe the overall chemistry of the atmospheric regions, can be facilitated and readily placed into context, a brief description of the atmospheric plasma medi-

um (Sect. 2) will be presented, including the neutral composition, the ionizing radiations and the ion composition in the various regions. Then, following the detailed discussion of elementary processes in Sect. 3, which will concentrate on the most recent developments, the paper will be concluded (Sect. 4) by a brief summary of the current status of atmospheric ion chemistry.

2 Description of the Environmental Plasma

The combined influence of gravity and solar radiations on the Earth's atmosphere results in several distinct 'regions' which are designated according to such physical parameters as the ambient temperature and the ionization density. Photoionization and a subsequent complicated ion chemistry converts the simple primary positive and negative ions into the observed, generally more complex ions.

2.1 The Neutral Atmosphere: Composition and Temperature

Much has been written concerning the structures and properties of the neutral atmosphere [2-5], but the details are not relevant here. Only those general features which significantly influence the chemistry of the atmosphere will be discussed and then only very briefly.

In the absence of temperature gradients, that is for an isothermal atmosphere, the total pressure or total gas density would decrease very nearly exponentially with increasing altitude. However radiant heating ensures that such a simple structure does not pertain in the Earth's atmosphere and the total gas density decreases in the manner shown in Fig. 1. The altitudinal variation of ambient temperature is even more complicated and in the upper reaches of the atmosphere is a result of the absorption of short wavelength radiation whilst in the lower atmosphere it is due to the heating of the Earth's surface by longer wavelength radiation followed by conduction and convection. A typical neutral temperature versus altitude profile is shown in Fig. 2. From sea level, the *atmospheric temperature,* T_g, at first decreases with altitude as the distance from the heat source (the Earth's surface) increases. At about 15 km altitude a minimum in T_g appears, the so-called tropopause, the actual altitude of the tropopause being subject to both diurnal and seasonal variations as are most of the atmospheric physical features.

The increasing T_g at altitudes above the tropopause is largely due to the photochemical production of ozone via the well-known reactions [7]

$$O_2 \xrightarrow{h\nu} O + O \tag{1a}$$

$$O + O_2 + M \longrightarrow O_3 + M \tag{1b}$$
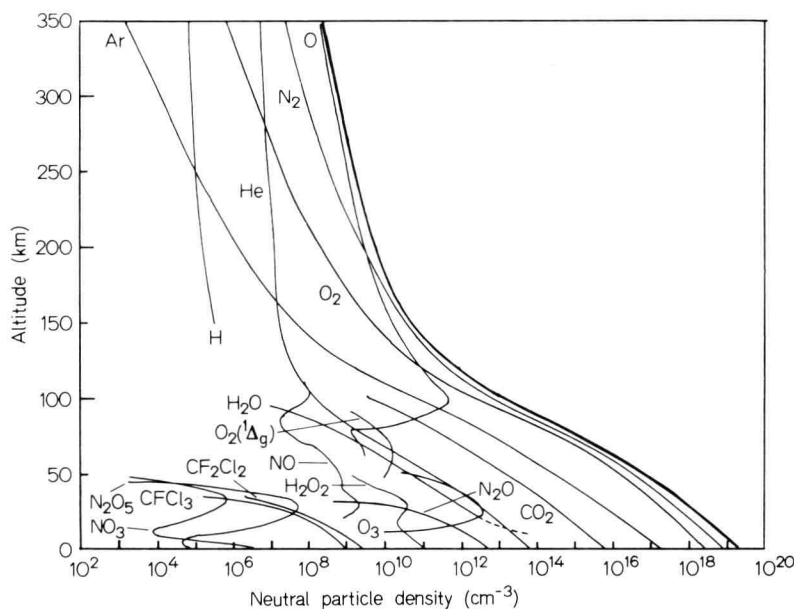
Fig. 1. The neutral composition of the Earth's atmosphere as a function of altitude. The sources of the altitudinal profile data are: H, He, O, N_2, O_2, Ar, Ref.[6]; O_3, Ref.[7]; H_2O, Refs.[8] and [10]; NO, Refs.[9] and [10]; $O_2(^1\Delta_g)$, Ref.[11]; O below 90 km, Ref.[12]; CF_2Cl_2 and $CFCl_3$, Ref.[13]; N_2O, Ref.[14]; H_2O_2, NO_3 and N_2O_5, from model calculations given in Ref.[15]; CO_2 is assumed to have a constant mixing ratio of 300 p.p.m. Clearly many other minority species are present in the lower atmosphere (e.g. OH, HO_2; see Ref.[15]) but these have been omitted for clarity. The thick line indicates the total neutral particle density

