CHANGES IN ATMOSPHERIC CHEMISTRY RELATED TO SOLAR FLUX VARIATIONS

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ABSTRACT

Changes in atmospheric chemistry, which are due to solar flux variations, must be explained by solar activity effects in the spectral ranges of the O_2 photodissociation between 100 and 240 nm. Special attention is given to various spectral regions from Lyman-α at 121.6 nm to the Herzberg continuum threshold at 242 nm. Various molecules containing $H(H_2O, \ldots)$, $N(N_2O, \ldots)$, $Cl(CCl_4, CF_2Cl_2, CFCl_3, \ldots)$, which are photodissociated in these spectral regions, are also related to specific variations of spectral solar irradiances. For absorption by O_3, the solar flux variations have not an important role, but particular attention must be given to the production of the excited atom $O(^1D)$ leading, by reaction with H_2O, CH_4, H_2, N_2O, \ldots , to their dissociation and subsequent reactions.

1. INTRODUCTION

The chemical reactions in the atmosphere depend ultimately on the photodissociation of atmospheric constituents by solar radiation at wavelengths greater than 100 nm (e.g., Nicolet, 1975). First, O_2 is photodissociated successively by radiation in several wavelength bands: less than 175 nm in the Schumann-Runge continuum, less than 200 nm in the Schumann-Runge band system, and less than 242 nm in the Herzberg continuum. Hydrogen Lyman-α radiation from the chromosphere is especially important because of its high intensity and its relatively low absorption in O_2.

Second, O_3 is important because of the high absorption of solar radiation in the Hartley band, which extends to 310 nm. At greater wavelengths, the Huggins bands extend up to about 350 nm, and the Chappuis bands into the visible region.

Thus, absorption by O_2 and O_3 determines the degree of penetration of solar radiation into the terrestrial atmosphere. In consequence, the way in which the chemistry of the atmosphere can be influenced by variations in the solar radiation flux, both at the top of the atmosphere and at lower levels, is controlled by O_2 and its direct product O_3.

2. ATMOSPHERIC ABSORPTION

The height at which maximum absorption occurs, i.e., where the optical thickness equals unity, varies considerably and depends on the absorption cross-sections of O_2 and O_3. In the Schumann-Runge continuum, the cross-section reaches 10^{-17} cm², and there is total absorption above the mesopause in the thermosphere. The O atoms produced above 100 km drift downwards and recombine at heights below 100 km. The rotational structure of the Schumann-Runge bands leads to great variations in the absorption cross-section, which varies by a factor of 10^4 (10^{-19} to 10^{-23} cm²) between 200 and 175 nm; the absorption is spread over the whole of the mesosphere from above the mesopause, the (18-0) band, to below the stratopause, the (2-0) band.
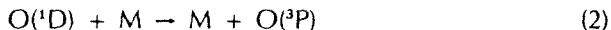
For the Herzberg continuum, the cross-section is small and, even at its maximum near 195 nm, probably does not exceed 10^{-23} cm². It overlaps the first of the Schumann-Runge bands, (2-0) to (5-0), and in this region both systems contribute to the absorption.

As the wavelength increases from 200 to 240 nm, the O_2 absorption decreases, while that of O_3 increases. In consequence, near 210 ± 20 nm, the optical thickness of the atmosphere is very sensitive to the relative contributions of the absorption due to O_2 and O_3. Later, we shall examine this question in the light of our present knowledge of the solar spectrum and of the characteristics of the molecules in this spectral region.
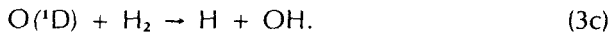
The O_3 Hartley band has an absorption maximum of 10^{-17} cm² near 250 nm and gives rise to the photodissociation of O_3 up to about 310 nm through the following reaction:

$$O_3 + h\nu(\lambda < 310 \text{ nm}) \rightarrow O_2^* + O^* + O \tag{1}$$
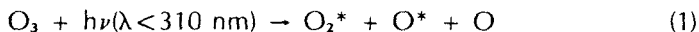
where O_2^* and O^* represent excited states. Up to 90% of the O atoms are in the metastable state $O(^1D)$; those which escape to de-excitation by collision with N_2 or O_2:

$$O(^1D) + M \rightarrow M + O(^3P) \tag{2}$$

react rapidly with water vapor, CH_4 or H_2:

$$O(^1D) + H_2O \rightarrow OH + OH \tag{3a}$$

$$O(^1D) + CH_4 \rightarrow CH_3 + OH \tag{3b}$$

$$O(^1D) + H_2 \rightarrow H + OH. \tag{3c}$$

Thus the photodissociation of O_3 in the Hartley band is the starting point for the whole of tropospheric and stratospheric chemistry.

