The influence of solar radiation on atmospheric chemistry (*)

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ABSTRACT. Analysis of the penetration into the terrestrial atmosphere of solar UV radiation of wavelengths greater than 100 nm indicates that a certain number of physical parameters playing an important role in atmospheric chemistry are not yet known with sufficient accuracy. Solar UV fluxes are not known with the precision that is required for the photolysis rates particularly when the oxygen absorption exhibits complex pressure and temperature dependencies. Observed Lyman- α irradiances show clearly various trends due to instrumental drifts and differences due to systematic errors in the absolute fluxes.

The atmospheric transmissivity depends on the absorption of O_2 and O_3 which control exclusively the penetration of solar UV radiation above 100 nm. A precision better than $\pm 10\%$ in the transmissivity requires a knowledge of the atmospheric optical depth with a precision better than ± 0.1 . A critical analysis of the various absorption cross-sections used in the standard models leads to a clear indication of various deficiencies in different spectral regions and to an estimate of the possible uncertainty in the experimental measurements in several cases. Further experimental and theoretical data are needed to determine the correct atmospheric transmissivity and the exact influence of solar radiation on atmospheric chemistry.

Key words : solar radiation, atmospheric chemistry.

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INTRODUCTION

At all levels in the atmosphere (troposphere, stratosphere, mesosphere and thermosphere) the chemistry depends essentially on action of the solar radiation. It is necessary first to know the absolute value of the solar spectral irradiance with sufficient accuracy. Second, the variation of the ultraviolet radiation with solar activity must be determined as a function of wavelength. Finally, the changes that the UV radiation undergoes as it passes through the atmosphere must be specified in terms of the various atmospheric parameters.

At present, it must be admitted that there are several outstanding problems and that much work remains to be done before it will be possible to understand completely the chemistry of the atmosphere at all levels.

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THE ULTRAVIOLET SPECTRAL IRRADIANCE

Although the total solar irradiance (solar constant) can be measured with great accuracy from satellites, this is not the case for spectral irradiance in the UV above 100 nm. The best calibrations give an accuracy of better than ± 10 %, but comparisons between different sets of observations that have been regarded as satisfactory reveal differences of ± 20 %. If a reexamination is made of the rocket observations of the past 10 years (e.g. Simon, 1981), it is found that, in certain cases, there are differences of as much as a factor of 2. As shown in figures 1 and 2, recent values obtained using satellites and rockets (Heath, 1981; Mentall *et al.*, 1981; Mount and Rottman, 1983) have mean values at 1 nm which differ by as much as 10 %.

The values of Mount and Rottman are systematically greater than those of Mentall *et al.* between 200 and 300 nm, while those of Mentall *et al.* are consistently less than those of Heath between 200 and 250 nm. If a comparison is made between the data of Heath and those of Broadfoot (1972), it can be seen that there are systematic differences ranging from a ratio of 1.4, at 210 nm, down to 0.9 at 310 nm, but both spectral irradiances are identical at 290 nm (figs. 3, 4).

The differences mentioned above are due ultimately to the difficulties of making accurate measurements, and

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Figure 1

Comparison of mean spectral irradiances in a 1 nm band-width between 200 and 255 nm. The values of Mentall et al. (1981) are compared with those of Heath (1981), and those of Mount and Rottman (1983) with those of Mentall et al. (1981).



Figure 2

Comparison of mean spectral irradiances from 255 to 310 nm. Continuation of figure 1.



Figure 3

Comparison of mean spectral irradiances between 210 and 260 nm in a 1 nm bandwith. The values of Broadfoot (1972) are compared with those of Heath (1981).

are quite unconnected with changes in solar activity. Figure 5, published by Heath (1981), is based on the 27-day variations in solar activity. It shows that the effect first seems to appear between 250 and 260 nm, that, as already known, it becomes clear at 210 nm, and that it continues to increase with decreasing wavelength. However, one of the problems encountered in making satellite observations of the UV spectrum is that of the degradation of the measuring instruments with time. This results in a drift in the observed irradiance values which is clearly shown in figures 6a and 6b.



Figure 4 Comparison of spectral irradiances between 260 nm and 315 nm. Continuation of figure 3.

At 280 nm, fluctuations of about $\pm 2\%$ can be seen; at 205 nm there is a systematic decrease with time instead of the expected increase due to the increase in solar activity. These results can certainly be attributed to a deterioration of the instrument which varies with wavelength. A recent study by Bossy and Nicolet (1981), based on observations of Lyman-alpha between 1969 and 1982, illustrates how difficult it is to obtain values that are sufficiently good for making atmospheric studies (fig. 7). It has been pointed out by Nicolet (1983) that even the most careful calibrations do not give great enough accuracy. For a quiet sun, the Lyman-alpha irradiance is given by :

$$F_{\rm Ly-\alpha} = (3 \pm 0.75) \times 10^{11} \, \rm photons \, \rm cm^{-2} \, \rm sec^{-1}$$
,

that is, with an accuracy of about $\pm 25-30$ %. Although the points plotted in figure 7 seem to suggest a variation by a factor of 5 between minimum and maximum solar activity, the analysis of the data carried out by Bossy and Nicolet (1981 and in press) show that :

$$F_{Ly-\alpha} = 3 \times 10^{11} \left(1 + 0.2 \frac{F_{10.7} - 65}{100} \right)$$

photons cm⁻² sec⁻¹

where $F_{10.7}$ cm is the solar radio flux at 10.7 cm, and that the $E_{Ly-\alpha}$ does not vary by more than a factor of 2 during the solar cycle.

