

SPECTRAL SOLAR IRRADIANCES AND AERONOMIC PHOTOLYTIC PROCESSES
IN THE MESOSPHERE

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INTRODUCTION

The advances in space observations during the past thirty years have overshadowed many fundamental aspects of aeronomy which dominated the first days of rocket observations. In particular, the mesosphere has suffered from a lack of attention before the development of the MAP (Middle Atmosphere Programme). On the other hand, the mass of material obtained by the SME (Solar Mesosphere Explorer) satellite should lead the progress in our understanding of the mesosphere with its various aeronomic processes.

The principal gases in the thermosphere, molecular nitrogen, atomic oxygen and molecular oxygen, limit the atmospheric penetration of solar radiation at wavelengths less than 100 nm. Since absorption cross-sections are not less than 10^{-18} cm² between 100 nm and 10 nm, the solar radiation in this spectral range is absorbed above 100 km and ionizes N₂, O and O₂ and other minor constituents.

At 175 nm, the O₂ Schumann-Runge continuum begins and its absorption leads to the direct photodissociation of that molecule. Thus, the total number of photons available at the top of the earth's atmosphere at wavelengths less than 175 nm represents the total number of oxygen molecules which can be photodissociated in a vertical column of the atmosphere. The continuum of the Schumann-Runge system has an absorption cross-section varying from about 10^{-17} cm² at the absorption peak to more than 10^{-19} cm² at the threshold. Therefore, the penetration of solar radiation into the atmosphere is limited to the thermosphere and cannot reach the mesosphere. But, it must be realized (Nicolet and Mange, 1954; Nicolet, 1954; Mange, 1955, 1957, 1961) first that the dissociated atoms move downward and recombine below 100 km, above the mesopause, and second that molecular oxygen is not in photochemical equilibrium and is subject to an upward transport trying to reach diffusive equilibrium conditions. Furthermore, the effective recombination of the oxygen atoms is still an unsolved problem since the O concentration peak in the neighbourhood of 95 km (see, for example, Howlett et al., 1980; Dickinson et al., 1980; Sharp, 1980; Offerman et al., 1981; Dickinson et al., 1985) is an aeronomic parameter with a value varying even outside of the limits of 10^{11} and 10^{12} atoms cm⁻³.

Finally, the solar irradiance and its variation with solar activity in

the spectral range of the O₂ Schumann-Runge continuum is not yet an aeronomic parameter known with the required accuracy. Figure 1 gives the observational results (Nicolet, 1981) which were obtained between 1970 and 1980, after the analysis of the first observational results made by Ackerman (1971). However, if recent observations such as the SME solar irradiances (Rottman, to be published) or rocket observations (Mentall, to be published) are considered, it seems possible to conclude that the lowest observational values of the solar flux for quiet and active sun conditions may be accepted with a variation with solar activity smaller than a factor of 2.

In conclusion, the production of oxygen atoms in the mesosphere clearly includes not only the absorption by O₂ beginning at 240 nm in the Herzberg continuum, where the value of the cross section has always been acknowledged as uncertain due to the experimental pressure effects in the laboratory determination, but also the extremely variable absorption between 200 and 175 nm by the Schumann-Runge bands as a result of their predissociation. These aspects will be taken into consideration in our analysis with other aspects such as the penetration of solar radiation to greater depths than 10¹⁹ O₂ molecules cm⁻² occurring in various "windows" between 122 and 110 nm. An important window with a cross section of the order of 10⁻²⁰ cm² is situated at 121.6 nm corresponding to the solar-chromospheric Lyman-alpha line of atomic hydrogen and is responsible for various photodissociation processes in the mesosphere.

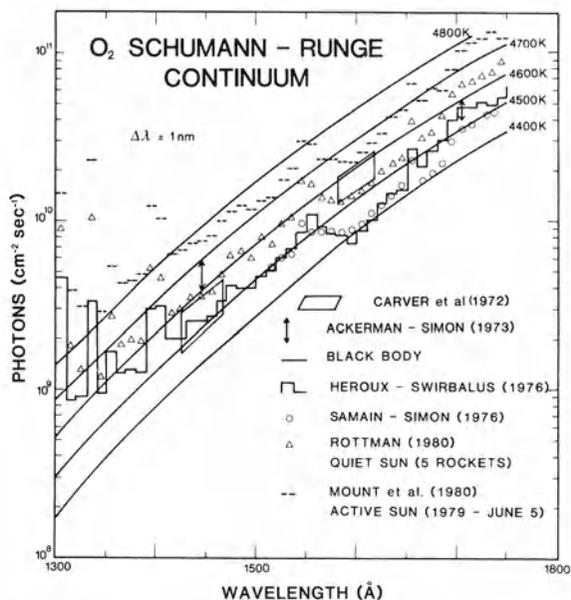
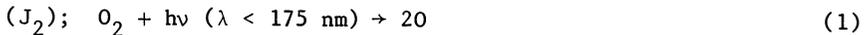


Figure 1

Spectral distribution of the solar irradiance in the region corresponding to the Schumann-Runge continuum of molecular oxygen leading for $\lambda < 175$ nm to about 5×10^{11} photons $\text{cm}^{-2} \text{s}^{-1}$ (possible minimum value) to 1.5×10^{12} photons $\text{cm}^{-2} \text{s}^{-1}$ (too high maximum value probably to be reduced to a possible maximum of about 1×10^{12} $\text{cm}^{-2} \text{s}^{-1}$). See references in Nicolet (1981).

THE CHEMICAL REACTIONS IN THE MESOSPHERE

When Chapman (1930a) introduced the atomic oxygen region, he had in mind a possible explanation for the airglow emission of the green line that arises from a forbidden transition of atomic oxygen. The photodissociation was due to the absorption of solar radiation (a black body at 6000K) in the O₂ Schumann-Runge continuum, a thermospheric process since the Herzberg continuum was not yet known:



with recombination of oxygen atoms in the presence of a third body (N₂, O₂, O)

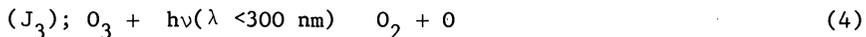


and with the possibility (M=O) to excite the third body O(³P) in the metastable state O(¹S).

In addition, Chapman (1930b) introduced also for his study of atmospheric ozone the association of oxygen atoms with oxygen molecules



with a possible photodissociation (Hartley band)



and also the two-body reaction between O₃ and O



leading to the re-formation of oxygen molecules and the final destruction of ozone.