M can be any third body which carries away the energy liberated in the reaction but almost invariably will be N_2 or O_2. Destruction of the ozone also results in atmospheric heating:

$$O_3 \xrightarrow{\ h\nu\ } O_2 + O \tag{2a}$$

$$O_3 + O \longrightarrow O_2 + O_2 \tag{2b}$$

Reactions (1) and (2) essentially convert solar radiant energy into thermal energy. The parameters which determine the rate of ozone formation (UV photon flux, atomic and molecular oxygen number density and the total gas number density) are not constant with altitude and so the ozone concentration and hence T_g varies with altitude. The net result is that T_g increases thoughout the stratosphere until a maximum is reached at the stratopause whence T_g begins to decrease again.

The presence of the ozone layer ensures that solar UV radiation (in the wavelength range 2—300 nm) which is harmful to living things is prevented [by reaction (2a)] from reaching the Earth's surface. Since ozone is known from laboratory studies to be destroyed by some atmospheric pollutants and the photofragments thereof [17], pollution of the atmosphere (particularly by freons) has recently been the
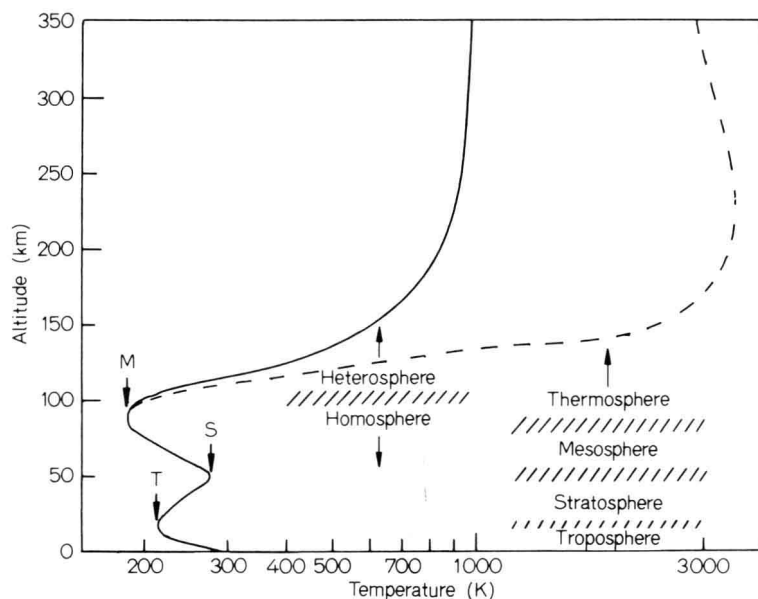
Fig. 2. A typical altitudinal variation of the neutral gas temperature[6] (*solid curve*) and the plasma electron temperature[16] (*dashed curve*) in the Earth's atmosphere. Note that the temperature scale (*absissa*) is logarithmic. The atmospheric regions are as indicated and M, S and T indicate the mesopause, stratopause and tropopause, respectively

cause of much discussion. This has led to experiments specifically designed to determine the concentration of such pollutants in the troposphere and the stratosphere [18]. The various techniques which have been used for this and some of the results obtained have recently been reviewed by Ehhalt[13].

The region of the atmosphere above the stratopause in which T_g continuously reduces towards a second minima, the mesopause, is termed the *mesosphere*. The mesopause occurs at an altitude of about 80 km and is the lowest temperature point in the atmosphere, values of T_g approaching 100 K having been recorded, although temperatures nearer to 200 K are more typical. Significantly, it is the relatively high pressure, low temperature mesosphere in which "cluster" ions were first detected in the atmosphere (Sect. 2.2).