In consequence, it is necessary to adopt a very critical attitude towards any study of atmospheric chemistry that has been based on the assumption of very large variations in solar activity.

In the absence of better information, Nicolet (1981) has given, in his table 4, the values of solar irradiance to be adopted for the Schumann-Runge O_2 bands from 200 to 175 nm, while table 8 gives the values for the Herzberg continuum of O_2 between 200 and 242 nm, and for the Hartley O_3 band to 305 nm; these data are the same as those used in the NASA-WMO Workshop at Hampton, Virginia, in 1981. However, it must not be assumed that all the values in the two tables have the same accuracy. For example, a comparison of the results for a spectral range of 1 nm at 291 nm obtained by Broadfoot (1972), Heath (1981), Mentall *et al.* (1981) and Mount and





Data taken from Heath (1981). Upper diagram : Spectral irradiances on 7 November 1978. Black body curves from 5 770 K to 4 500 K indicating the decrease of the radiation temperature with decreasing wavelength. Lower diagram : This illustrates the effect of solar activity for 27-day periods; it may begin near 250 nm, is quite distinct at 210 nm and continues to increase beyond 170 nm.



Figure 6a

Variations with time of spectral irradiances at 181.6 nm, 205 nm and 280 nm according to Heath (1981).



Figure 6b

Ratio of the spectral irradiances, as a function of wavelength, at the beginning and end of the 10-month period between 7 November 1978 and 23 August 1979, according to Heath (1981). Although solar activity was greater on 23 August 1979 (radioflux at 10.7 cm about 220 units) than on 7 November 1978 (radioflux about 175 units) there is a decrease in the ratio instead of the expected increase. This is due to an instrumental deterioration. This decrease in the ratio, which begins between 3 600 and 3 100 A, becomes more important and is most pronounced (-10%) at 2 050 A, whereas an increase of several percentage points would have been expected.

Rottman (1983) shows that exactly the same value was found by the four groups : 8.9×10^{10} cm⁻² sec⁻¹; but at 290 nm, there are differences of as much as 15 %. The reason for this is that mean values based on measurements made using different spectral resolutions are influenced by errors in the determination of the wavelength, and by important variations in the intensity as a function of wavelength, as well as by errors of measurement. Figure 8, taken from Kohl *et al.* (1978) shows the specific mean intensity at the centre and the limb of the Sun's disc, and it is clear that there are pronounced variations in intensity with wavelength, even over



Figure 7

Irradiance at Lyman- α observed between 1969 and 1982. The large scatter of the points is due to inaccuracies in the absolute values as well as to specific differences for same levels of solar activity. For references, see Nicolet (1983).



Figure 8

The mean specific intensity of solar radiation as a function of wavelength averaged over intervals of 0.5 nm. Upper curve, centre of disc, $\mu = 1$, Lower curve : near the limb, $\mu = 0.23 \pm 0.04$ (Kohl et al., 1978).

intervals of 0.5 nm. The accuracy of a measured spectral irradiance value must depend on how close the measurement was made to one of the intense Fraunhofer lines. However, it must be admitted that, in the context of atmospheric applications, the absorption of O_2 and O_3 is continuous, and that positive and negative errors may cancel each other out. Only absolute global values may be considered.

It is concluded that the absolute value of the solar flux in the UV is not known to better than $\pm 10 \%$, or to $\pm 20 \%$ in certain parts of the spectrum. Comparisons of the most recent results tend to show that differences of $\pm 10 \%$ are normal at wavelengths above 200 nm. Above 200 nm, variations in solar activity must be taken into account from 210 nm, and perhaps also from 250 nm, in any assessment of the accuracy of flux measurement.

TRANSMISSION OF SOLAR RADIATION THROUGH THE ATMOSPHERE

Absorption by oxygen and ozone

UV radiation at wavelengths above 100 nm is absorbed by molecular oxygen up to 240 nm, and by ozone beyond 320 nm.

The absorption spectrum of oxygen is characterised below the first photodissociation limit at 242 nm by the Herzberg continuum, from 200 nm by the predissociation bands of the Schumann-Runge system, from 175 nm by the Schumann-Runge continuum, and finally at 121.6 nm by the presence of Lyman-alpha radiation of hydrogen.

The ozone absorption spectrum that begins with the Hartley band extends from about 310 nm to shorter wavelengths; this is followed by the Huggins bands at wavelengths greater than 300 nm, and finally the Chappuis bands in the visible region.

It is the O_2 and the O_3 molecules which control the penetration of solar radiation into the atmosphere at wavelengths greater than 100 nm.

The absorption cross-section of oxygen varies greatly as a function of wavelength. In the Herzberg continuum, the absorption is very weak; the effective cross-section is less than 10^{-23} cm² and is not more than 10 times that due to Rayleigh scattering in the atmosphere. Then the predissociation Schumann-Runge bands, with their rotational structure, are responsible for variations of the effective cross-section which depend on the temperature and on the total number of absorbing O_2 molecules. In the Schumann-Runge continuum, the effective cross-section is very high and reaches 10^{-17} cm² near 150 nm. Hence the absorption coefficient varies by a factor of 10⁶ between the minimum at 200 nm and the maximum at 150 nm; thus it refers to a 100 km deep section of the atmosphere extending from the thermosphere to the lower stratosphere.