The discovery by Meinel (1950) that the vibrational rotational bands of the hydroxyl radical OH appear in the airglow aroused the interest in the photochemistry of hydrogen-oxygen compounds (Bates and Nicolet 1950a,b), and in particular, of water vapour (Bates and Nicolet, 1950c). Their results were based on very rough estimates of the various aeronomic parameters involved. Figure 2 gives their results for the mesospheric distributions of the various forms of hydrogen: atomic hydrogen, molecular hydrogen, the hydroxyl and per-hydroxyl radicals, water vapour. Their analysis not only explained the observations on the airglow but had several other points of interest such as the presence of hydrogen reducing the equilibrium concentrations on both O and O₃, the presence of hydrogen in atomic and molecular form (H and H₂) leading to the upward escape of hydrogen into interplanetary space and also the rapid decrease of water vapour concentration in the upper mesosphere by increasing photodissociation. But, it should be remembered that these results were only rough estimates based on photochemical equilibrium conditions with absorption cross sections determined by extrapolation in various parts of the O₂ spectrum (without introducing the predissociation in the O₂ Schumann-Runge bands) and, at that time with several unknown reaction rate coefficients.

The principal reactions in a hydrogen-oxygen mesosphere start from the dissociation of water vapour by various photodissociative channels (see Nicolet, 1984 and references infra)

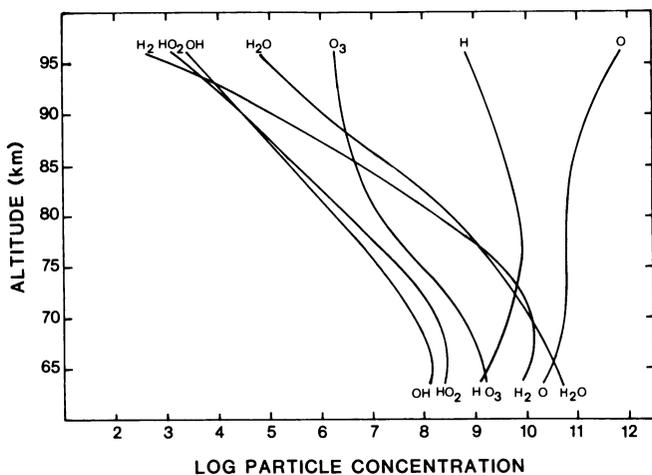
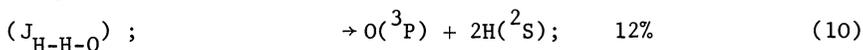
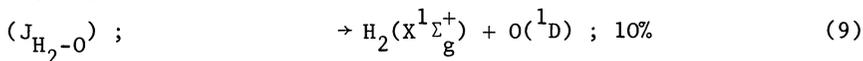
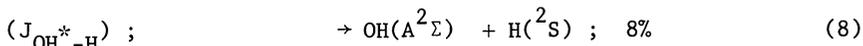
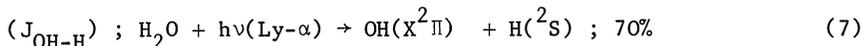
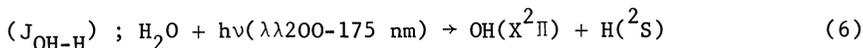
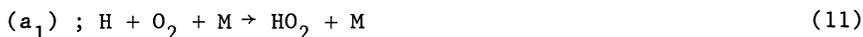


Figure 2

Approximate mesospheric distributions under photochemical equilibrium conditions of atomic oxygen and ozone in an oxygen-hydrogen atmosphere with its additional constituents H_2O , H_2 , H , OH and HO_2 . After Bates and Nicolet⁻(1950); first aeronomic analysis of hydrogen compounds in the terrestrial atmosphere.



With the production of H atoms and OH radicals, various reactions are possible (see Figure 3). In the mesosphere the principal processes are



the production of the perhydroxyl radical and



the production of the excited hydroxyl radical leading to the airglow emission in the infrared.

These two reactions are followed by processes involving OH and HO_2



and



i.e. the first introduction of a catalyst (hydrogen) leading to a loss process of atomic oxygen (and ozone).

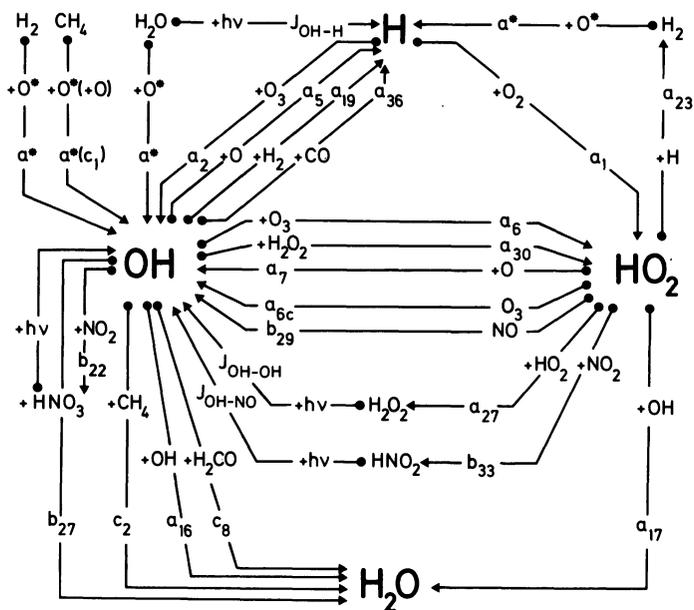


Figure 3

Fundamental reaction scheme in which atomic hydrogen (H), hydroxyl radical (OH) and perhydroxyl radicals (HO₂) may be involved. Their reactions with ozone and nitrogen oxides are essentially stratospheric processes. CH₄ and H₂O₂ do not play a significant role in the mesosphere.

After its photodissociation, H₂O can be re-formed by the reaction



Reactions with O₃ or leading to H₂O₂ can be neglected at mesospheric levels. Reactions between H and HO₂



cannot play an important role in the general behaviour of the mesosphere. Reaction (18) must be associated with the photodissociation process (9), both being a mesospheric source of molecular hydrogen.

THE CHEMICAL EQUATIONS IN THE MESOSPHERE

The equation governing the rate of change of the concentration of an atmospheric constituent XY is of the form

$$\frac{\partial n(\text{XY})}{\partial t} + \text{div} [n(\text{XY})w(\text{XY})] = P - L \quad (19)$$

where P and L denote the production and loss terms due to the photochemical or chemical processes, respectively, and div [nw] corresponds to the

transport term which is always introduced when atmospheric exchanges are more significant than chemical processes. This transport term is often used now as a significant mechanism responsible for apparently inoperative aeronomic processes.

