

PHOTODISSOCIATION EFFECTS OF SOLAR U.V. RADIATION

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Abstract—This paper reviews the current knowledge of u.v. solar irradiances beyond 120 nm measured during solar cycle 21. Parameters required to calculate the atmospheric attenuation of the u.v. radiation and the photodissociation rate of neutral constituents are discussed. The effect of scattering is also considered.

1. INTRODUCTION

The chemical and the thermal structure of planetary atmospheres is driven by the radiation emitted by the Sun and its absorption by optically active atmospheric constituents. An accurate knowledge of the solar irradiance and its variation is therefore fundamental in aeronomy and in climatology. Most of the solar energy is confined in the wavelength range below 4000 nm while the radiation emitted by the Earth and the surrounding atmosphere has a wavelength greater than 4000 nm.

Photochemical processes of the neutral constituents in the middle atmosphere and in the lower thermosphere are initiated by u.v. radiation in the wavelength interval ranging from 120 nm to the visible part of the spectrum. Furthermore the HI Lyman α line is responsible for the ionization of nitric oxide (Nicolet, 1945) leading to the formation of the D region.

When penetrating in the atmospheric layers, the solar irradiance is progressively attenuated by absorption and scattering. The main absorbing gases are molecular oxygen and ozone. An accurate analysis of the radiative transfer in the u.v. requires therefore a perfect knowledge of (1) the solar irradiance at the top of the atmosphere, (2) the absorption cross sections of O₂ and O₃, (3) the integrated amount of these absorbing species, (4) the scattering cross section and (5) the albedo.

The distribution of the trace species concentration depends directly on the photodissociation rates in the atmosphere. The photodissociation frequency of a

molecule X is given by

$$J(X; z, \chi) = \int_{\lambda} \varepsilon(X; \lambda) \sigma(X; \lambda) q(\lambda, z, \chi) d\lambda \quad (1)$$

where $q(\lambda, z, \chi)$ is the total photon flux into a volume element at an altitude z , for a solar zenith angle χ and for wavelength λ . $\sigma(X, \lambda)$ is the absorption cross section and $\varepsilon(X, \lambda)$ the photodissociation efficiency for the given molecule. The absorption and scattering processes will therefore influence the atmospheric composition.

The purpose of this paper is to review the key parameters which are used as input data in photochemical models of the atmosphere. In particular, the solar irradiance, the absorption cross section of molecular oxygen and ozone and the Rayleigh scattering will be discussed. In order to clarify the analysis, the solar spectrum will be divided according to the various spectral regions of molecular oxygen corresponding to the penetration of solar radiation in different atmospheric layers.

2. SOLAR IRRADIANCE

Solar u.v. irradiance measurements from 135 to 400 nm will be reviewed. The solar HI Lyman α line will not be discussed here since its absolute value and its variations are analyzed by Bossy (1983, this volume). On the other hand, measurements obtained since the first observation reported by Friedman *et al.* (1951) have been discussed in several papers (e.g. Vidal-Madjar, 1977; Simon, 1978; Simon, 1981).

2.1. The wavelength interval 135–175 nm

During solar cycle 20, several rocket measurements have been made in the wavelength interval corresponding to the Schumann–Runge continuum of molecular oxygen. Heroux and Swirbalus (1976) and Samain and Simon (1976) have published the lowest irradiance

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values. The latter values refer to a quiet solar full disk. Rottman (1981) has proposed revised values for his observations performed in 1972 and 1973. With three other flights made in 1975, 1976 and 1977, he has defined a so-called reference spectrum corresponding to minimum conditions between solar cycle 20 and 21, by taking an average value provided by the five flights.

The irradiance values obtained during cycle 21 for a high solar activity level have been published by Mount *et al.* (1980) and Mount and Rottman (1981). They are systematically higher than the reference spectrum of Rottman (1981). The differences represent long-term variability which is confirmed by the AE-E satellite observations reported by Hinteregger (1981) even if the latter correspond to a limited field of view on the solar disk of 6 arc min \times 6 arc min situated near the disk center. New data obtained in 1982 have been very recently published by Mount and Rottman (1983). These observations, corresponding to an intermediate level of solar activity, are comparable to the minimum values proposed by Rottman (1981). They are even lower than the values obtained in 1976 and 1977 with a similar instrument. Values obtained by Heath (1980) during the rising phase of solar cycle 21 in November 1978 are also in better agreement with the minimum values proposed by Rottman (1981) rather than with those obtained during the maximum of solar cycle 21.

On the basis of the former observations performed since 1978, the enhancement of solar irradiance with the 11-year solar activity seems correlated only with the highest activity levels around the cycle maximum in 1979 and 1980. This is in contradiction with the two-component plage model of Cook *et al.* (1980) which proposes a linear relationship between the solar irradiance in the 117.5–210 nm wavelength interval and the Zurich sunspot number. A three-component model recently published by Lean *et al.* (1982) and based on spatially resolved observations of the Ca II K chromosphere is in better agreement with the 11-year cycle variation deduced from the LASP data (Rottman, 1981; Mount *et al.*, 1980; Mount and Rottman, 1981). According to this latter model, the irradiance increase in the 155–160 nm wavelength interval reaches levels higher than 25% after the beginning of 1978 or before mid 1971 corresponding to smooth sunspot numbers larger than 50.

The ratios of irradiance values integrated over 5 nm from 135 to 175 nm taking as a reference the irradiance values proposed by Brasseur and Simon (1981) are given in Fig. 1. This graph clearly shows that the previous values of Heroux and Swirbalus (1976) are 30% lower than the reference spectrum. On the other hand, the divergences between the five observations of Rottman (1981) give a good idea of the reproductibility

reached in this wavelength range by means of snapshot measurements which include the variability related to the 27-day solar rotational period.

Observations made by the *Solar Mesosphere Explorer* (SME) indicate a 27-day variability of the order of 12% in the integrated 130–175 nm wavelength range (Rottman *et al.*, 1982). A detailed discussion of this question is given by Rottman (1983, this volume).