The absorption of Lyman-alpha at 121.6 nm occurs in an atmospheric window between two oxygen absorption bands; the effective cross-section is not greater than 10^{-20} cm² and corresponds to conditions in the meso-sphere.

Absorption by molecular oxygen

The Herzberg continuum

The data used for studies of oxygen absorption in the Herzberg continuum below 242.4 nm are based on the measurements made at relatively high pressures by Ditchburn and Young (1962); Ogawa (1971); Hasson and Nicholls (1971) and Shardanand and Prasad Rao (1977); these data are then extrapolated to give low pressure values applicable to the stratosphere. However, a mean value based on these experimental values is not sufficiently accurate (Nicolet, 1979) because there is a difference, by a factor of 2, between the minimum and the maximum values. The values of Shardanand and Prasad Rao were deduced by extrapolation, from pressures of 1 to 25 atmospheres, of measurements made in tubes of length 10, 50, 200 and 300 cm; they are the lowest values obtained in the region 240 nm to 200 nm. The spectral range below 200 nm includes the predissociation bands of the Schumann-Runge system. Its role has been studied theoretically by Jarmain and Nicholls (1967) and their curve has been calibrated, in terms of absolute values, by using some experimental data obtained by Ditchburn and Young (1962), as shown in figure 9. If the data of Shardanand and Prasad Rao (1977) are used to calibrate the theoretical curve, the maximum obtained at 195 nm is 10⁻²³ cm² instead of 1.3×10^{-23} cm² (fig. 10). Thus the modified curve shows a difference of 30 % (1.3/l) as already indicated by Blake (1979).

It is important to point out that, in their studies of atmospheric absorption in the Schumann-Runge bands, all the authors (Ackerman *et al.*, 1970; Hudson and Mahle, 1972; Fang Wofsy and Dalgarno, 1974; Kockarts, 1976; Nicolet and Peetermans, 1980; Frederick and Hudson, 1980*a*, *b*) used the theoretical values of Jarmain and Nicholls which are too high.

It should be added that the calibration of the theoretical curve using the latest experimental data does not guarantee the accuracy of the effective cross-section of O_2 in the Herzberg continuum. The experimental values have been extrapolated from very high pressures at laboratory temperatures. Thus it is possible that the theoretical values ought to be reduced by a factor of 2 before they are used in studies of atmospheric chemistry. However, in this case it is absolutely necessary to take into account the effect of Rayleigh scattering which must be associated with the absorption of solar radiation near 200 nm. Figure 9 illustrates the various experimental and theoretical considerations described above. As can be seen, given a considerable reduction in the absorption cross-section of O₂, and taking account of Rayleigh scattering, it is possible to account for the observational results obtained by Frederick and Mentall (1982) and Hermann and Mentall (1982) in the region 200-220 nm.

The Schumann-Runge bands

The structure of the predissociation bands of the Schumann-Runge system has been studied experimentally (Biaumé, 1972; Frederick and Hudson, 1979; Lewis *et al.*, 1978, 1979, 1980; Gies *et al.*, 1981; Yoshino



Figure 9

Experimental and theoretical values of the absorption cross-section in the Herzberg continuum of O_2 . The extreme experimental values differ by a factor of 2. If absorption due to atmospheric Rayleigh scattering is taken into account, the theoretical value of Jarmain-Nicholls could be reduced by a factor of 2 to account for the observational cross-sections deduced by Herman-Mentall and Frederick-Mentall.

et al., 1983) in order to determine the oscillator strength of each band and also the width of the rotational lines. These two parameters must be known if calculations are to be made of how the effective cross-section varies with temperature and wavelength. Such calculations are necessary for the determination of the effective absorption in the atmosphere, which depends on the vertical temperature distribution and on the total number of oxygen molecules absorbing the solar radiation. Thus it is necessary to take account also of the overall decrease in absorption, by a factor of about 10⁵ between 175 and 205 nm, arising from the Franck-Condon effect and of variations within the same band of up to 100/1. Table 1 illustrates the differences between earlier oscillator strengths and the more accurate values of Yoshino et al. (1983). But the problem that still remains is that of the exact width of the predissociation lines from (1-0) to beyond (18-0). Table 2 quotes various numerical





Adjustment of the theoretical curve for absorption cross-section (Jarmain and Nicholls, 1967) to fit the more recent experimental values (Shardanand and Prasad Rao, 1977). The absorption cross-section of O_3 is also shown in order to emphasise the importance of precise experimental values at 210 ± 20 nm where solar radiation penetrates easily into the stratosphere.

Table 1

Oscillator strengths of the system of the Schumann-Runge of molecular oxygen.