The rate of change of $n(O)$ in the mesosphere should be written (see, for example, Nicolet, 1979) in general form

$$\begin{aligned}
 & \frac{\partial n(O)}{\partial t} + \text{div}^- [n(O)w(O)] \\
 & + 2k_{1M}n^2(O) + k_{2M}n(O_3)n(O) \\
 & + n(O) [k_3n(O_3) + a_5n(OH) + a_7n(HO_2) + a_{24}n(H_2)] \\
 & + n(O^*) [a_{H_2O}^*n(H_2O) + a_{H_2}^*n(H_2)] \\
 & = 2n(O_2)J_2 + n(O_3)J_3 + n(H_2O) [J_{H_2-O} + J_{2H-O}] + n(HO_2)J_{HO_2} \\
 & + n(H) [a_{20}n(HO_2) + a_{22}n(OH)] \tag{20}
 \end{aligned}$$

where O^* is the excited oxygen atom in the metastable state 1D .

The associated equation to (20) corresponding to the rate of change of $n(O_3)$ in the mesosphere is

$$\frac{dn(O_3)}{dt} + n(O_3) [J_3 + k_3n(O) + a_2n(H)] = k_{2M}n(O_2)n(O) \tag{21}$$

In these equations the reactions of OH and HO_2 with O_3 have been neglected since they are compared with their reactions with O in the combination of the two equations (20) and (21).

The practice which is followed throughout this article is to write $\langle XY \rangle$ instead of $\frac{\partial n(XY)}{\partial t} + \text{div} [n(XY)w(XY)]$ or only $\text{div} [n(XY)w(XY)]$ for a stationary state and $\{XY\}$ instead of $\frac{dn(XY)}{dt} = P - L$ for the rate of change of the concentration $n(XY)$. When $\{XY\} = 0$, there is photo-equilibrium.

$$\begin{aligned}
 & \text{The practical equation for the mesosphere is, therefore, } \langle O \rangle + \{O_3\} \\
 & + 2k_{1M}n^2(O) + n(O_3) [2k_3n(O) + a_2n(H)] \\
 & + n(O) [a_5n(OH) + a_7n(HO_2) + a_{24}n(H_2)] \\
 & + n(O^*) [a_{H_2O}^*n(H_2O) + a_{H_2}^*n(H_2)] \\
 & = 2n(O_2)J_2 + n(H_2O) [J_{H_2-O} + J_{2H-O}] + n(HO_2)J_{HO_2} \\
 & + n(H) [a_{20}n(HO_2) + a_{22}n(OH)] \tag{22}
 \end{aligned}$$

where $k_{1M} = k_1n(M)$ and $k_{2M} = k_2n(M)$.

The rate of change of the concentration of water vapour in the mesosphere can be written:

$$\begin{aligned} <H_2O> + n(H_2O)[J_{OH-H} + J_{2H-O} + J_{H_2-O} + a_{H_2O}^* n(\rho^*)] \\ = a_{20}n(H)n(HO_2) + a_{17}n(OH)n(HO_2) \end{aligned} \quad (23)$$

The water vapour dissociation can be described in the mesosphere by its photodissociation and at the stratopause level by its reaction with the excited atom $O(^1D)$. H_2O is subject to a permanent transport in the mesosphere related to its photodissociation and reformation from the reaction between OH and HO_2 .

The associated equation for the hydroxyl radical is

$$\begin{aligned} \{OH\} + n(OH) [a_5n(O) + a_{17}n(HO_2)] \\ = n(H) [a_2n(O_3) + 2a_{15}n(HO_2)] + n(HO_2) [a_7n(O) + J_{HO_2}] \\ + n(H_2)a_{H_2}^* n(O^*) + n(H_2O) [J_{OH-H} + 2a_{H_2O}^* n(O^2)] \end{aligned} \quad (24)$$

The last three equations (22), (23) and (24) lead to an expression determining the mesospheric conditions:

$$\begin{aligned} <O> + \{O_3\} = <H_2O> + \{OH\} \\ + 2k_{1M}n^2(O) + 2k_3n(O)n(O_3) + 2a_5n(O)n(OH) \\ = 2n(O_2)J_2 + 2n(HO_2) [J_{HO_2} + \{a_{15} + a_{20}\}n(H)] \end{aligned} \quad (25)$$

The terms involving HO_2 can be neglected compared with the atomic oxygen production by O_2 photodissociation. Furthermore, if the photo-equilibrium conditions (low solar zenith angles) are applied to O_3 and OH, i.e. $\{O_3\} = 0$ and $\{OH\} = 0$ in equation (25), then

$$a_7n(O)n(HO_2) = a_{1M}n(O_2)n(H) \quad (26)$$

and

$$\frac{n(OH)}{n(HO_2)} = \frac{a_7}{a_5} \left[1 + \frac{a_2n(O_3)}{a_{1M}n(O_2)} \right] \quad (27)$$

while

$$\frac{n(O_3)}{n(O)} = \frac{k_{2M}n(O_2)}{J_3 + a_2n(H) + k_3n(O)} \quad (28a)$$

In applying numerical values in (28a) for a standard atmosphere, it can be seen that the ratio $n(O_3)/n(O) = 1$ near 60 km (daytime conditions), i.e. in the lower mesosphere above the stratopause level where photo-equilibrium conditions can be 9550 med for almost all aeronomic parameters. Furthermore, $k_3n(O) < J_3 + a_2n(H)$ and instead of (28a) we see that

$$n(O_3)/n(O) = k_{2M}n(O_2)/J_3 + a_2n(H) \quad (28b)$$

can be introduced into (25) giving the simple formula

$$\begin{aligned}
& \langle O \rangle + \langle H_2O \rangle \\
& + 2k_{1M} \left[1 + \frac{k_{2M}}{k_{1M}} \cdot \frac{k_3 n(O_2)}{J_3 + a_2 n(H)} \right] n^2(O) \\
& + 2 a_5 n(OH) n(O) = 2 n(O_2) J_2
\end{aligned} \tag{29}$$

This shows the action of the photodissociation of oxygen and of water vapour on the aeronomic behaviour in the mesosphere. Their photodissociation rates must be known with good accuracy.

It may be added here that the production of H_2 depends strongly on the photodissociation of H_2O . Its mesospheric distribution is given by

$$\begin{aligned}
& \langle H_2 \rangle + n(H_2) [a_{24} n(O) + a_{H_2}^* n(O^*)] \\
& = n(H) a_{23} n(HO_2) + n(H_2O) J_{H_2-0}
\end{aligned} \tag{30a}$$

or in its simplest form

$$\langle H_2 \rangle = n(H_2O) J_{H_2-0} \tag{30b}$$

i.e. a continuous production by the photodissociation of water vapour at Lyman-alpha which leads to a transport for its production peak downwards through the lower mesosphere and upwards into the thermosphere.