Above the mesopause, T_g increases rapidly. In this region, termed the *thermosphere* (Fig. 2), absorption of short wavelength solar radiation is occurring (Fig. 3) which results in the efficient photodissociation of molecular oxygen, and the photoionization of the O atoms so produced and of the O_2 and N_2 molecules. Thus, T_g increases beyond 1000 K, approaching 2000 K at times. Whereas below 100 km the neutral gas particles, the ions and the electrons in the plasma all possess the same kinetic temperature, above 100 km, due to the lower pressure and the subsequent reduced electron/heavy particle collision frequency and the large amount of energy imparted to the photoelectrons, the electron temperature, T_e increases above T_g (and T_i the ion temperature, which is $\sim T_g$, see Fig. 2).

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Fig. 3. The absorption spectrum for solar radiation in the Earth's atmosphere[19]. On the ordinate is plotted the altitude at which the radiation intensity is reduced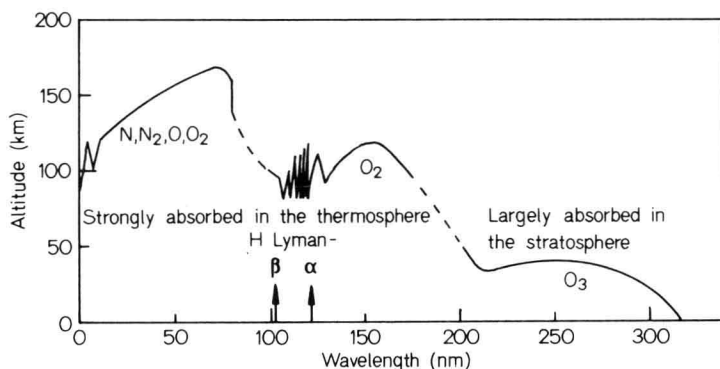 by a factor e^{-1} from its unattenuated value. The species predominantly responsible for the absorption in the various wavelength ranges are as indicated. The wavelength of the H Lyman-α radiation closely coincides with a window in the O_2 absorption spectrum

The temperature gradients, gravity and photochemistry exercise an important influence on the neutral composition of the atmosphere. The mesopause divides the atmosphere into two distinct regions in terms of their gas dynamical properties. Below about 100 km, large scale dynamical effects result in mass transport throughout the region, i. e. effective mixing of the major and the more stable minor neutral constituents (e. g., CO_2, H_2O) occurs and the "mixing ratio" of a particular species remains approximately constant. Hence the term "homosphere" is often applied to this region. The transport of minor neutral constituents from the troposphere into the stratosphere and mesosphere has a profound influence on the chemistry of these regions.

Above an altitude of about 100 km (in the thermosphere), convective mixing of the various gases of differing molecular weight is no longer effective and gravitational separation of the neutral species becomes evident (Fig. 1). Thus the relative concentrations of the lighter species H, He and O increases with increasing altitude. Hence the term *"heterosphere"* is often applied to this region of the atmosphere. No complex molecules can survive in the heterosphere because of the prevailing intense solar radiation and so the chemistry is relatively simple (Sect. 3.2.2 and 4).

In summary, large variations in the pressure, composition and temperature exist in the atmosphere, the greatest variations occurring in the lower atmospheric regions which, as will be seen, are reflected by the much more complex chemistry occurring in these regions, a chemistry which is thought to be dominated by the minor neutral constituents, doubtlessly some of which have yet to be identified.