Band	Yoshino <i>et al.</i> 1983	Lewis <i>et al.:</i> 1978-1979	Gies <i>et al.</i> 1981	Frederick and Hudson 1979-1980	Hudson and Mahle 1972	Allison <i>et al.</i> 1971
1-0	$3.15 \pm 0.32 \times 10^{-9}$				3.05×10^{-9} (0.97)	3.31×10^{-9} (1.05)
2-0	$1.89 \pm 0.19 \times 10^{-8}$	$2.26 \pm 0.05 \times 10^{-8}$		$2.77 + 0.07 \times 10^{-8}$	2.7×10^{-8}	2.03×10^{-8}
		(1.20)		(1.47)	(1.43)	(1.07)
3-0	8.45 ± 0.42	9.7 ± 0.2		7.51 + 0.13 - 0.09	7.1	8.62
		(1.15)		(0.89)	(0.84)	(1.02)
4-0	$2.82 \pm 0.14 \times 10^{-7}$	$2.65 \pm 0.05 \times 10^{-7}$		$3.04 + 0.02 \times 10^{-7}$	2.5×10^{-7}	2.86×10^{-7}
		(0.94)		(1.08)	(0.89)	(1.01)
5-0	7.42 ± 0.37	7.7 ± 0.2		7.39 + 0.90	6.1	7.87
		(1.04)		(1.00)	(0.82)	(1.06)
6-0	$1.62 \pm 0.08 \times 10^{-6}$	$1.74 \pm 0.03 \times 10^{-6}$		$1.62 + 0.05 \times 10^{-6}$	1.7×10^{-6}	1.85×10^{-6}
		(1.07)		- 0.03	(1.05)	(1.14)
7-0	3.43 ± 0.17	3.73 ± 0.07	$3.68 \pm 0.10 \times 10^{-6}$	3.15 + 0.10	3.5	3.75
		(1.09)	(1.07)	- 0.07 (0.92)	(1.02)	(1.09)
8-0	6.31 ± 0.32	7.32 ± 0.15	6.92 ± 0.20	5.78 + 0.04	6.0	6.71
		(1.16)	(1.10)	(0.92)	(0.95)	(1.06)
9-0	$1.00 \pm 0.05 \times 10^{-5}$	$1.28 \pm 0.04 \times 10^{-5}$	$1.13 \pm 0.05 \times 10^{-5}$	$1.04 + 0.36 - 0.20 \times 10^{-5}$	1.0×10^{-5}	1.08×10^{-5}
		(1.28)	(1.13)	(1.04)	(1.00)	(1.08)
10-0	1.54 ± 0.08	1.77 ± 0.03	1.52 ± 0.04	1.60 + 0.47	1.6	1.58
		(1.15)	(0.99)	(1.04)	(1.04)	(1.03)
11-0	$2.26 \pm 0.11 \times 10^{-5}$	$2.50 \pm 0.05 \times 10^{-5}$	$2.16 \pm 0.05 \times 10^{-5}$	1.80 + 0.53	1.7×10^{-5}	2.14×10^{-5}
		(1.11)	(0.96)	(0.80)	(0.75)	(0.95)
12-0	2.43 ± 0.12	3.13 ± 0.07	2.74 ± 0.06	2'09 + 0.08	2.5	2.67
		(1.29)	(1.13)	(0.86)	(1.03)	(1.10)
13-0		3.48 ± 0.10	2.87 ± 0.12	2.69 + 0.36		3.07
14-0		4.22 ± 0.10	3.21 ± 0.14	(3.25)		3.25
15-0			2.95 ± 0.12	(3.18)		3.18
16-0			2.63 ± 0.08	(2.93)		2.93
17-0			2.64 ± 0.15	(2.56)		2.56
18-0			2.14 ± 0.15	(2.09)		2.09

() is the ratio to values of column 2.

values; these illustrate the present difficulties that are met in obtaining accurate line widths, and which arise from insufficient resolving power. The lack of accuracy leads to errors in studies of the atmosphere, because it is necessary to take account of the effect of low atmospheric temperatures on the rotational structure, and how this affects the determination of optical thicknesses greater than unity.

Although the oscillator strengths make it possible to compare the overall absorption in the various bands, the amount of predissociation determines the type of absorption in each band, and thus the optical thickness in the atmosphere as a function of wavelength. Judging from tables 1 and 2, it must be admitted that the experimental data do not have the required accuracy. For example, Frederick and Hudson (1979b) found that the oscillator strengths for the bands (2-0) and (12-0) were 2.77×10^{-8} and 2.9×10^{-5} respectively, but the values given by Yoshino *et al.* (1983) are very different : 1.89×10^{-8} and 2.43×10^{-5} , respectively.

Thus, it can be seen that, in addition to the problem of the continuum associated with the Schumann-Runge bands, there is also the question of the width of the rotational lines. It is for this reason that, in any atmospheric study, all the relevant information must be examined at the same time.

Depending on whether an investigation refers to the mesosphere, the stratosphere or the troposphere, the uncertainties will have effects that are quite different. At the level of the mesopause, the bands (19-0) to (15-0) have effects of the same order of magnitude as the other groups : (14-0) to (10-0), (9-0) to (6-0) and (5-0) to (2-0), but at 60 km their effects are negligible even for an overhead sun.

Table 2 Mean line width of the O_2 Schumann-Runge bands.