It must be mentioned that the small cross-sections in the Huggins bands, 10^{-19} to 10^{-23} cm², are very sensitive to temperature. There is a reduction of about 5%, near 290 nm, in passing from laboratory temperature to that in the strato-

sphere; this value rises to over 20% at 320 nm, and reaches 50% near 340 nm. The cross-section in the Chappuis bands does not change with temperature; between 500 and 800 nm it exceeds 10^{-21} cm^2, but is less than 5×10^{-21} cm^2 at its maximum near 600 nm. However, when discussing spectral effects in the atmosphere at wavelengths above 300 nm, it is necessary to bear in mind also those due to Rayleigh scattering and the albedo.

3. SOLAR RADIATION

Although absolute values of solar irradiance must be considered, it is important to remember that the accuracy of the observational values is not better than $\pm 10\%$ (e.g., Nicolet, 1981). Hence, if two independent observations are compared, a difference of 5% is not significant. In view of this, errors of interpretation are bound to occur if insufficient attention is given to the errors of observation arising from the difficulties in making the measurements. Two spectra obtained using rockets do not necessarily refer to strictly identical experimental conditions. Data acquired over a period of time using satellites must inevitably be influenced by changes in the sensitivity of the instruments, and it is important to know whether such changes are gradual or subject to fluctuations, whether they are linear or not, etc. Without this information, it is not possible to deduce accurately the way in which solar activity varies at different wavelengths. For example, an examination of the data obtained by Nimbus 7 (Heath, 1981) and by the Solar Explorer Satellite (Rottman, 1983) leads to the conclusion that solar activity changed by less than 1% above 240 nm, the spectral region responsible for the photodissociation of O_3; on the other hand, at the lower wavelengths responsible for the photodissociation of O_2, the changes in activity must be considered. Nevertheless, the Nimbus 7 data for 1978 and 1979 clearly show a drift due to aging of the instruments near 200 nm, and it is essential to avoid confusing this with a solar effect. The 27-day cyclic changes in solar activity are clearly seen; they begin near 240 nm, corresponding to the ionization of MgI in the photosphere, and increase towards 210 nm where the continuum due to the ionization of AlI begins. This variation increases with decreasing wavelength and reaches a maximum in the Schumann-Runge continuum below 175 nm. Finally, Lyman-α radiation is closely associated with the level of solar activity but, although many observations have been made during both high and low solar activity, they are not sufficiently consistent with each other. Indeed, the absolute flux of solar Lyman-α is not known to an accuracy better than 25%.
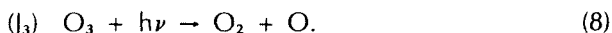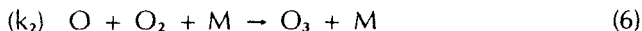
4. OZONE FORMATION

If the production and destruction of O_3 in the simple case of a pure O_2

atmosphere are considered, the photochemical equilibrium equation for the stratosphere can be written:

$$n^2(O_3) = (J_2/J_3)n(M)n^2(O_2)(k_2/k_3) \tag{4}$$

where the symbols have the following meanings:

$$(J_2) \quad O_2 + h\nu \rightarrow O + O \tag{5}$$

$$(k_2) \quad O + O_2 + M \rightarrow O_3 + M \tag{6}$$

$$(k_3) \quad O + O_3 \rightarrow 2O_2 \tag{7}$$

$$(J_3) \quad O_3 + h\nu \rightarrow O_2 + O. \tag{8}$$

The concentration of O_3 is proportional to the square root of the ratio J_2/J_3 of the dissociation frequencies for O_2 and O_3, respectively. In consequence, any change in solar activity must result in an increase in O_3 production, since J_2 depends on the radiation at wavelengths less than 240 nm, while J_3 depends mainly on the longer wavelengths. The ratio k_2/k_3 is an exponential function of the temperature ($e^{+x/T}$), and hence the concentration of O_3 increases with decreasing temperature. However, an increase in the O_3 concentration leads to an increase in the temperature, and this in turn results in a decrease in the initial rise in a region where there is photochemical equilibrium. This illustrates why the influence of solar radiation on stratospheric chemistry must take account of the interactions between the various processes.

5. OZONE DESTRUCTION

It is now well known that the basic reaction for the destruction of O_3, its reaction with atomic O (7), is often less important than others involving catalytic reactions with molecules containing H, N or a halogen (e.g., Nicolet, 1975) such as the pair:

$$k_x \quad X + O_3 \rightarrow O_2 + XO \tag{9}$$

$$k_{xo} \quad XO + O \rightarrow O_2 + X. \tag{10}$$
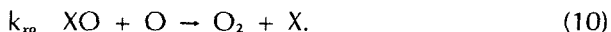
The simple expression (4) for photoequilibrium concentrations of stratospheric O_3 can be applied also to reactions (9) and (10) provided that k_3 is replaced by:

$$k_{3x} = k_3 [1 + k_{xo} n(XO)/k_3 n(O_3)] \tag{11}$$

that is, by a correction term which increases the rate of destruction and which depends on the ratio of the concentrations of the oxide XO and of O_3. The present objective is not to discuss the specific effect of the various reactions.