Accuracy and precision of the irradiance observations need to be improved in order to quantitatively measure the solar variability during the 11-year cycle. The accuracy of $\pm 8\%$ at the two σ level quoted by Mount and Rottman (1983) in the wavelength interval of 115–186.5 nm seems very promising in regard to the previous observations usually made with an accuracy of $\pm 15\%$ at the one σ level. This improvement has been reached by using the Synchrotron Users Radiation Facility (SURF) at the National Bureau of Standards as a calibration standard.

2.2. The wavelength interval 175–210 nm

Solar irradiance and its variability are very poorly known in the wavelength range corresponding to the Schumann–Runge bands of molecular oxygen. Figure 1 gives the ratios of several observed irradiance values integrated over 5 nm taking as a reference the values obtained by Samain and Simon (1976) corresponding to a quiet Sun and quoted by Brasseur and Simon (1981). Differences at wavelengths below 185 could probably be due to long-term solar variability. Divergences between individual observations are not uniform with wavelength. It should be mentioned that, according to the two-component model of Cook *et al.* (1980) and the three-component model of Lean *et al.* (1982), the variability during the rising phase of solar cycle 21 beyond 182 nm does not exceed 30%. Ratios from 180 to 190 nm obtained on the basis of Rottman's measurement should be excluded because of larger errors. In addition, the data of Mount *et al.* (1980) are not reliable beyond 190 nm because of experimental problems (Mount and Rottman, 1981). Consequently, the quantitative variation over the 11-year cycle is still masked by the uncertainties of all measurements in this wavelength range. Additional observations with accuracy and precision higher than or at least comparable to those obtained by Mount and Rottman (1983) are required.

The variability of the solar irradiance with the 27-day rotation period has been observed by *Nimbus 7* (Heath, 1980) and by SME (Rottman *et al.*, 1982). Heath (1980) observes a maximum variability of 5% around 180 nm while Rottman *et al.* (1982) report a variability of 10% for the whole spectral interval of 175–190 nm.

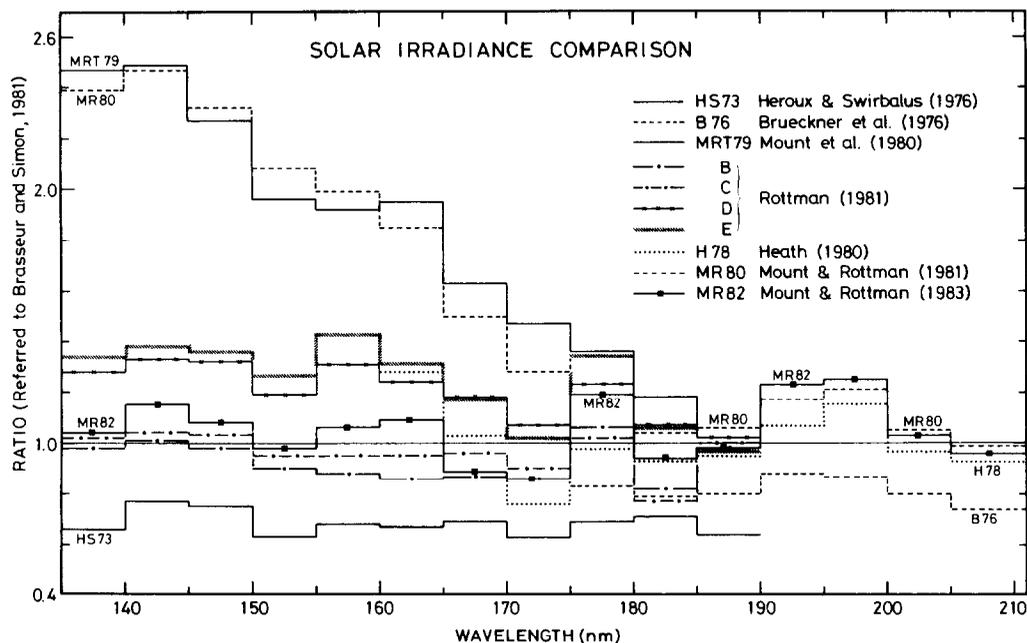


FIG. 1. OBSERVED SOLAR IRRADIANCE IN THE SPECTRAL RANGE 135–210 nm EXPRESSED AS RATIOS RELATIVE TO THE SOLAR REFERENCE SPECTRUM OF BRASSEUR AND SIMON (1981). Values are integrated over 5 nm intervals.

2.3. The spectral region beyond 210 nm

Figure 2a presents the ratio of irradiance values integrated over 5 nm from 205 to 270 nm taking as a reference the values proposed by Brasseur and Simon (1981). Systematic divergences clearly appear between most measurements in the 205–240 wavelength interval. They are probably due to experimental errors. Differences between all the flights do not exceed 20%. They are within 12% when considering only the balloon observations reported by Simon *et al.* (1982a, b) and within 10% when keeping only the 1980 and 1982 rocket flight results published by Mount and Rottman (1981, 1983). All these measurements confirm that the values of Broadfoot (1972) have to be lowered by at least 25% below 260 nm. The lowest values of Mount *et al.* (1980) are not reliable in this wavelength range because of experimental problems encountered during this flight (Mount and Rottman, 1981). Above 240 nm, the divergences are within 15%. Data reported by Mount and Rottman (1981) have been revised on the basis of improved calibration methods obtained with the Synchrotron Users Radiation Facility (SURF) at the National Bureau of Standards (see Mount and Rottman, 1983).

Figure 2b represents the same comparison for integrated irradiance values over 5 nm between 270 and 350 nm. The agreement between all the observations is

good ($\pm 10\%$) up to 295 nm. Beyond this wavelength, the data obtained in 1980 and revised by Mount and Rottman (1983), as well as those of Broadfoot (1972), become significantly lower than the others. Balloon observations also exhibit larger discrepancies up to 15%, at larger wavelengths. It should be noted that the quantum yield of the solar blind detectors used for rocket and balloon observations decreases rapidly beyond 250 nm and becomes very small for wavelengths greater than 300 nm. Nevertheless, the agreement with the values obtained by Heath (1980) is within 5% for the 1979 balloon observation (Simon *et al.*, 1982b).