Band	Hudson and Mahle (1972)	Lewis <i>et al.</i> (1978)	Frederick and Hudson (1979-1980)	Gies <i>et al.</i> (1981)
0-0	(0.001)			
1-0	(0.002)			
2-0	0.34 ± 0.15	0.62 ± 0.08	0.24 ± 0.2	
3-0	1.25 ± 0.35	1.2 ± 0.1	1.84 ± 0.08	
4-0	3.30 ± 0.20	3.0 ± 0.4	4.18 ± 0.09	
5-0	2.20 ± 0.20	1.9 ± 0.3	2.3 ± 0.5	
6-0	1.70 ± 0.10	1.43 ± 0.07	1.1 ± 0.2	
7-0	2.25 ± 0.05	1.63 ± 0.11	1.70 ± 0.13	1.62 ± 0.10
8-0	2.21 ± 0.20	1.35 ± 0.08	1.43 ± 0.16	1.36 ± 0.09
9-0	0.72 ± 0.08	0.67 <u>+</u> 0.04	0.76 ± 0.4	0.67 ± 0.04
10-0	0.34 ± 0.05	0.69 ± 0.05	0.42 ± 0.7	0.70 ± 0.04
11-0	1.80 ± 0.12	0.98 ± 0.06	1.3 ± 0.4	0.94 ± 0.06
12-0	0.48 ± 0.05	0.60 ± 0.02	0.81 ± 0.06	0.66 ± 0.03
13-0	0.08 ± 0.05	0.14 ± 0.01	0.13 ± 0.01	0.20 ± 0.005
14-0	0.06 ± 0.05	0.08 ± 0.01	0.06	0.16 ± 0.02
15-0	0.20 ± 0.05		0.20	0.32 ± 0.04
16-0	0.25 ± 0.05		0.26	0.33 ± 0.03
17-0	(0.4)		0.40	0.25 ± 0.03
18-0	(0.4)		0.40	0.16 ± 0.03
19-0	(0.4)		0.40	$0.22~\pm~0.12$

The effect of the spectral region of (14-0) to (10-0) is important down to the stratopause, but it decreases considerably in the stratosphere where the effect of the region (8-0) to (2-0) is more important. A detailed calculation shows that, when the total number of O_2 molecules exceeds 2.5×10^{23} cm⁻², it is necessary to consider only the bands (5-0) to (2-0) which extend over the region 200 nm to 190 nm.

Ozone absorption

Prior to the experimental work of Bass (1982, private communication) the absorption cross-sections were based essentially on the data of Vigroux (1952*a*, *b*, *c*, *d*, 1953, 1969) and Inn and Tanaka (1953, 1959), and on complementary data from Hearn (1961), De More and Raper (1964) and Griggs (1968). Moreover, the quantum efficiency for the production of $O(^{1}D)$ atoms during the photo-dissociation of ozone

$$O_3 + h\nu \rightarrow O_2(^1\Delta_a) + O(^1D)$$

is based on the results of Moortgat (cf. Arnold *et al.*, 1977; Moortgat *et al.*, 1975, 1977, 1978) and of Wiesenfeld (cf. Aminoto *et al.*, 1979, 1980; Fairchild *et al.*, 1978; Sparks *et al.*, 1980). The results of Davenport add nothing new to this series of early measurements, apart from a clear indication of the temperature effect beyond 300 nm, and perhaps some confusion arising from the inaccuracy of certain uncorrected data.

Figure 11 illustrates the experimental results and uses the data of Bass as a reference. It can be seen that, at short wavelengths, the effective cross-section reaches its maximum, and that there is good agreement $(\pm 1 \%)$ between the various experimental values; the agreement is not so good at 290 nm with a scatter of $\pm 3 \%$, and at 320 nm with a scatter of $\pm 4 \%$. Beyond 320 nm, the disagreement is so great that it is not possible to suggest an accurate value. These differences are all the more important because, from 280 nm, it is necessary to take account of the effect of temperature on the effective



Figure 11

Comparison of absorption cross-sections of O_3 measured at laboratory temperatures. The values are normalized with respect to the values of Bass, and refer to spectral intervals of 5 nm.

absorption cross-section. Thus at the wavelengths quoted below, it can be seen (Bass'data) that for T = 243 K and 295 K, the ratios decrease with increasing wavelength :

λ (A)	2837	2963	3007	3053	3200
243/295 K	0.95	0.92	0.90	0.89	0.77

This temperature effect is of great importance in the lower stratosphere and the troposphere, as shown in figures 12 and 13 which give the transmission factor from 242 nm to 305 nm between 50 km and 10 km for zenith angles of 0° and 60° . It is clear that the effect of low temperature (below 230 K) must be introduced



Figure 12

Atmospheric transmissivity, between 50 km and 10 km, due to absorption by ozone alone. The standard atmospheric temperatures are shown in order to emphasise the importance of temperature on the opacity of the atmosphere, especially below 30 km. Solar zenith angle = 0° .



Figure 13 As for figure 12, but solar zenith angle $= 60^{\circ}$.

above 30 km. The penetration of solar radiation at wavelengths above 280 nm is closely connected with the effect of the temperature on the absorption of ozone.

Finally, when studying the photodissociation of ozone, it is necessary to take into account (as in figure 14), and particularly in the lower stratosphere, at the level of the tropopause and in the troposphere, the absorption characteristics of the Huggins bands where the crosssection is very sensitive to the temperature, but has not yet been determined with the required accuracy. Although there is no temperature effect in the Chappuis bands centred near 600 nm in the visible, it is clear (fig. 14) that they have important effects below 35 km.