It should be noticed also that above the mesopause where the three-body association $H + O_2 + M$ decreases rapidly with height, the transport conditions must be considered for atomic hydrogen.

THE MESOSPHERIC PHOTODISSOCIATION OF O_2

Several difficulties occur in the determination of oxygen dissociation in the mesosphere. The first difficulty comes from the fact that the experimental absorption cross sections in the O_2 Herzberg continuum obtained before 1980 yield to an inaccurate mean value since there is a difference by a factor of 2 between the greatest and least values (see for references, Nicolet, 1983 and Bucchia et al., 1985). However, recent laboratory and theoretical determinations (Johnston, et al., 1984; Jenouvrier et al., 1986; Cheung et al., 1986; Saxon and Slanger, 1986) permits us to determine the aeronomic photodissociation of molecular oxygen between 242 and 200 nm with an acceptable accuracy (Nicolet, 1986). The various aeronomic parameters given in Table I lead to a correct value of the O_2 photodissociation frequency (Table II) and also of various photodissociation rates (Table III) for wavelengths greater than 200 nm. The recent O_2 absorption cross section determination are illustrated in figure 4. Thus, it can be concluded that the mesospheric O_2 photodissociation frequency is of the order of $5 \times 10^{-10} s^{-1}$ with a mean accuracy of about $\pm 5\%$ in the O_2 absorption cross section and an accuracy of 5 to 10% in the solar spectral irradiances. This photodissociation $J_\infty(HER) = 5 \times 10^{-10} s^{-1}$ corresponds to the mean of the extreme values indicated by Nicolet (1984), i.e.

$$J_\infty(HER) = (5 \pm 2) \times 10^{-7} s^{-1} \tag{31}$$

with an uncertainty limit of $\pm 40\%$. There is, therefore, an improvement since it seems that both systematic and random errors are not more than $\pm 10 - 15\%$.

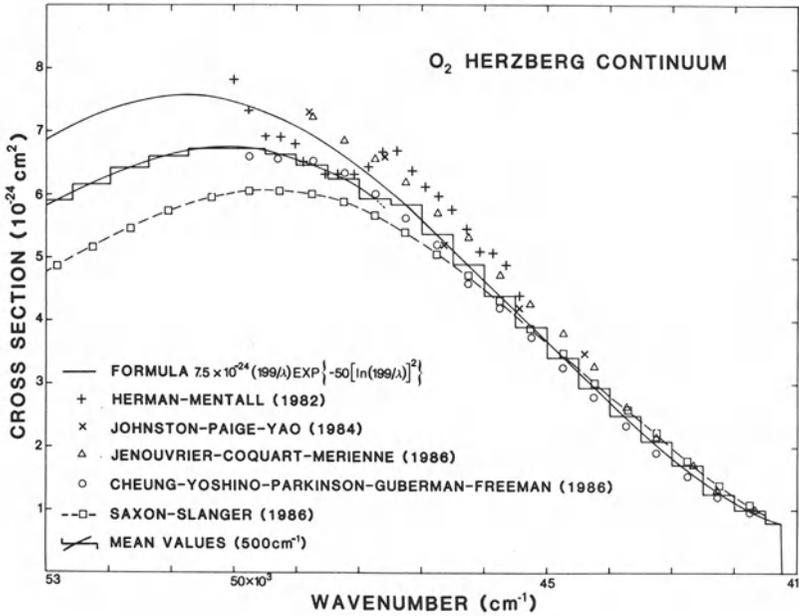


Figure 4

Recent experimental and theoretical absorption cross sections of molecular oxygen in the spectral region of the Herzberg continuum. Nicolet (1986).

Table 1. Solar spectral irradiances for $\Delta\nu=500 \text{ cm}^{-1}$ and corresponding attenuation cross sections in the spectral region of the Herzberg continuum (Nicolet, 1986).

$\nu(\text{cm}^{-1})$ (1) $\pm 250 \text{ cm}^{-1}$	$q_{\infty}(\text{cm}^{-2} \text{ s}^{-1})$ (2)	$\sigma(\text{O}_3)$ (3) (cm^2)	$\sigma_{\text{MS}}(\text{air})$ (4) (cm^2)	$\sigma(\text{O}_2)$ (5) cm^2
41250	2.04×10^{13}	9.00×10^{-18}	0.14×10^{-24}	0.80×10^{-24}
41750	1.33	7.97	0.15	1.00
42250	1.51	6.86	0.16	1.26
42750	1.26	5.79	0.17	1.73
43250	1.49	4.83	0.18	2.10
43750	1.31	4.00	0.19	2.51
44250	1.26	4.24	0.20	2.96
44750	1.52	2.55	0.21	3.42
45250	1.11	1.97	0.22	3.92
45750	1.06	1.52	0.23	4.39
46250	7.91×10^{12}	1.17	0.25	4.90
46750	8.19	8.57×10^{-19}	0.26	5.38
47250	7.12	6.50	0.27	5.84
47750	4.37	5.10	0.29	5.94
48250	2.54	4.15	0.30	6.25
48750	2.07	3.51	0.32	6.47
49250	1.69	3.18	0.34	6.63
49750	1.49	3.18	0.35	6.72

- (1) Mean wave number for spectral ranges of 500 cm^{-1} .
(2) Solar irradiances adapted from Heath (1981) and Mentall et al. (1981)
(3) Ozone absorption cross section. See details in Nicolet (1986).
(4) Molecular scattering cross section from air. Bates (1984) and Nicolet (1984).
(5) Adopted mean absorption cross section of O_2 by Nicolet (1986).

Table 2. O_2 photodissociation frequency (s^{-1}) between 242 and 200 nm in the mesosphere.

Altitude (km)	$\text{sec } \chi = 1$ $J(\text{O}_2)\text{HER}$	$\text{sec } \chi = 1.414$ $J(\text{O}_2)\text{HER}$	$\text{sec } \chi = 2$ $J(\text{O}_2)\text{HER}$	$\text{sec } \chi = 3$ $J(\text{O}_2)\text{HER}$
∞	5.06×10^{-10}	5.06×10^{-10}	5.06×10^{-10}	5.06×10^{-10}
65	5.03	5.02	5.01	4.98
60	5.00	4.97	4.93	4.87
55	4.98	4.82	4.73	4.58
50	4.62	4.45	4.23	3.89

Table 3. O₂ photodissociation rates between 242 and 200 nm in the mesosphere.