Beyond 330 nm, new irradiance values have been published by Neckel and Labs (1981). These latter values which supersede those previously published by Labs and Neckel (1970) are probably the most reliable in the near u.v. and in the visible. According to Table 3 in Simon (1981), they are in good agreement with the observation reported by Heath (1980). The measurements of Arvesen *et al.* (1969) have to be carefully adjusted because of errors in their wavelength scale below 400 nm and because of uncertainties due to changes in the spectral irradiance scale of the National Bureau of Standards in 1973.

Long-term variability in this spectral range is generally considered as being negligible from the

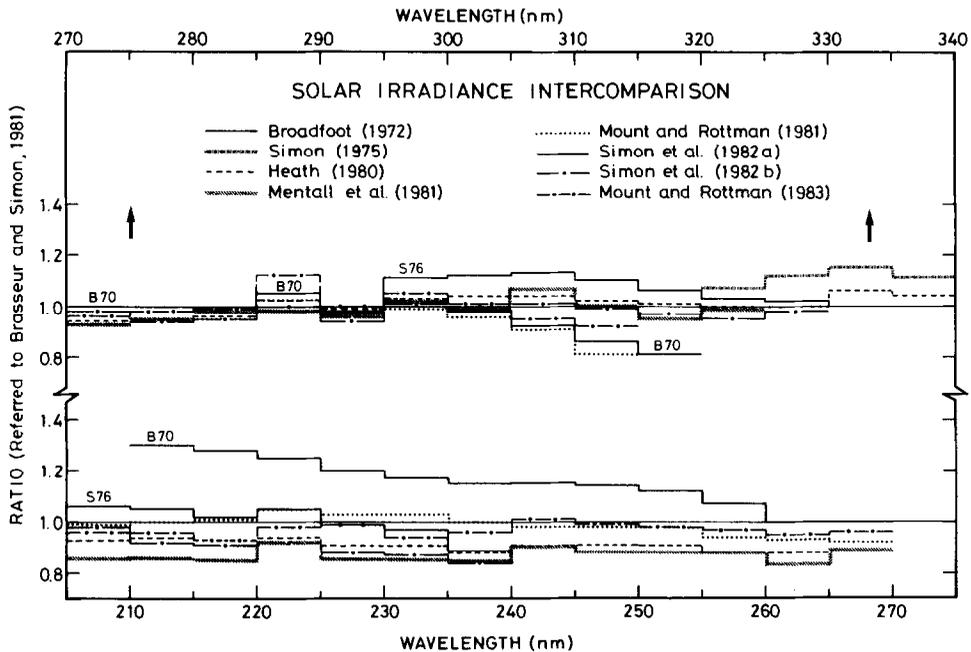


FIG. 2. OBSERVED SOLAR IRRADIANCE IN THE SPECTRAL RANGES 205–275 nm (BOTTOM) AND 270–340 nm (TOP) EXPRESSED AS RATIOS RELATIVE TO THE SOLAR REFERENCE SPECTRUM OF BRASSEUR AND SIMON (1981). Values are integrated over 5 nm intervals. The labelling is as follows: B 70, Broadfoot (1972); S 76, Simon *et al.* (1982a) flight dated 1 July 1976.

aeronomic point of view and is also masked by the uncertainties in available measurements. Variations less than 2% related with the 27-day rotational period of the Sun have been reported by Heath (1980) from *Nimbus 7* observations. They are confirmed by the recent SME observations (Rottman, 1983).

2.4. Summary

In conclusion, solar irradiance values are probably known with an uncertainty of $\pm 20\%$ from 135 to 175 nm for solar minimum conditions. The long-term variations are certain, reaching a factor of 2 around 150 nm between the maximum and the minimum of activity during the rising phase of solar cycle 21. In the wavelength interval of 175–200 nm, the uncertainty is not smaller ($\pm 20\%$) and the long-term variations are still masked by the accuracy and the precision of available observations. Solar irradiances can be estimated within $\pm 15\%$ of accuracy around 210 nm and with $\pm 5\%$ at 300 nm. Further observations with an accuracy of $\pm 5\%$ and a precision better than $\pm 2\%$ are still needed in order to provide useful irradiance values and to determine the possible long-term variability beyond 175 nm. Such goals are only achievable by referring the calibration to a common stable source as the synchrotron to insure the continuity of future

observations. It is also required to compare the different instrument performances when observing the Sun from the same platform. Intercomparison of solar spectrometers should make future measurements on board balloon, rocket and space shuttle more comparable and should help to the validation of satellite observations, particularly for the instrument drift in orbit.

3. THE ABSORPTION CROSS SECTION OF MOLECULAR OXYGEN

3.1. The Lyman α window region

Below 130 nm, the absorption cross section of molecular oxygen varies rapidly with wavelength. Near the H1 Lyman α solar line, the minimum values of the oxygen cross section allows the solar radiation to reach the mesosphere, down to the altitude of 70 km. Since this solar line is responsible for the dissociation of water vapor, methane, carbon dioxide and the ionization of nitric oxide, an accurate knowledge of the optical depth in this wavelength region is required.

Many laboratory measurements have been made (e.g. Watanabe, 1958; Ogawa, 1968; Dose *et al.*, 1975) leading to the working value of 1×10^{-20} cm² at 121.6 nm. Hall (1972) has pointed out that the variation in the molecular oxygen cross section across the solar Lyman

α , the line which has the appearance of a doublet (Purcell and Tousey, 1960) requires the calculation of an effective cross section depending on the oxygen content above a given altitude. On the other hand, Smith and Miller (1974) and Weeks (1975) have pointed out the temperature dependence of the molecular oxygen absorption cross section near Lyman α . Carver *et al.* (1977) have measured the oxygen absorption cross sections at 0.02 nm intervals between 121.4 and 121.86 nm at three temperatures of 294, 195 and 82 K. The effective cross sections have been calculated as a function of the integrated Lyman α extinction for the three temperatures. Results are significantly lower than the effective cross sections published by Hall (1972) and based on Ogawa's measurements.