Figure 14

Photodissociation of ozone (%) as a function of altitude and solar zenith angle (sec $\chi = 1, 2$ and 4) for the main spectral regions : Herzberg continuum to 240 nm, Hartley band to 310 nm and Huggins bands beyond 310 nm. The Chappuis bands cover the visible region.

It is for this reason that the state of the atmosphere must be considered in studies of photodissociation. It is a question, in particular, of anisotropic multiple scattering and of the albedo in the solar radiation field.

Transmission characteristics of the atmosphere

In a pure dry atmosphere, solar radiation undergoes anisotropic multiple scattering (Meier *et al.*, 1982) which is amplified by the albedo of the ground or clouds. The two examples in figure 15 illustrate the amplification at ground level (relative to the direct solar flux) resulting from both Rayleigh scattering and the albedo for solar zenith angles of 45° and 60° .

It is clear, therefore that, in any study of atmospheric chemistry, it is necessary to know the solar radiation field as a function of anisotropic multiple scattering and of the variable albedo conditions. Figure 16 shows the pronounced effect of multiple scattering in the troposphere and the lower stratosphere on the production of the $O(^{1}D)$ atom; this is involved in the reactions with H₂O, CH₄, and N₂O which are fundamental in atmospheric chemistry. In figure 17, the importance of the albedo is illustrated for the Huggins bands, and especially for the Chappuis bands. In no case can the albedo be neglected. This shows how important the cloud cover is in modifying the chemistry of the stratosphere; the conditions will be different depending on whether the sky is cloudless or not, and whether the ground below is grey or green, or the surface of the ocean; in all these cases, the reflection conditions are very different. especially in the UV.

CONCLUSIONS

The study of the basic parameters, namely the solar radiation responsible for molecular dissociation in the atmosphere and its absorption by various molecules, particularly O_2 and O_3 , indicates that there is a need for an improvement in observations of solar spectral irradiance, and that the experimental determinations of absorption in certain spectral regions must be made more accurately.

The investigation of UV irradiance must also include studies of the effects of solar activity, which play a role in the spectral range of the absorption of molecular oxygen, as well as of N_2O , HNO_3 and chlorofluoro-carbons such as CCl_4 , CF_2Cl_2 , $CFCl_3$.

Experimental work must aim at more accurate measurements of effective absorption cross-section. For molecule O_2 , there is a need for a determination of the effective cross-sections between 10^{-24} and 10^{-23} cm² in the Herzberg continuum.

The data on the Schumann-Runge bands cannot be used in precise atmospheric studies until there is a major improvement in the values of the width of the rotation lines, and better information on the importance of the associated continuum.

As for ozone, it is necessary to have new experimental determinations of its absorption particularly at the two limits of its UV spectrum : that is at wavelengths greater than 280 nm and less than 220 nm.



Figure 15a

Amplification ratio for direct solar radiation at ground level resulting from the effect of multiple anisotropic scattering and albedo, for solar zenith angle of 45°.



Figure 15b As for figure 15a, but solar zenith angle = 60° .

The effect of temperature on the effective cross-section must be known more accurately, especially between 300 nm and 340 nm. The effect of temperature must be determined, or redetermined, for most of the absorbing constituents near 200 nm and beyond 300 nm, since the available values are not sufficiently accurate for use in

REFERENCES

Ackerman M., Biaumé F., Kockarts G., 1970. Absorption cross sections of the Schumann-Runge bands of molecular oxygen, *Planet*. *Space Sci.*, **18**, 1639.



Figure 16

Photodissociation frequencies of O_3 in the troposphere and stratosphere as a function of solar radiation (curves 1) including the effect of multiple anisotropic scattering (curves 2) and in addition the effect of various albedos : 0.25, 0.50 and 0.75 (curves 3, 4 and 5, respectively). All the curves relate to a solar zenith angle of 60° to a mean temperature for the quantum yields of 263 K and to Standard Atmosphere Conditions for concentrations. The rates for the $O(^{1}D)$ and $O(^{3}P)$ atom productions are shown separately in order to illustrate the altitude effect. The rates vary from 10^{-6} to 3×10^{-3} sec⁻¹ between the ground and stratopause.



Figure 17

Photodissociation frequency of O_3 in the lower stratosphere and upper stratosphere, between 10 and 30 km, resulting from the absorption in the Huggins and Chappuis bands (production of unexcited $O(^3P)$ atoms). The rates cover the range 10^{-4} to $10^{-3} \sec^{-1}$. Note, in particular, that the frequency does not change with altitude in Chappuis bands (optical thickness near 0) but that it is strongly dependent on multiple anisotropic scattering and albedo.

investigations of photodissociation as a function of height.

Finally, the atmospheric conditions must be taken into account so that effects due to anisotropic scattering and the albedo on the solar radiation field can be treated.

Amimoto S. T., Force A. P., Gulotly Jr. R. G., Wiesenfeld J. R., 1979. Collisional deactivations of $O(2 \ ^1D_2)$ by the atmospheric gases, J. Chem. Phys., 71, 3640.

Amimoto S. T., Force A. P., Wiesenfeld J. R., Young R. H., 1980. Direct observation of $O({}^{3}P_{0})$ in the photolysis of O_{2} at 248 nm, *J. Chem. Phys.*, 73, 1244.

Arnold I., Comes F. J., Moortgat G. K., 1977. Laser flash photolysis : quantum yield of $O(^{1}D)$ formation from ozone, *Chem. Phys.*, 24, 211.