2.2 The Ionized Atmosphere: Ion Composition and Number Density

The presence of ionization in the upper atmosphere was first demonstrated about half a century ago by reflecting radio waves from the ambient plasma [1], and by this technique it was shown that the ionosphere was clearly structured, several "ledges"

in the electron density being evident (Fig. 4). Below 80 km, no radio reflection could be detected and it was concluded that no significant ionization existed below that altitude. This conclusion is now known to be incorrect since, although the ionization
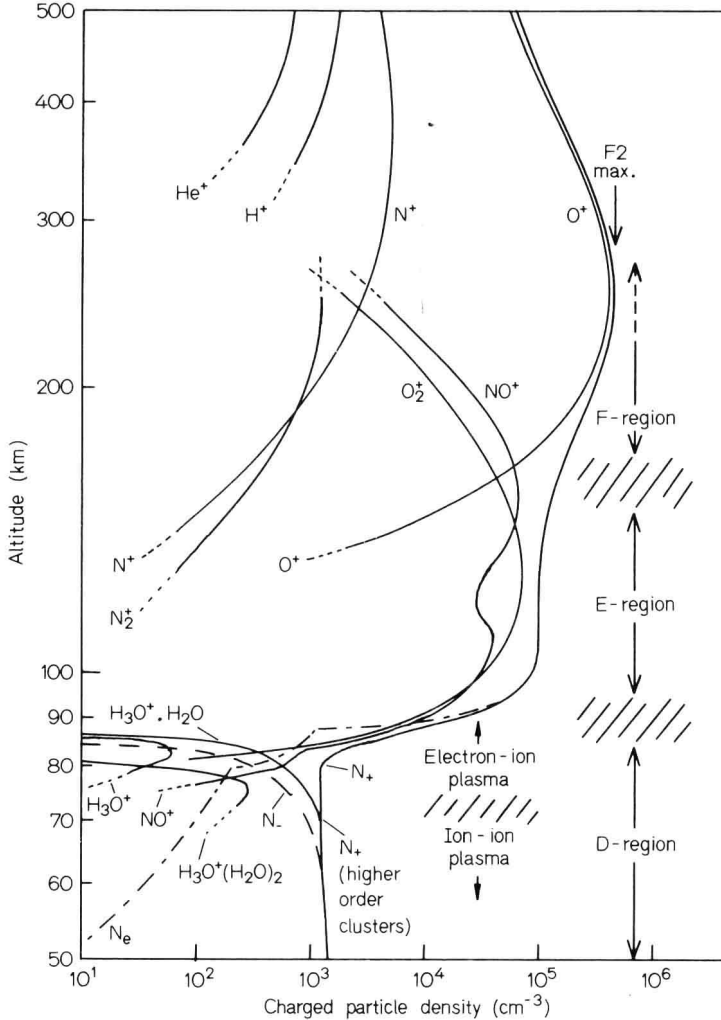
Fig. 4. The ionized regions of the Earth's atmosphere. The F, E and D regions are designated according to the "ledges" observed in the electron density. Typical altitudinal profiles of the various positive ion densities in the positive ion-electron plasma (from Refs.[20] and [21]) are also shown. The negative ion types in the positive ion-negative ion plasma of the lower D-region are known but the detail altitudinal profiles of density are not well characterised and so only the approximate total negative ion density, N_-, (dashed line) as obtained from Refs.[22] and [23] is shown. The profiles of the electron density, N_e, and the total positive ion density, N_+, are also included. It is assumed that quasi-neutrality exists throughout the atmosphere, that is $N_e \approx N_+$ in the thermosphere, $N_e + N_- \approx N_+$ in the mesosphere, and $N_- \approx N_+$ in the strato-sphere and troposphere

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density below this altitude does decrease due to the rapid dissociative recombination of electrons with the water cluster ions which are efficiently formed in this region (Sect. 3.2.3), the process of electron attachment (Sect. 3.2.2) is also sufficiently rapid to convert some of the free electrons to negative ions which do not efficiently reflect radio waves and therefore remained undetected. Thus above 80 km an electron-positive ion plasma exists, whilst below this altitude a gradual transition towards a negative ion-positive ion plasma takes place which is complete below an altitude of about 60 km. These gross features of the Earth's ionosphere have been confirmed using several other techniques such as rocket-borne electrostatic probes [24] and radar backscatter [25].