Nicolet and Peetermans (1980) using the data of Carver *et al.* (1977), have deduced simple expressions, adopting an average temperature of 190 K, for the photodissociation rate calculations.

The optical depth is given by the expression

$$\tau_{\text{Ly}\alpha}(\text{O}_2) = 4.17 \times 10^{-19} N(\text{O}_2)^{0.917} \quad (2a)$$

for $N(\text{O}_2) > 1 \times 10^{19}$ molecules cm^{-2} corresponding to an effective cross section given by

$$\sigma_{\text{Ly}\alpha}(\text{O}_2) = 4.17 \times 10^{-19} N(\text{O}_2)^{-0.083}. \quad (2b)$$

For $N(\text{O}_2) \leq 1 \times 10^{19}$ molecules cm^{-2} , a cross section value of 1×10^{-20} cm^2 can be adopted.

3.2. The Schumann–Runge continuum

The heating in the lower thermosphere as well as the formation of the atomic oxygen due to the photodissociation of molecular oxygen in this atmospheric layer has to be attributed to the absorption of solar radiation in the 135–175 nm wavelength interval.

The absorption cross section of molecular oxygen in this range has been reviewed several times. The first analysis was made by Nicolet and Mange (1954) and followed by those of Watanabe (1958), Ackerman (1971) and Hudson and Mahle (1971). The latter author has also extensively discussed the sources of errors in the u.v. absorption cross section measurements. He claimed that the total uncertainty with the laboratory techniques available at that time, is larger than 5%. Furthermore, errors on the cross section values are larger when photographic emulsions are used instead of photoelectric techniques detection. Actually, the first investigations of molecular oxygen absorption cross section have been conducted using photographic techniques and yielded values 20–25% higher than those obtained by photoelectric measurements. Later on, the data obtained by Goldstein and Mastrup (1966) did not confirm the higher cross section values obtained by photographic emulsions. Figure 3 compares several photoelectric measurements between 135 and 160 nm obtained since 1953 at room temperature with those of Goldstein and Mastrup (1966). The divergences between the photoelectric observations do not exceed

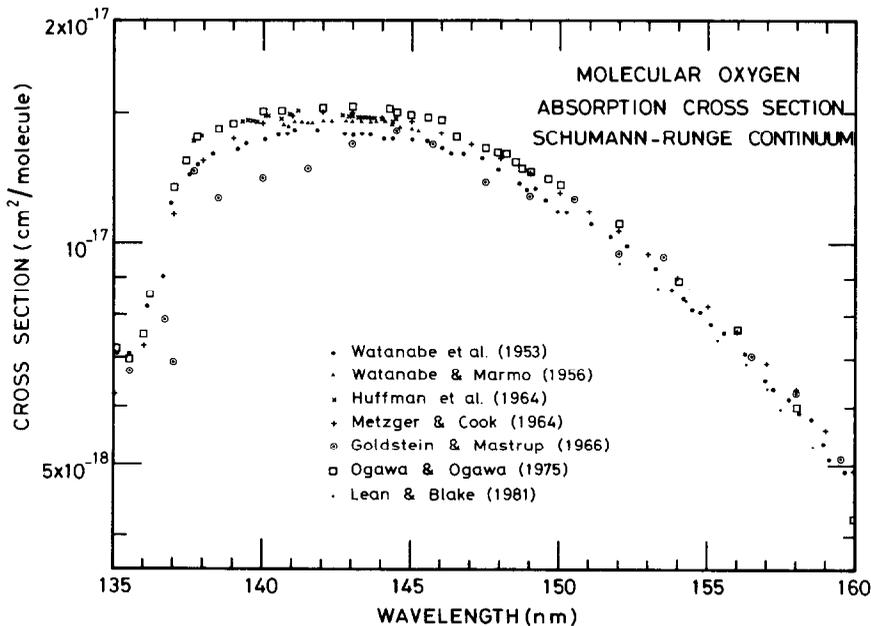


FIG. 3. ABSORPTION CROSS SECTION OF MOLECULAR OXYGEN BETWEEN 135 AND 160 nm.

10% and are therefore within the $\pm 10\%$ of accuracy quoted by most investigators. Specific measurements have been performed only around the peak of the absorption spectrum in order to obtain reliable cross section values of the order of $1.5 \times 10^{-17} \text{ cm}^2$ in this region (e.g., Watanabe and Marno, 1956; Huffman *et al.*, 1964). Measurements performed between 160 and 180 nm are displayed in Fig. 4. The positive temperature dependence of the absorption cross section is illustrated by the data obtained around 300 and 600 K by Hudson *et al.* (1966) and by Lean and Blake (1981). The temperature effect becomes significant for wavelengths greater than 160 nm and should be taken into account in photodissociation calculations in the thermosphere. According to Blake *et al.* (1980), the temperature coefficient becomes negative at shorter wavelengths but the change is limited to less than -4% at 149 nm instead of the -10% at 160 nm as measured by Hudson *et al.* (1966). A semi-empirical two terms model of the temperature dependence of the molecular oxygen absorption cross section is proposed by Lean and Blake (1981).

The Schumann–Runge continuum adjoins the Schumann–Runge band system at 175 nm and underlies the bands up to 183 nm. Therefore,

this continuum contributes to the absorption cross section minima in the band system and should be taken into account in cross section calculations discussed in the following section.

3.3 The Schumann–Runge band system

The attenuation of the solar radiation in the wavelength range of 175–200 nm is driven by the absorption of the molecular oxygen in the Schumann–Runge band system. The absorption takes place mainly in the mesosphere, between the altitudes of 60 and 90 km. However, the penetration is large enough so that the radiation in this spectral range contributes significantly to the photodissociation of several constituents in the stratosphere.