Bass A. M., Paur R. J., 1982. UV absorption cross-sections for ozone : the temperature dependence, *EOS*, 63, 331.

Biaumé F., 1972. Détermination de la valeur absolue de l'absorption dans les bandes du Système de Schumann-Runge de l'oxygène moléculaire, *Aeronomica Acta*, Bruxelles, A nº 100.

Blake A. J., 1979. An atmospheric absorption model for the Schumann-Runge bands of oxygen, J. Geophys. Res., 84, 3272.

Broadfoot A. L., 1972. The solar spectrum 2100-3200 A, Astrophys. J., 173, 681.

Bossy L., Nicolet M., 1981. On the variability of Lyman-alpha with solar activity, *Planet. Space Sci.*, 29, 907.

Davenport J. E., 1981. Parameters for ozone photolysis as a function of temperature at 280-330 nm. U.S. Department of Transp., Fed. Aviation Adm., FAA 80-44R, May.

De More W. B., Raper O. F., 1964. Hartley band extinction coefficients of ozone in the gas phase and in liquid nitrogen, carbon monoxide and argon, J. Phys. Chem., 68, 412.

Ditchburn R. W., Young P. A., 1962. The absorption of molecular oxygen between 1850 and 2500 A, J. Atm. Terr. Phys., 24, 127.

Fairchild C. E., Stone E. J., Lawrence G. M., 1978. Photofragment spectroscopy of ozone in the UV region 270-310 nm and 600 nm, *J. Chem. Phys.*, 69, 3632.

Fang T. M., Wofsy S. C., Dalgarno A., 1974. Opacity distribution functions and absorption in Schumann-Runge bands of molecular oxygen, *Planet. Space Sci.*, 22, 413.

Frederick J. E., Hudson R. D., 1980a. Atmospheric opacity in the Schumann-Runge bands and the aeronomic dissociation of water vapor, J. Atmos. Sci., 37, 1088.

Frederick J. E., Hudson R. D., 1980b. Dissociation of molecular oxygen in the Schumann-Runge bands, J. Atmos. Sci., 37, 1099.

Frederick J. E., Mentall J. E., 1982. Solar irradiance in the stratosphere : Implications for the Herzberg continuum absorption of O_2 , *Geophys. Res. Lett.*, 9, 461.

Gies H. P. F., Gibson S. T., McCoy D. G., Blake A. J., Lewis B. R., 1981. Experimentally determined oscillator strengths and line widths for the Schumann-Runge band system of molecular oxygen. III. The (7-0) to (19-0) bands, J. Quant. Spectrosc. Radiat. Transfer, 26, 469.

Greenblatt G. D., Wiesenfeld J. R., 1983. Time-resolved resonance fluorescence studies of $O({}^{1}D_{2})$ yields in the photodissociation of O_{3} at 248 and 308 nm, *J. Chem. Phys.*, **78**, 4924.

Griggs M., 1968. Absorption coefficients of ozone in the ultraviolet and visible regions, J. Chem. Phys., 49, 857.

Hasson V., Nicholls R. W., 1971. Absolute spectral absorption measurements on molecular oxygen from 2640-1920 Å: II Continuum measurements 2430-1920 Å, J. Phys. B. Atomic Molec. Phys., 4, 1789.

Hearn A. G., 1961. The absorption of ozone in the ultra-violet and visible region on the spectrum, *Proc. Phys. Soc.*, **79**, 932.

Heath D., 1981. A review of observational evidence for short and long term ultraviolet flux variability of the sun, p. 447 in Soleil et Climat, Journées internationales CNES, CNRS DGRST, Toulouse, 30 sept.-3 oct. 1980.

Herman J. R., Mentall J. E., 1982. O₂ absorption cross sections (187-225 nm) from stratospheric solar flux measurements, *J. Geophys. Res.*, 87, 8967.

Hudson R. D., Mahle S. H., 1972. Photodissociation rates of molecular oxygen in the mesosphere and lower thermosphere, *J. Geophys. Res.*, 77, 2902.

Inn E. C. Y., Tanaka Y., 1953. Absorption coefficient of ozone in the ultraviolet and visible regions, J. Opt. Soc. Amer., 43, 870.

Inn E. C. Y., Tanaka Y., 1959. Ozone absorption coefficients in the visible and ultraviolet regions in Ozone Chemistry and Technology Advances in Chemistry Series 21, p. 263-268. American Chemical Society, Washington D.C.

Jarmain W. R., Nicholls R. W., 1967. A theoretical study of the v'' = 0, 1, 2 progressions of bands and adjoining photodissociation continua of the O_2 Herzberg I system, *Proc. Phys. Soc.*, **90**, 545.

Kockarts G., 1976. Absorption and photodissociation in the Schumann-Runge bands of molecular oxygen in the terrestrial atmosphere, *Planet. Space Sci.*, 24, 589.

Kohl J. L., Parkinson W. H., Kurnez R. L., 1978. Center and limb solar spectrum in high spectral resolution 225.2 nm to 319.6 nm, Harvard-Smithsonian Center for Astrophysics, Harvard University Printing Office, Cambridge. Lewis B. R., Carver J. H., Hobbs T. I., McCoy D. G., Gies H. P. F., 1978, 1979. Experimentally determined oscillator strengths and linewidths for the Schumann-Runge band system of molecular oxygen. I. The (6-0)-(14-0) bands, J. Quant. Spectrosc. Radiat. Transfer, 20, 191. II. The (2-0) to (5-0) bands, J. Quant. Spectrosc. Radiat. Transfer, 22, 213.