Several distinct regions of ionization exist (Fig. 4) which have characteristic and predictable shapes, resulting from the interaction of a specific wavelength or a broad wavelength band of ionizing radiation with an atmosphere of varying composition. They have been designated the F, E and D layers (or regions) in order of descending altitude and as can be seen from Fig. 4, the electron density ranges from about $10^6 cm^{-3}$ at the F 2 maximum to zero in the lower D-region. The ion and neutral compositions as well as the particular solar radiations which are most strongly absorbed in these regions have been determined using rocket-borne mass spectrometers and radiation detectors. Above the F 2 maximum, the ionization results predominantly from the action of EUV and X-rays on the dominant neutrals (see Fig. 3) producing the observed ions He^+, N^+ and O^+ [20], that is , there is a correspondence between the ambient ions and neutrals. Ionic reactions however, are occurring, for example the nearly *thermoneutral charge transfer reaction* [26]

$$H^+ + O \longrightarrow O^+ + H \tag{3}$$

will be continuously influencing the relative concentrations of H^+ and O^+ ions. Below the F 2 maximum the ion-to-neutral correspondence disappears and although N_2^+ and O^+ are expected to be the major primary ions, since *molecular nitrogen* is by far the most abundant neutral and the molecular oxygen is largely dissociated, the most abundance ion is NO^+ even though neutral NO is present in only an insignificant concentration (Fig. 1). As is now well known [20, 27], this is the result of the ionic reactions which occur such as the charge exchange and ion-atom interchange reactions:

$$N_2^+ + O \longrightarrow NO^+ + N$$
$$\longrightarrow O^+ + N_2 \tag{4a}$$

$$O^+ + N_2 \longrightarrow NO^+ + N \tag{4b}$$

$$N_2^+ + O_2 \longrightarrow O_2^+ + N_2 \tag{4c}$$
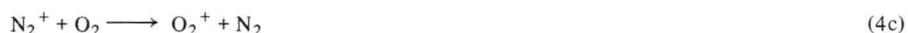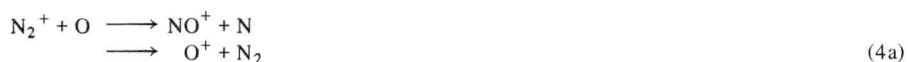
So the chemistry of the F-region is generally well-understood and detailed chemical models have been constructed which can predict reasonably well the observed electron density and ionic composition [28, 29]. These models are based on laboratory data for ion-neutral reactions such as (4), and dissociative recombination reactions (Sect. 3.2.4), such as

$$NO^+ + e \longrightarrow N + O \tag{5a}$$

$$O_2^+ + e \longrightarrow O + O \tag{5b}$$

which control the loss of ionization in these regions. Many excellent reviews have been written on this subject [30-32]. However several intriguing questions still remain especially with respect to the rôle of metastable excited states of both neutrals and ions and of doubly-charged ions and this will be referred to in Sect. 3.2.2 and 4. The possible importance of metastable ions, e. g. O^+ (^2D), has been discussed from time to time [33-36] and they have recently been detected in the ionosphere (Sect. 3.2.2). The radiations in the E and F regions are sufficiently energetic to produce some doubly-charged species and it is worthy of note that the Atmosphere Explorer C (AE-C) satellite has recently detected O^{2+} in the F-region [37]. Such observations to- gether with reliable laboratory data relating to excited ion [38-41] and doubly-charged ion [42-45] reactions (such data are just beginning to appear in the literature) will clarify the role of these species in ionospheric chemistry.

In the E-region where the most energetic solar UV and X-ray photons have been filtered out, the ions which are most efficiently produced are O_2^+ and O^+, the latter being quickly converted to NO^+ *via* reaction (4b). Hence the most abundant ions ob- served are O_2^+ and NO^+ (Fig. 4) which are relatively unreactive with the ambient neutrals present at these altitudes and so they persist until they are lost via reaction (5). However, this chemically less interesting region exhibits an unusual feature in the mid-latitude zones, the so-called "Sporadic-E" layers of enhanced ionization den- sity within a layer a few kilometres thick is enhanced several-fold above the ambient ionization. Rocket-borne mass spectrometers have shown that *metallic ions* (Mg^+, Na^+, Si^+ and Fe^+) are concentrated in these layers[46] and more recently rocket flights have shown that metallic ions are also plentiful in the D-region [21,47, 48]. It seems that the metallic species originate from ablation of meteors in the atmosphere at D and E-region altitudes [48, 49]. Some data are available relating to metal ion reac- tions[50-54] although this is an area where more work is required.