Several studies of the photodissociation of molecular oxygen in the middle atmosphere have been performed by many authors such as Kockarts (1971), Hudson and Mahle (1971), Fang *et al.* (1974), Park (1974), Kockarts (1976), Blake (1979), Nicolet and Peetermans (1980) and Frederick and Hudson (1979).

In situ observations at 40 km altitude of solar irradiance between 184 and 202 nm have been reported by Frederick *et al.* (1981) and have provided a check on the absorption cross sections of molecular oxygen. The

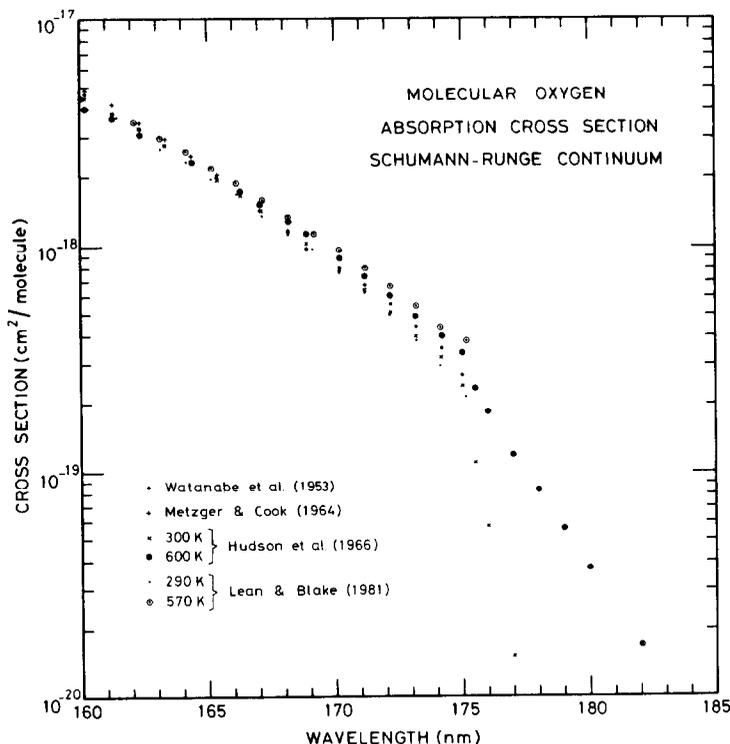


FIG. 4. ABSORPTION CROSS SECTION OF MOLECULAR OXYGEN BETWEEN 160 AND 185 nm.

differences with detailed attenuation calculations are of the order of 10% above 194 nm, 20% between 189 and 194 nm and as large as 40% below 189 nm. According to Frederick *et al.* (1981), such disagreements could be attributed to uncertainties in spectroscopic data but errors associated with the observations should not be neglected.

The cross section values in the Schumann–Runge band system which vary by about five orders of magnitude between 175 and 205 nm are calculated on the basis of experimental spectroscopic parameters for the Schumann–Runge rotational lines, adding the contribution of underlying continua which become important near both ends of the band system. Nicolet and Peetermans (1980) emphasize the difficulties of obtaining accurate experimental values of the oscillator strength and of the predissociation linewidth. Figure 5 illustrates the linewidth measured since the work of Ackerman and Biaumé (1970), including the new values recently obtained by Gies *et al.* (1981). Theoretical values deduced from models are not reported in this figure. The large differences between the available data should play an important role on the photodissociation rates of several trace species. Indeed, if smaller linewidths are used, the absorption by

molecular oxygen is more concentrated in the line centers. Consequently the solar radiation in the wavelength interval of 175–200 nm penetrates more deeply in the stratosphere and enhances the photodissociation rates at lower altitudes.

Recent studies on the photodissociation of the molecular oxygen in the Schumann–Runge bands (Kockarts, 1976; Blake, 1979; Nicolet and Peetermans, 1980; Frederick and Hudson, 1979) are based on detailed computation of the rotational structure of the band system. They require lengthy computation and, in order to reduce the computer time and cost, these authors have also developed parameterization methods which can be applied either to calculate the photodissociation rate of molecular oxygen itself or the penetration of the solar radiation in the wavelength range of 175–200 nm. These approximations are only valid when the absorption cross section of the trace species can be averaged over each given wavelength interval (1 nm, 500 cm^{-1} , intervals between successive band heads). On the contrary, when constituents such as nitric oxide are characterized by rotational structures in their cross sections, special treatments are required (Nicolet, 1979; Allen and Frederick, 1982).

Kockarts (1971) has introduced reduction factors

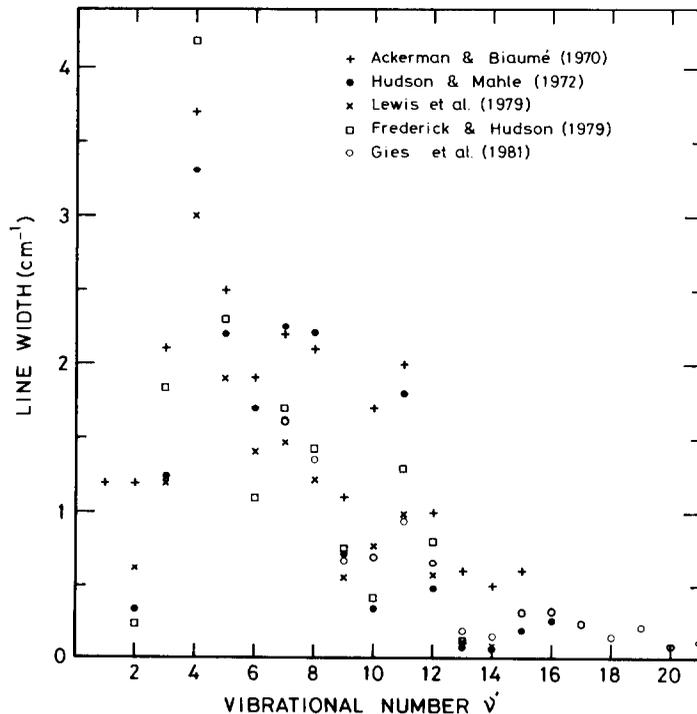


FIG. 5. EXPERIMENTAL VALUES OF THE LINEWIDTH (cm^{-1}) IN THE SCHUMANN–RUNGE BANDS OF MOLECULAR OXYGEN.

defined by the expressions:

$$R_b(M) = \frac{1}{n} \sum_{i=1}^{n_b} \exp(-\tau_{ib}) \quad (3)$$

and

$$R_b(O_2) = \frac{1}{n} \sum_{i=1}^{n_b} \varepsilon_b \sigma_{ib} \exp(-\tau_{ib}) \quad (4)$$

where

- b denotes each band in the Schumann–Runge band system,
- σ_{ib} the O_2 cross section calculated every 0.5 cm^{-1} ,
- ε_b the predissociation probability corresponding to band b ,
- τ_{ib} the optical depth every 0.5 cm^{-1} and
- n_b the number of intervals in band b .