Altitude (km)	sec $\chi = 1$ (cm ⁻³ s ⁻¹)	sec $\chi = 1.414$ (cm ⁻³ s ⁻¹)	sec $\chi = 2$ (cm ⁻³ s ⁻¹)	sec $\chi = 3$ (cm ⁻³ s ⁻¹)
85	1.75 x 10 ⁴	1.75 x 10 ⁴	1.75 x 10 ⁴	1.75 x 10 ⁴
80	4.40	4.40	4.40	4.40
75	9.50	9.50	9.50	9.50
70	1.92 x 10 ⁵	1.92 x 10 ⁵	1.92 x 10 ⁵	1.92 x 10 ⁵
65	3.65	3.64	3.63	3.61
60	6.64	6.61	6.56	6.48
55	1.19 x 10 ⁶	1.18 x 10 ⁶	1.15 x 10 ⁶	1.12 x 10 ⁶
50	2.07	1.99	1.89	1.74

The second difficulty in the determination of the mesospheric photodissociation of O₂ is the calculation of the absorption of the ultraviolet radiation between 175 and 200 nm in the spectral region of the Schumann-Runge bands (see, for example, Ackerman et al., 1970; Fang et al., 1974; Kockarts, 1976; Frederick and Hudson, 1979; Lewis et al., 1978 and 1979; Nicolet and Peetermans, 1980; Allen and Frederick, 1982; Yoshino et al., 1983). In our present analysis, we have adopted the reference solar spectrum adopted recently by a working group in the World Meteorological Organization, Report no. 16 entitled "Global Ozone Research and Monitoring Project" (1985).

However, we have determined a new set of transmission functions based mainly on the cross sections of Yoshino et al. (1983). The final results show that the photodissociation frequency J_∞(SRB) for the spectral range of the Schumann-Runge bands between 175 and 200 nm is

$$J_{\infty}(\text{SRB}) = 1 \times 10^{-7} \text{ s}^{-1} \quad (32)$$

corresponding to the quiet sun conditions adopted by Nicolet (1984). This result indicates that there is now a general decrease in the observational results of the spectral solar irradiances. Finally, the results of a detailed calculation between N(O₂) = 10¹⁹ cm⁻² and N(O₂) = 10²² cm⁻² i.e. in the mesosphere depicted in Figure 5 for temperatures between 180 K (mesopause) and 270 K (stratopause) can be represented with a precision better than ± 10% by the formula:

$$J_{\text{SRB}}(\text{O}_2) = 3 \times 10^7 / N^{0.795} \text{ s}^{-1} \quad (33)$$

The roles of the two spectral regions 240 - 200 nm and 200 - 175 nm in the mesospheric photodissociation of O₂ are shown in Figure 6. At the mesopause (85 km), it can be seen that more than 90% of J(O₂) depend on the predissociation in the Schumann-Runge bands. At the stratopause (50 km), the role of the Herzberg continuum increases since J_{SRB}(O₂) reaches only 30% for an overhead sun. Nevertheless, it is important to note that these estimates based on more recent data give

$$J(\text{O}_2)_{85 \text{ km}} = 1.5 \times 10^{-8} \text{ s}^{-1}, \quad (34)$$

for the total photodissociation frequency at 85 km for an overhead sun decreasing to

$$J(\text{O}_2)_{50 \text{ km}} = 6.75 \times 10^{-10} \text{ s}^{-1} \quad (35)$$

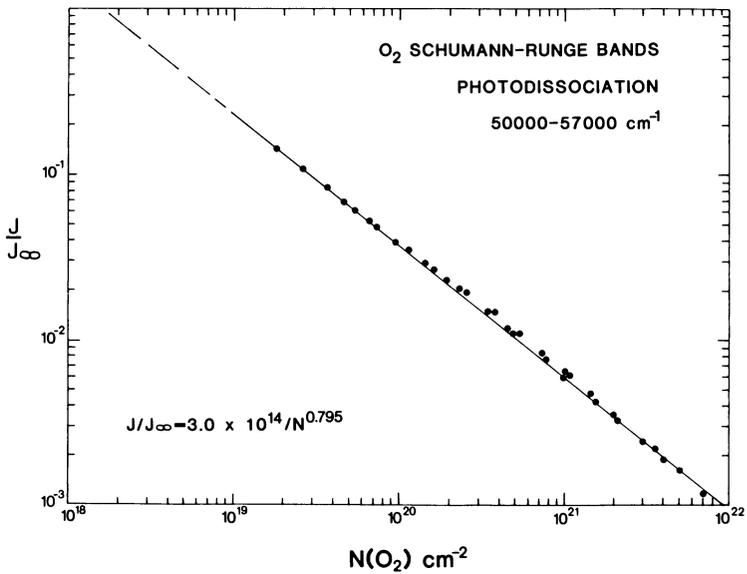


Figure 5

Relative photodissociation frequency of O₂ in the mesosphere for the spectral interval 175-200 nm corresponding to the Schumann-Runge bands. Standard solar spectral irradiances conditions and temperatures varying from 180 K (mesopause) to 270 K (stratopause).

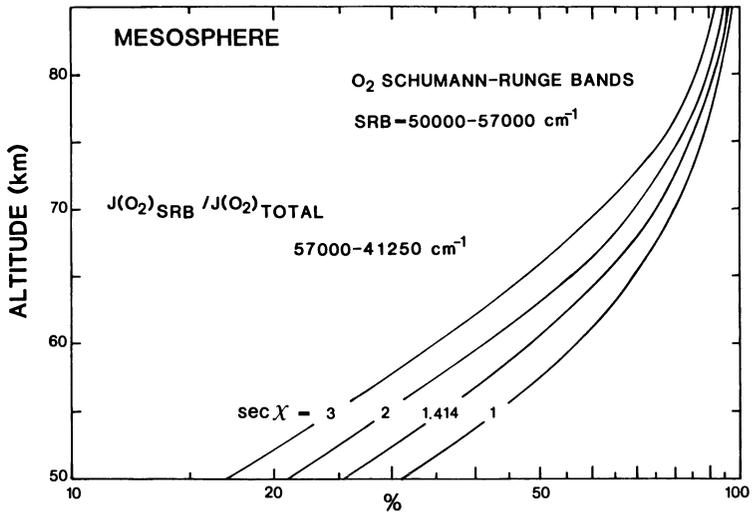


Figure 6

Ratios of the O₂ photodissociation rates in the Schumann-Runge bands interval (175-200 nm) to the total spectral range (175-242 nm) in the mesosphere.

at 50 km again for an overhead sun. These values correspond to the total O_2 photodissociation rates depicted in Figure . At the mesopause

$$2 \times 10^5 \leq n(O_2)J(O_2) \leq 5 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1} \quad (36)$$

for solar zenith angles χ in the range of $3 \leq \sec \chi \leq 1$, and at the stratopause the photodissociation rate is between 2 and $3 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ for the same solar conditions. The detailed values show that the Rayleigh scattering and the ozone absorption do not play any role for a total number of O_2 molecules less than $3 \times 10^{21} \text{ cm}^{-2}$, i.e. at and above 60 km.