Lewis B. R., Carver J. H., Hobbs T. I., McCoy D. G., Gies H. P. F., 1980. Rotational variation of predissociation linewidths for the Schumann-Runge bands of molecular oxygen, J. Quant. Spectrosc. Radiat. Transfer, 24, 365.

Meier R. R., Anderson Jr., D. E., Nicolet M., 1982. Radiation field in the troposphere and stratosphere from 240-1000 nm. I. General analysis, *Planet. Space Sci.*, **30**, 923.

Mentall J. E., Frederick J. E., Herman J. R., 1981. The solar irradiance from 200 to 330 nm, J. Geophys. Res., 86, 9881.

Moortgat G. K., Kudszus E., 1978. Mathematical expression for the $O(^{1}D)$ quantum yields from the O_{3} photolysis as a function of temperature (230-320 K) and wavelength (295-320 nm), *Geophys. Res. Lett.*, **5**, 191.

Moortgat G. K., Kudszus E., Warneck P., 1977. Temperature of $O(^2D)$ formation in the near UV photolysis of ozone, *J. Chem. Soc., Faraday Trans.*, **II**, 73, 1216.

Moortgat G. K., Warneck P., 1975. Relative O(¹D) quantum yields in the near UV photolysis of ozone at 298 K, Z. Naturforsch. 30A, 835.

Mount G. H., Rottman G. J., 1983. Solar absolute spectral irradiance 1150-3173 A : May 17, 1982, J. Geophys. Res., 88, 5403.

Nicolet M., 1979. Etude des réactions chimiques de l'ozone dans la stratosphère, Institut Royal Météorologique, Bruxelles.

Nicolet M., 1981. The solar spectral irradiance and its action in the atmospheric photodissociation processes, *Planet. Space Sci.*, 29, 951.

Nicolet M., 1982. Penetration of solar radiation into the mesosphere and stratosphere, EOS, 63, 331.

Nicolet M., 1983. Changes in atmospheric chemistry related to solar flux variations in solar-terrestrial influences on weather and climate, Ed. B. M. McCormac, Un. Colorado Press.

Nicolet M., Meier R. R., Anderson Jr., D. E., 1981. Effect of temperature and of anisotropic scattering on the $O(^1D)$ production in the troposphere and stratosphere, Proc. Quadrennial Int. Ozone Symposium, Boulder, Colorado, p. 892.

Nicolet M., Meier R. R., Anderson Jr., D. E., 1982. Radiation field in the troposphere and stratosphere. II. Numerical analysis, *Planet.* Space Sci., 30, 935.

Nicolet M., Peetermans W., 1980. Atmospheric absorption in the O_2 Schumann-Runge band spectral range and photodissociation rates in the stratosphere and mesosphere, *Planet. Space Sci.*, 28, 85.

Ogawa M., 1971. Absorption cross-sections of O_2 and CO_2 continua in the Schumann- and far-UV regions, J. Chem. Phys., 54, 2550.

Shardanand, Prasad Rao A. D., 1977. Collision induced absorption of O₂ in the Herzberg continuum, J. Quant. Spect. Rad. Transfer, 17, 433.

Simon P. C., 1981. Solar irradiance between 120 and 400 nm and its variations, *Solar Physics*, 74, 273.

Sparks R. K., Carlson L. R., Shobatake K., Kowalczyk M. I., Lee Y. T., 1980. Ozone photolysis : a determination of the electronic and vibrational state distributions of primary products, J. Chem. Phys., 72, 1401.

Vigroux E., 1952a. Mesures absolues des coefficients d'absorption de l'ozone dans la région des bandes de Huggins à 18°, C.R. Acad. Sci., Paris, 234, 2351.

Vigroux E., 1952b. Absorption de l'ozone dans la région des bandes de Huggins, Influence de la température, C. R. Acad. Sci. Paris, 234, 2439.

Vigroux E., 1952c. Absorption de l'ozone à 18° au-dessous de 3 130A, C. R. Acad. Sci. Paris, 234, 2529.

Vigroux E., 1952d. Absorption de l'ozone dans le domaine spectral situé au-dessous de 3 130 Å. Effet de la température, C. R. Acad. Sci., Paris, 234, 2592.

Vigroux E., 1953. Contribution expérimentale de l'absorption de l'ozone, Ann. Phys. Paris, 12^e Sér., **8**, 709.

Vigroux E., 1969. Coefficients d'absorption de l'ozone dans la bande de Hartley, Ann. Géophys., 25, 169.

Wine P. H., Ravishankara A. R., 1981. Kinetics of $O(^{1}D)$ interactions with the atmospheric gases N_2 , N_2O , H_2O , H_2 , CO_2 and O_3 , Chem. Phys. Lett., 77, 103.

Yoshimo K., Freeman D. E., Esmond J. R., Parkinson W. H., 1983. High resolution absorption cross-section measurements and band oscillator strengths of the (1,0)-(12,0) Schumann-Runge bands of O₂. *Planet. Space Sci.*, **31**, 339.