The reductions factors are calculated using the molecular parameters taken from Ackerman *et al.* (1970). Approximations of these reduction factors taking into account the atmospheric temperature profile have been given by Kockarts (1976):

$$\ln R_b(x) = -a \exp \left[\sum_{i=1}^6 c_i (x - x_0)^i \right] \quad (5)$$

where x is the natural logarithm of the total content of molecular oxygen in cm^{-2} . The same expressions can also be applied for intervals of 500 cm^{-1} and 1 nm . The coefficients x_0 , a and c_1 through c_6 are given in Tables 2, 3, 5, 6, 8 and 9 of Kockarts (1976) for each type of wavelength intervals. The calculations are only valid for altitudes above 30 km . The errors, using these approximations, are generally less than 5% for most of the intervals. The same set of coefficients can be used for different solar zenith angles and the choice of the wavelength interval is guided by the aeronomic problem to be studied.

In his model, Blake (1979) has adjusted the linewidth values, used as a parameter, in order to improve the agreement between the calculated and the measured cross section value. The best fit is obtained with a linewidth in good agreement with those observed by Lewis *et al.* (1978) and the cross section model is in good agreement with the measurements of Ackerman *et al.* (1970) except at a few wavelengths. Blake (1979) proposed an expression giving the mean transmission T in the middle atmosphere for two wavelength intervals, namely 1.0 and 0.2 nm :

$$T = \exp \left[- \frac{X}{(1 + \beta \times N(O_2))^{1/2}} + Y \right] N(O_2) \quad (6)$$

where N designates the oxygen column density. X , Y and β are coefficients given by Blake (1979) in his Tables 3 and 4.

The effective local cross section σ_e is obtained with a polynomial function:

$$\ln(\sigma_e) = \exp \left[\sum_{n=0}^7 a_n X^n \right] \quad (7)$$

where

$$X = \{ \log [N(O_2)] - 20 \} / 3.5. \quad (8)$$

The a_n coefficients are given by Blake (1979) in his Tables 5 and 6. The standard deviation over all points is 6% for the 1.0 nm model and 7% for the 0.2 nm model.

Nicolet and Peetermans (1980) have calculated an effective cross section following the expression:

$$\sigma_e(O_2) = \sigma_m [\sigma_M / \sigma_m]^{1/(1+e^p)} \quad (9)$$

where σ_M and σ_m are the maximum and the minimum photodissociation cross section defined by:

$$\overline{\sigma_M(T)} = \frac{1}{n} \sum_{i=1}^n \sigma_i(T) \quad (10)$$

when $N(O_2) \rightarrow 0$, and by:

$$\sigma_m(T) = [\sigma_i(T)]_m \quad (11)$$

which corresponds to the smallest values of σ in the adopted range when $N(O_2) \rightarrow \infty$. In these expressions, $\sigma_i(T)$ is the absorption cross section corresponding to a narrow interval labelled i and n is the number of intervals. Values of σ_M and σ_m are given for three temperatures, 190 , 230 and 270 K in Table 7 in Nicolet and Peetermans (1980). Parameter p is a function given by the polynomial expression:

$$p = \sum_{i=0}^n p_i [\ln N(O_2)]^i. \quad (12)$$

Values using only two terms ($n = 1$) in expression (12) are given by Nicolet and Peetermans (1980) in their Table 8 for the aforementioned temperatures. The transmission related to the mean optical depth $\tau(O_2)$ is defined by the expression:

$$\exp[-\tau(O_2)] = \exp(-e^d) \quad (13)$$

where d is given by a second polynomial function:

$$d = \sum_{i=0}^n d_i [\ln N(O_2)]^i \quad (14)$$

for which coefficient values using only two terms ($n = 1$) are given in Table 9 of Nicolet and Peetermans (1980).

The temperature effect cannot be neglected when accurate values are required. Moreover precise calculations should take into account the specific effect of the solar zenith angle since, due to the temperature dependence of the cross section values, optical paths with the same O_2 column content but different

zenith angles can lead to significantly different solar attenuation and dissociation rates. When the calculation with a 10% precision is sufficient, the expressions with two terms can be used with an average temperature of 230 K and for a maximum total content of molecular oxygen less than 5×10^{23} molecules cm^{-2} , corresponding to stratospheric levels above 30 km.

Allen and Frederick (1982) have also recently published a simple polynomial representation of the effective photodissociation cross section, taking into account the effect of the altitude z and of the zenith angle χ :

$$\log \sigma_i^e(z, \chi = 0^\circ) = \sum_j a_{ij} X_i(z)^{j-1} \quad (15)$$

where $X_i(z)$ is either the temperature $T(z)$ or the logarithm of the pressure $\log P(z)$. The coefficients a_{ij} are presented by Allen and Frederick (1982) in Table 2, where index i refers to the 500 cm^{-1} wavelength intervals in the spectral region of the Schumann–Runge bands. The error averaged over all altitudes is 9% with a maximum value of 22% at 50 km. Allen and Frederick (1982) stated that such an error is within the uncertainties of the detailed calculations made by Frederick and Hudson (1979), namely $\pm 40\%$.