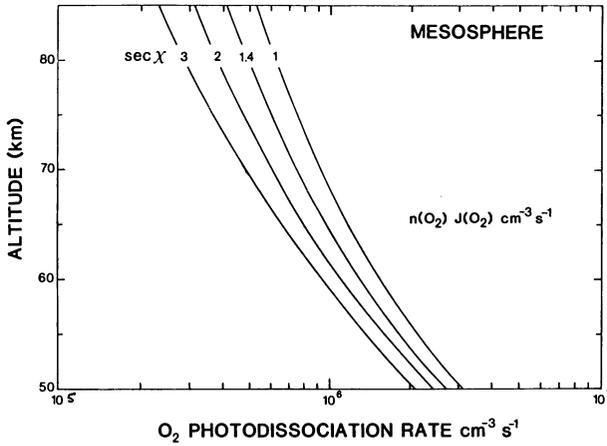


Figure 7

O_2 photodissociation rates ($\text{cm}^{-3} \text{ s}^{-1}$) in the mesosphere for various solar zenith angles.

At 55 km, their effects for various solar angles ($\sec \chi = 1$ to 4) is always less than 2% and at the stratopause (50 km); each effect is still less than 2% for solar zenith angles less than 60° but can reach 3 to 6% for $\sec \chi = 3$ and 4. Thus, the mesospheric transmittance is related only to the absorption of molecular oxygen.

Finally, since the atomic oxygen production between 50 and 60 km is of the order of $2 - 5 \times 10^6 \text{ atoms cm}^{-3} \text{ s}^{-1}$, it is clear that, in less than 10^4 seconds, the observed O_3 concentration observed in this region can be produced. It is, therefore a region of photochemical equilibrium where the aeronomic (calculated and measured) parameters should agree without the introduction of a transport effect.

Nevertheless, it is possible to consider the possibility of other dissociation processes in the mesosphere. The first additional process is related to the hydrogen Lyman-alpha radiation which reaches the middle mesosphere and will be discussed in connection with the photodissociation of water vapour. As far as the photodissociations of $^{16}O^{18}O$ molecules or of $O_2(^1\Delta_g)$, proposed by Cicerone and McCrumb (1980) and Frederick and Cicerone (1985) respectively, are concerned, they cannot constitute significant sources of atomic oxygen (see, for example, Blake et al., 1984, and Simonaitis and Leu, 1985, respectively). The $^{16}O^{18}O$ molecules cannot give more than $3 \pm 1\%$ of the $^{16}O_2$ production of oxygen atoms at mesopause levels near 70 ± 10 km. Again the absorption from $O_2(^1\Delta_g)$ is far too small to produce enough oxygen atoms.

THE SOLAR H LYMAN-ALPHA LINE

Besides causing photoionization of NO, Lyman-alpha radiation can also cause photodissociation of H_2O , CH_4 , CO_2 and O_2 . The experimental data obtained by Lewis et al. (1983) have been adopted by Nicolet (1985) to determine the aeronomic parameters for an analysis of the photodissociation processes in the mesosphere.

In the case of Lyman-alpha, it is necessary to take into account the variation with wavelength of the O_2 absorption cross section and of the profile of the solar line simultaneously. Both are illustrated in Figure 8. The variation of the solar H Lyman-alpha line, i.e. of the source function defined by $q_{i, Ly\alpha}(\Delta\lambda = 0.1\text{\AA})/q_{\infty, Ly\alpha}(\Delta\lambda = 3.5\text{\AA})$, for increasing number of O_2 molecules, is shown with its deformation for $N(O_2) = 0, 10^{19}, 10^{20}, 2.2 \times 10^{20}, 5 \times 10^{20}$ and 10^{21} cm^{-2} , i.e. from above the mesopause to 60 km for overhead sun. The ratios $q(Ly\alpha)/q_{\infty}(Ly\alpha)$ are also given for the various profiles; the effective transmittance of the H Lyman-alpha irradiance varies from 0.9 for $N(O_2) = 10^{19} \text{ cm}^{-2}$ to 2.4×10^{-4} for $N(O_2) = 10^{21} \text{ cm}^{-2}$, i.e. a decrease by a factor of about 10^4 . For that reason the calculations have not been extended beyond an optical thickness of 10. The numerical results show that the effect of temperature ($230 \pm 40\text{K}$) is not important for $N(O_2) < 10^{20} \text{ cm}^{-2}$. Nevertheless, the adoption of a reference temperature of 230 K, adjusted by ± 20 K for $N(O_2) > 10^{20} \text{ cm}^{-2}$ leads to the following simple expression $T_{O_2}(Ly\alpha)$ with an accuracy better than $\pm 2\%$,

$$T_{O_2}(Ly\alpha) = q(Ly\alpha)/q_{\infty}(Ly\alpha) = \exp [-2.155 \times 10^{-18} N^{0.8855}] \quad (37)$$

Figure 9 shows how the effective optical depth increases from 0.1 to 10 as the total number of O_2 absorbing molecules increases from 10^{19} to 10^{21} cm^{-2} .

In aeronomic work it is necessary to know with great accuracy the absolute value of the irradiance of H Lyman-alpha and how this varies during the solar cycle. The question will not be discussed here and we will adopt $3 \times 10^{11} \text{ photons cm}^{-2} \text{ s}^{-1}$ as a conventional value considering that the irradiance for a very quiet sun cannot be less than $2 \times 10^{11} \text{ photons cm}^{-2} \text{ s}^{-1}$ and for an active sun cannot be more than $5 \times 10^{11} \text{ photons cm}^{-2} \text{ s}^{-1}$.