In the D-region, the solar radiations capable of ionizing the major constituents of the region, ie. N_2 and O_2 have been filtered out and but for a fortuitous combi- nation of circumstances, the ionization density in the D-region would be much smaller than actually exists ($\sim 10^3 - 10^4$ cm^{-3}). The existence of windows in the O_2 ab- sorption spectrum allows H Lyman-α and H Lyman-β radiation, (intense lines in the solar radiation spectrum), to penetrate to the D-region and photoionize the minor neutral constituents NO and O_2 ($^1\Delta_g$) respectively (see Fig. 1). The metastable O_2 ($^1\Delta_g$) is produced by photo-excitation of O_2 ground state and by photodissociation of O_3 by long wavelength radiation which can also penetrate to these altitudes. Thus the primary positive ions will be predominantly NO^+ and O_2^+.

The technology of mass spectrometric sampling of the relatively high pressure D-region is more challenging than that for higher altitudes. However many of the problems have been solved and the in-situ experiments carried out by Narcisi and his colleagues [55, 56] have produced entirely unexpected results. Large concentrations of the *hydrated hydronium ions* $H_3O^+(H_2O)_n$, often called water cluster ions, were detected which in later, more refined experiments (designed to minimise the break- up of these weakly bound species during the sampling procedure) have been shown

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to dominate the positive-ion content of the lower D-region [47, 57]. More recent experiments by Arnold and his colleagues [58-61] have confirmed the dominance of these cluster ions (n is seen to be $\lesssim 20$) and any doubts which exist regarding the nature of the dominant D-region positive ions are ones of detail, i. e., what are the fractions of the various hydrates in a given altitude region and are the larger hydrates being satisfactorily sampled without collisional destruction, etc.

The origin and behaviour of these cluster ions has been the basis of much of the work on atmospheric ion chemistry during the last decade. The problem which is still not resolved in detail, is to explain how the primary ions NO^+ and O_2^+ are converted to the observed water clusters, i. e.

$$NO^+, O_2^+ \longrightarrow H_3O^+ (H_2O)_n \tag{6}$$

always remembering that water vapour is a very minor constituent of the atmosphere at these altitudes (mixing ratio $\sim 10^{-6}$). Due to the collective effort of several laboratory groups [63-69] and aeronomists [70-72] (notably E. E. Ferguson and his colleagues at NOAA, Boulder, Colorado) a clear insight into the likely reactions involved has been obtained, and this will be discussed in Sect. 3 and 4. D-region chemistry has been the subject of several reviews [8, 73-75] and it is sufficient to say here that both the conditions of high pressure and low temperature in the D-region (and indeed in the stratosphere and troposphere) are conducive to ternary association reactions and to the production of weakly-bonded association ions viz:

$$O_2^+ + O_2 + N_2 \rightleftharpoons O_2^+ \cdot O_2 + N_2 \tag{7}$$

Such reactions, together with binary "switching" reactions of the kind

$$O_2^+ \cdot O_2 + H_2O \longrightarrow O_2^+ \cdot H_2O + O_2 \tag{8}$$

have been shown in laboratory experiments [76] to be very effective in promoting the overall reaction indicated by reaction sequence (6).

A distinctive feature of the D-region is the occasional appearance of the highest cloud formation known to exist in the Earth's atmosphere. These so-called *"noctilucent clouds"* occur at or near the mesopause. Goldberg and Witt [48] using rocket-borne mass spectrometers have shown that the positive ions in these clouds are heavily clustered with water molecules and that hydrated hydronium ions are prominent. However, in addition, other hydrated species are present with masses that suggest that the core ions are Fe^+, FeO^+, FeO_2^+ and perhaps Mg^+ also, the metals presumably being of meteoritic origin. The co-existence of cluster ions with visible cloud formations adds some support to the view that the cluster ions play an important role as nucleation sites for droplet (aerosol) formation [77].