The effective cross section variation with the zenith angle χ is given by

$$\sigma_i^e(z, \chi) / \sigma_i^e(z, 0) = (\sec \chi)^{-C_i(z)} \quad (16)$$

where $C_i(z)$ is given by

$$\log C_i(z) = \sum_j b_{ij} [\log N(z)]^{j-1} \quad (17)$$

where $N(z)$ is the zenith oxygen column density above the altitude z . Coefficients b_{ij} are presented by Allen and Frederick (1982) in Table 3.

3.4. The Herzberg continuum

The penetration of the solar radiation in the wavelength range of 200–240 nm is driven by the absorption of the molecular oxygen in the Herzberg continuum but also by the absorption of ozone which becomes predominant beyond 220 nm. In addition, extinction by Rayleigh scattering contributes to at least 10% of the total attenuation. It contributes also to the minimum values in the Schumann–Runge band system as the underlying Herzberg continuum. The absorption cross sections of molecular oxygen are very weak beyond 200 nm (lower than 10^{-23} cm^2) and accurate values are difficult to obtain. Laboratory measurements require long path lengths or high pressure in the absorption cell. In this latter case, the absorption is contaminated by the presence of O_4 which is formed by association of two oxygen molecules. Several

determinations of the absorption cross section of molecular oxygen in the Herzberg continuum have been performed in the last 20 years. The values measured by Hasson and Nicholls (1971) are somewhat higher than the data obtained by Ditchburn and Young (1962) on which the tables published by Ackerman (1971) are based. The absorption spectrum reported by Shardanand and Prasad Rao (1977) is characterized by the smallest cross section at wavelengths shorter than 230 nm i.e. in the region which contributes the most to the photodissociation frequency in the middle and lower stratosphere. Other data such as the values by Ogawa (1971) or the tabulation by Hudson and Reed (1979) or by Nicolet (1978) are intermediate.

Recently, Frederick and Mentall (1982) as well as Herman and Mentall (1982b) have derived the molecular oxygen absorption cross section spectrum which is required to explain the observed attenuation of the solar irradiance between two different heights located in the range of 30–40 km. The observations have been performed by means of the same balloon borne double monochromator.

Frederick and Mentall (1982), have deduced from their observations on 15 September 1980, that, in the 200–210 nm range, the Hasson and Nicholls (1971) cross sections should be multiplied by factors in the range of 0.52–0.68 and the Shardanand and Prasad Rao (1977) values by factors in the range of 0.85–0.93. It should be noted however that, when applied to the two sets of laboratory data, these factors do not lead to the same value of the corrected cross sections. In principle, they are calculated by assuming that the cross section of ozone is perfectly known and that the ozone column between the two levels of observation is measured without error.

Herman and Mentall (1982a) have derived with the same instrument on 15 April 1980 absorption cross sections which are about 30% smaller than the laboratory results of Shardanand and Prasad Rao (1977) from 200 to 210 nm and about 50% smaller than those of Hasson and Nicholls (1971). These values deduced from *in situ* measurements are thus somewhat smaller than those suggested by Frederick and Mentall (1982).

Figure 6 shows that the dispersion in the available data is quite important and leads to significant uncertainties in the photodissociation rate of several trace species. One dimensional models have been used very recently by Froidevaux and Yung (1982) and by Brasseur *et al.* (1983) in order to estimate the importance of the stratospheric composition changes due to absorption cross section values 30–50% lower than those currently used in photodissociation calculation.

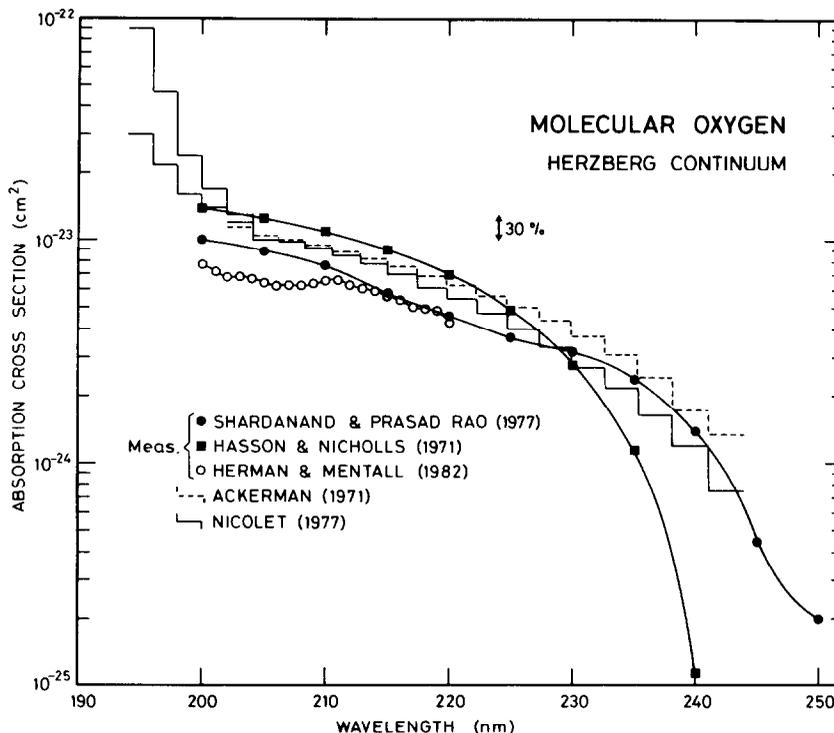


FIG. 6. ABSORPTION CROSS SECTION OF MOLECULAR OXYGEN BETWEEN 200 AND 250 nm.

4. THE ABSORPTION CROSS SECTION OF OZONE

The ozone absorption cross section has been measured in the u.v. up to 350 nm and in the visible range from 400 to 200 nm. Only one absorption cross section spectrum with an estimated uncertainty of $\pm 10\%$ is available below 200 nm (Tanaka *et al.*, 1953). Numerical values have been deduced from this work for modelling purposes (Ackerman, 1971).