Since the absorption near Lyman-alpha by oxygen depends on both temperature and wavelength, the photodissociation frequency $J_{Ly\alpha}(O_2)$ defined by

$$J_{Ly\alpha}(O_2) = \sigma_D(O_2)q_{\infty}(Ly\alpha)e^{-\tau_q(O_2)} \quad (38)$$

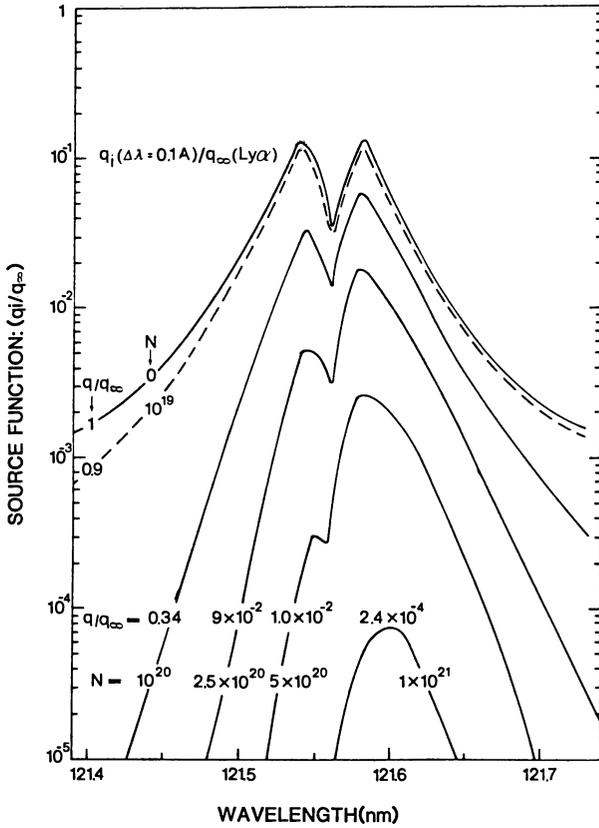


Figure 8

Variation of the profile of the solar H Lyman-alpha line with its penetration into the mesosphere. Six curves from $N(O_2)=0$ to $N(O_2) = 10^{21} \text{ cm}^{-2}$ show the deformation of the profile and the corresponding decrease of the transmittance.

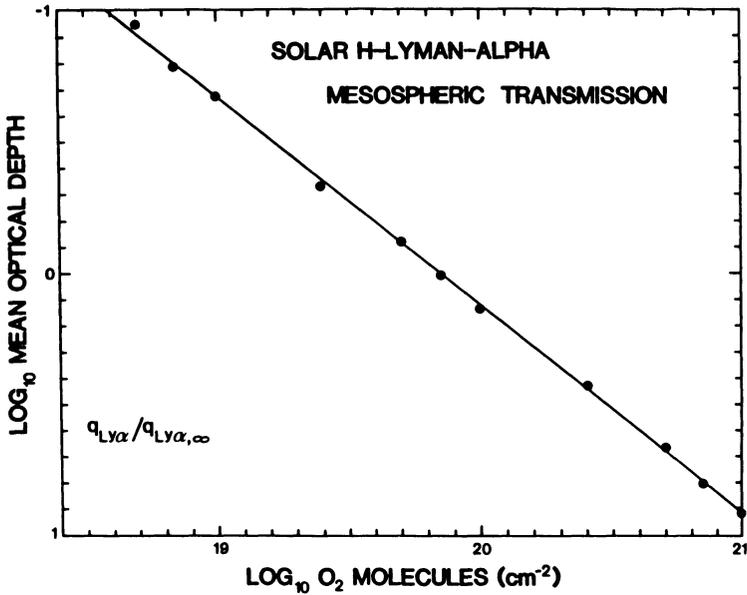


Figure 9

Mesospheric absorption of the solar H Lyman-alpha radiation represented by its effective optical depth. The straight line is obtained from the formula, equation (37), for $T = 230$ K.

is determining using a complete and detailed expression based on intervals of 0.1Å. With the conventional value $q_{\infty}(\text{Ly}\alpha) = 3 \times 10^{10}$ photons $\text{cm}^{-2} \text{s}^{-1}$, the O_2 photodissociation frequency at the top of the earth's atmosphere and for the mean distance between the Sun and the Earth is

$$J_{\text{Ly}\alpha, \infty}(\text{O}_2) = 3.8 \times 10^{-9} \text{ s}^{-1} \quad (39)$$

and the ratio (see Figure 10) as

$$J_{\text{Ly}\alpha}(\text{O}_2)/J_{\text{Ly}\alpha, \infty}(\text{O}_2) = \exp [-4.923 \times 10^{-17} N^{0.8216}] \quad (40)$$

If equation (40) is used in conjunction with the result obtained in equation (23), the effective absorption-photodissociation cross-section $\sigma_{\text{D}}(\text{O}_2)$, (equation 38), is

$$\sigma_{\text{D}}(\text{O}_2)_{\text{Ly}\alpha} = 1.15 \times 10^{-18} / N^{0.1175} \text{ cm}^2 \quad (41)$$

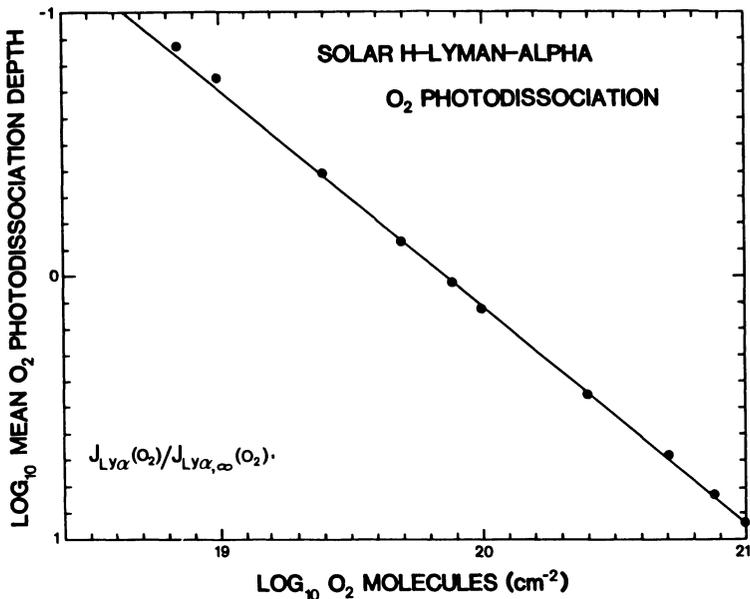


Figure 10

Equivalent optical depth of the O₂ photodissociation frequency expressed here as a "mean photodissociation depth" from 0.1 to 10 vs the total number of molecules. The straight line is obtained from formula, (equation 40), for T = 230 K.

A calculation based on these formulas shows that the O₂ photodissociation frequency due to Lyman-alpha is 10⁻⁹ s for N(O₂) = 10²⁰ cm⁻², i.e. increases by 25% the total photodissociation frequency between 75 km (overhead sun) and 80 km (solar zenith angle = 60°) resulting from the absorption between 175 and 242 nm. Thus, Lyman alpha plays a role in the photodissociation of O₂ in the upper mesosphere, and the photodissociation rates depicted in Figure 7 must be increased by about 25% when the Lyman alpha solar irradiance is 3 x 10¹¹ photons cm⁻²s⁻¹, and N(O₂) = 10²⁰ cm⁻².