In the upper reaches of the D-region, electrons are the dominant negatively-charged species and electron-ion dissociative recombination (e. g. Eq. 5) controls the loss of ionization from the plasma, this process being considerably more rapid when cluster ions are involved (Sect. 3.2.4). However, at lower altitudes electrons are gradually replaced by negative ions until below about 60 km (70–80 km during nighttime), free electrons represent a negligible fraction of the ionized component of the atmo-

sphere plasma. Loss of ionization from the ion-ion plasma is then due to the process of ion-ion mutual neutralization:

$$\text{e. g.,} \quad H_3O^+(H_2O)_n + NO_3^-(H_2O)_m \longrightarrow products \tag{9}$$
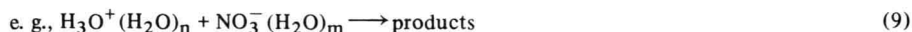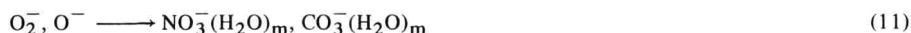
a process which is discussed in Sect. 3.2.5.

As is suggested by reaction (9), the ambient negative ions also are complex clusters. In-situ measurements of the negative ion composition have been made by Narcisi et al. [47] and Krankowsky et al. [58] and whilst there is no doubt that water clusters dominate, there remains some doubt as to the nature of the 'core' ions, i. e. whether the ions are predominantly $CO_3^-(H_2O)_m$ or $NO_3^-(H_2O)_m$. More of these very difficult sampling experiments are necessary to clarify the situation.

As in the case of the positive ion chemistry, the problem is to describe the chemical steps which convert the primary negative ions to the observed clusters. The primary negative ions can only be O^- and O_2^- formed in the electron attachment reactions:

$$e + O_2 + M \longrightarrow O_2^- + M \tag{10a}$$

$$e + O_3 \quad \longrightarrow O^- + O_2 \tag{10b}$$

So the negative ion chemistry is summarised by

$$O_2^-, O^- \longrightarrow NO_3^-(H_2O)_m, CO_3^-(H_2O)_m \tag{11}$$

which involves a number of parallel and sequential binary and ternary reactions. Some of the reactions considered to be involved will be discussed in Sect. 3.2.

Solar radiation sufficiently energetic to photoionize the ambient gas in the stratosphere cannot penetrate the atmosphere above it and the ionization in these regions is generated throughout the day and night by galactic cosmic rays. Thus the primary ions are O^+, O_2^+, N^+ and N_2^+, characteristic of the major atmospheric constituents O_2 and N_2. In-situ ion composition measurements in the stratosphere are fraught with difficulties and are only just beginning. The first observations were made by Arnold et al.[78, 79] again using rocket- and balloon-borne mass spectrometers. These revealed, as expected, a large number of different positive ions including the seemingly inevitable hydrated hydronium ions but with other clusters of the kind $X^+ \cdot (H_2O)_n$, the core ions, X^+, having not yet been convincingly identified. On the basis of the Arnold et al. data and the proton affinity data of Kebarle [80], Ferguson [81] has reasoned that some of the observed stratosphere-ions are of the type $(NaOH)_m H^+(H_2O)_n$. The recent balloon-borne mass spectrometer experiments of Olsen et al.[82] suggest that $H_3O^+(H_2O)_n$ ions dominate the positive ion content of the stratosphere down to 28 km. A similar conclusion has been arrived at by Arijs et al.[83] from their balloon flights but they also observed other ions some of which have masses corresponding to the proposed $(NaOH)_m H^+(H_2O)_n$ hydrates.

The negative ion content of the stratospheric plasma is even less certain. The only data so far available are those obtained very recently by Arnold [62] which are as yet