Beyond 200 nm, the Hartley bands peak around 250 nm with a value of $1.146 \times 10^{-17} \text{ cm}^2$ for the absorption cross section (Hearn, 1961) which decreases below to 10^{-22} cm^2 through to the Huggins bands beyond 300 nm. The values measured by Inn and Tanaka (1953) are widely used in the photodissociation calculation from 200 to 300 nm. Beyond this wavelength, the adopted temperature dependence of the absorption cross section has been based up to now on the work of Vigroux (1953).

Since the review published by Ackerman (1971) new measurements are now in progress at the National Bureau of Standards (USA) and at the University of Reims (France). Preliminary results for the wavelength range of 245–345 nm at 295 and 243 K have been reported by Bass and Paur (1981). These measurements are relative to peak absorption values measured by

Hearn (1961) at 254 nm. Absolute measurements performed by Daumont, Malicet and Brion (1983; private communication) at 293 and 223 K between 300 and 350 nm are systematically 12% lower than those reported by Bass and Paur (1981). The uncertainty in the new values of the cross section is estimated to be 2% or less for both groups. These latter measurements resolve with a better precision the features of the absorption spectrum (the instrumental width is about 0.02 nm). Consequently, these data with resolved structure, especially beyond 300 nm, can be used to analyze the solar backscattered radiation measured by satellites (McPeters and Bass, 1982).

The absorption of solar radiation by ozone takes place in the mesosphere and in the stratosphere for wavelengths greater than 180 nm. At higher altitude, the ozone density is too small to play any role in the penetration of the u.v. solar radiation. The photodissociation of ozone leading to the formation of the excited state of atomic oxygen has been investigated for a long time, particularly by Nicolet (1939).

5. SCATTERING

When penetrating in the atmosphere, the solar radiation is not only absorbed by optically active

constituents but also scattered by the gas molecules and the aerosols. The irradiance q at a given altitude z , wavelength λ and solar zenith angle χ is given by

$$q(\lambda, z, \chi) = q_\infty e^{-(\tau_a + \tau_s)} + \int_\Omega I(\lambda, z, \Omega) d\Omega \quad (18)$$

where $I(\lambda, z, \Omega)$ is the intensity of the light which is scattered in the solid angle Ω .

The optical depth corresponding to the absorption (τ_a) can be expressed as:

$$\tau_a(\lambda, z, \chi) = \sec \chi \left[\sigma_a(\text{O}_2; \lambda) \int_z^\infty n(\text{O}_2) dz' + \sigma_a(\text{O}_3; \lambda) \int_z^\infty n(\text{O}_3) dz' \right] \quad (19)$$

since the main absorbing gases are molecular oxygen and ozone. The attenuation due to scattering processes appears through a second contribution of the optical depth (τ_s) which can be written as:

$$\tau_s(\lambda, z, \chi) = \sec \chi \left[\sigma_R \int_z^\infty n_R dz' + \sigma_M \int_z^\infty n_M dz' \right] \quad (20)$$

where σ and n are respectively the scattering cross section and the concentration of the Rayleigh (R) and Mie (M) scatters.

The first effect is governed by air molecules while the second contribution is due to aerosol particles. As indicated by Meier *et al.* (1982), test calculations have shown that, for standard atmospheric load, Mie scattering has a small effect on the value of the solar irradiance. The cross section related to Rayleigh scattering is given by (Fröhlich and Shaw, 1980):

$$\sigma_R = \frac{32\pi(\mu - 1)}{3n_R^2\lambda^4} f(\delta) \quad (21)$$

where μ is the refractive index of the air which depends on the pressure, the temperature, the relative humidity and varies with wavelength. The function

$$f(\delta) = (6 + 3\delta)/(6 - 7\delta) \quad (22)$$

where δ is the depolarization factor, accounts for the anisotropy of the molecules. For a standard mixture of air it has a value close to 1.016 (Fröhlich and Shaw, 1980). When calculating explicitly the Rayleigh scattering cross section can be expressed as:

$$\sigma_R = \frac{3.93 \times 10^{-16}}{[\lambda(\text{nm})]^{4+x}} \quad (23)$$

where x is given by (Fröhlich and Shaw, 1980)

$$x = 74\lambda + 5 \times 10^{-5}/\lambda - 0.084, \quad (24)$$

λ being expressed in nm.

The effect of scattering on the u.v. and visible radiation field in the troposphere and stratosphere has been recently analyzed by Meier *et al.* (1982) and Nicolet *et al.* (1982). Their results show that multiple scattering and ground albedo can lead to large amplifications of the solar irradiance in the photochemically active spectral region. These authors have calculated the corresponding enhancement factors as a function of height, solar zenith angle and wavelength. Numerical tables of these factors are given in convenient format for computational use. Herman and Mentall (1982b) have determined from their solar u.v. observations performed at the altitude of 40 km, the relative importance of scattering vs absorption. Their analysis shows that the scattered flux in the upper stratosphere is of the order of 1% of the direct flux between 220 and 300 nm and becomes larger than 10% beyond 310 nm.

6. CONCLUSIONS

Significant improvements are required in solar irradiance measurements. Accuracy of the order of 5% is needed for the calculation of photodissociation frequencies. Such an objective is achievable by appropriate calibration and measurement strategies. In particular, the magnitude of the solar variability related to the rotation period of the Sun and the 11-year cycle should be further investigated.

New *in situ* measurements of the atmospheric attenuation of the solar irradiance have questioned the accepted values of the absorption cross section of molecular oxygen in the Herzberg continuum. The low absorption recently observed in this wavelength range needs to be confirmed.

The penetration of the solar radiation in the Schumann–Runge bands is strongly dependent on spectrometric parameters which are not sufficiently well known for an accurate determination of the photodissociation frequencies in this part of the spectrum.

The optical depth around 210 nm is also driven by the ozone absorption. New values of the corresponding cross section in the vicinity of this wavelength are required in order to confirm the presently available data. Determination of the solar penetration should also consider the effect of multiple scattering which plays an important role above 300 nm and cannot be neglected in the calculation of the attenuation around 200 nm.

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