THE PHOTODISSOCIATION OF WATER VAPOUR.

If the H₂O absorption cross section is based on the laboratory measurements of Lewis et al. (1983) with a constant mean value

$$\sigma_{D,Ly\alpha}(H_2O) = (1.57 \pm 0.05) \times 10^{-17} \text{ cm}^2 \quad (42)$$

the photodissociation of H₂O at Lyman-alpha (see successive analyses by Nicolet, 1981, 1984, 1985) can be found with a precision of about ± 3%. With the commonly used value q_∞(Lyα) = 3 x 10¹¹ photons cm⁻² s⁻¹ the photodissociation frequency at the top of the earth's atmosphere is

$$J_{\text{Ly}\alpha, \infty}(\text{H}_2\text{O}) = 4.7 \times 10^{-6} \text{ s}^{-1} \quad (43)$$

and the mesospheric distribution of the photodissociation is, (37),

$$J_{\text{Ly}\alpha}(\text{H}_2\text{O}) = 4.7 \times 10^{-6} \exp [-2.115 \times 10^{-18} N^{0.8855}] \quad (44)$$

where N is the total number of O_2 molecules determining the atmospheric transmittance.

Below the mesopause at 75 km (overhead sun) or 80 km (solar zenith angle = 60°), the photodissociation life time of water vapour due to the action of H Lyman-alpha is less than 200 hours, since

$J_{\text{Ly}\alpha}(\text{H}_2\text{O}) = 1.6 \times 10^{-6} \text{ s}^{-1}$ for $N(\text{O}_2) = 10^{20} \text{ cm}^{-2}$. It is clear that such a short life time must produce a decrease of the H_2O mixing ratio; the reaction (15) between OH and HO_2 cannot counterbalance production of H_2O its destruction by photodissociation and the transport conditions cannot provide an adequate support.

The hydrogen production (9) related to this H_2O photodissociation by Lyman-alpha may be of the order of $10^3 \text{ H}_2 \text{ molecules cm}^{-3} \text{ sec}^{-1}$ and that due to the reaction (18) $\text{H} + \text{HO}_2$ a value of the same order of magnitude.

The photodissociation of H_2O in the region of the Schumann-Runge bands is difficult to determine with precision since the solar flux and the H_2O absorption cross section are not known accurately enough. In addition, the transmittance of each O_2 Schumann-Runge band is very sensitive to the temperature. A general uncertainty of about a factor of 2 at the stratopause level is inherent in the various input data. We can say that, for a fixed solar spectral irradiance, it is possible to reach the following uncertainty limits: not more than $\pm 10\%$ at $N(\text{O}_2) = 10^{19} \text{ cm}^{-2}$, $\pm 20\%$ at $N(\text{O}_2) = 10^{20} \text{ cm}^{-2}$, $\pm 50\%$ at $N(\text{O}_2) = 10^{21} \text{ cm}^{-2}$ and reaching a factor of about 2 at $N(\text{O}_2) = 10^{22} \text{ cm}^{-2}$. A linear fit to the values of the variation of $\ln(J_{\text{H}_2\text{O}}/J_{\infty})_{\text{SRB}}$ can be obtained and provides an estimation of the photodissociation of H_2O in the mesosphere. This approximation is

$$J_{\text{SRB}}(\text{H}_2\text{O}) = 2 \times 10^{-6} \exp [-3.52 \times 10^{-5} N^{0.2412}] \quad (45)$$

Below the mesopause at 75 km (overhead sun) or 80 km (solar zenith angle = 60°), the photodissociation frequency $J_{\text{SRB}}(\text{H}_2\text{O})$ would be of the order of $1.9 \times 10^{-7} \text{ s}^{-1}$, i.e. about 10 times less than photodissociation by Lyman-alpha.

In any case, the photodissociation at 75 km and above is the leading aeronomic process determining the vertical distribution of water vapour in the upper mesosphere and lower thermosphere. At the stratopause level, the H_2O photodissociation frequency in the 200-175 nm region is less than 10^{-8} s^{-1} , and the reaction $\text{O}(\text{^1D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$ must be introduced.

Recent observations of the water vapour concentrations in the mesosphere (see for example Figure 11) described recently by Laurent et al. (1986) show that we must recognize that any estimate of the aeronomic behaviour of water vapour and its various products in the mesosphere based on available measurements and present theoretical determinations is still too uncertain. More atmospheric observations and laboratory experiments with permanent spectral solar irradiances are needed together with general improvement of the accuracy of the various aeronomic parameters.

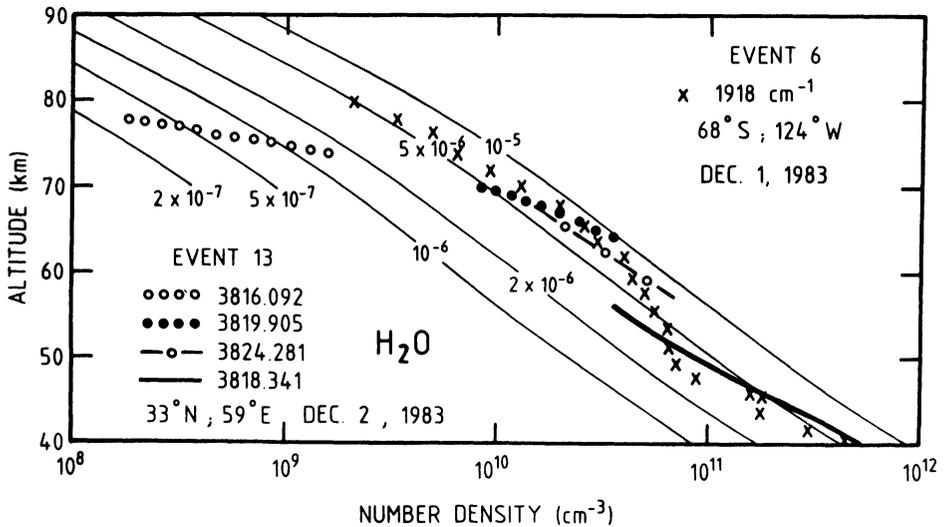


Figure 11

Observed vertical distributions of water vapour concentrations as a function of altitude at sunrise (event 6) and at sunset (event 13) by the Spacelab one grille spectrometer (see details in Laurent et al., 1986).

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