However, it is worth recalling that OH and HO_2, together with O_3, are involved in reactions in the lower stratosphere; the two radicals react strongly with atomic O in the upper stratosphere, and up to the greatest heights. In the middle stratosphere, X and XO must be associated not only with NO and NO_2, but also with the atom Cl and its monoxide ClO.

The presence in the atmosphere of the various atoms and molecules containing H, N and Cl gives rise to the problem of determining how they react to the incident solar radiation.

6. OH AND HO_2 RADICALS

As already explained, the presence of OH and HO_2 in the troposphere and the stratosphere is directly related to the oxidation of water vapor (Equations [1] and [2]) and of CH_4 and H_2. The action of the solar radiation results indirectly in the production of $O(^1D)$ atoms from the photodissociation of O_3, but this process cannot be regarded as related to solar activity, since it depends primarily on the absorbing properties of O_3 in the Hartley band which are temperature dependent above 280 nm. At 300 nm the cross-section in the stratosphere is 10% less than in the laboratory. On the other hand, the quantum yield for the production of the atom $O(^1D)$ by process (1) is a function of temperature, and hence varies with atmospheric temperature. Finally, in the troposphere and the lower stratosphere, it is necessary to take account of the effects due to multiple anisotropic scattering, and of the terrestrial or the cloud albedo, which increase the rate of photodissociation.
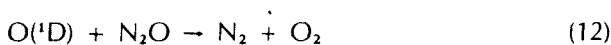
In the mesosphere, the photodissociation of H_2O by Lyman-α (e.g., Nicolet, 1980), and also by wavelengths less than 200 nm, provides a direct link between solar activity and the production of radicals containing H. Hence, since mesospheric chemistry is strongly linked to the reactions of H, OH and HO_2 with O and O_3, it it totally dependent on solar activity.

7. NITROGEN OXIDES

The presence of NO in the mesosphere is due almost entirely to its transport from the thermosphere as a result of ionic reactions above 100 km, particularly in the E region. Since the E region is formed as a result of the simultaneous effects of Lyman-β and CIII at 97 nm, and X-rays between 30 and 90 A, the production of NO, resulting from the reaction of N with O_2, is linked to the variations in the irradiances in these different spectral regions, which are very sensitive to solar activity.

Nitrogen oxides in the stratosphere occur essentially because of the presence of N_2O brought in by turbulent transport from the troposphere. Although N_2O undergoes photodissociation in the stratosphere, it is involved also in a reac-

tion with $O(^1D)$ which gives rise to NO:

$$O(^1D) + N_2O \rightarrow N_2 + \overset{.}{O}_2 \qquad (12)$$

$$\rightarrow NO + NO. \qquad (13)$$

As can be seen, the production of NO depends on the vertical distributions of both $O(^1D)$ and N_2O. An examination of the spectrum of N_2O leads at once to the conclusion that its photodissociation in the stratosphere is due, in almost equal proportions, to the solar fluxes above and below 200 nm: that is, to the O_2 Schumann-Runge bands below 200 nm, and to the Herzberg continuum above 200 nm (e.g., Table 9 in Nicolet, 1980). Thus, the effect of solar activity, combined with the temperature dependence of the cross-section of N_2O determines the degree of photodissociation of N_2O in the stratosphere and, finally, the production of NO as a function of height.

When considering the equilibrium between the different oxides of nitrogen in the stratosphere, it is necessary to take account of HNO_3 which is their sink at the level of the tropopause. It should be noted also that the solar flux above and below 200 nm influences the rate of photodissociation (e.g., Table 10 in Nicolet, 1980). Hence, the vertical distribution of HNO_3 in the middle and upper stratosphere is influenced by solar activity.

While admitting that the oxides of nitrogen depend also on the action of corpuscles originating in galactic cosmic rays, proton flares, etc., it can be concluded that the behavior of these oxides is related in many ways to fluctuations in the solar radiation flux resulting from changes in solar activity.

8. CHLORINE OXIDES

The presence of Cl in the stratosphere is due partly to the photodissociation, or the oxidation, of methylchloride CH_3Cl, a natural constituent of the troposphere, and partly to the direct photodissociation of industrial products such as carbon tetrachloride CCl_4, trichlorofluoromethane $CFCl_3$, dichlorodifluoromethane CF_2Cl_2, etc. It is important to remember that all these Cl compounds have absorption spectra which are temperature dependent to different degrees, and which lie both above and below 200 nm (e.g., Tables 11 to 14 in Nicolet, 1980). It follows that the influence of solar activity must result in different rates of dissociation depending on the precise characteristics of the respective spectra. Hence, all the minor atmospheric constituents associated with O_3 chemistry are subject, in one form or another, to the effects of variations in the solar flux.

9. DISCUSSION

Before drawing final conclusions on how variations in solar activity influence

the solar irradiance between 240 nm and Lyman-α, it is necessary to look at the question in the light of the experience of several cycles of solar activity. There are important differences, for example, between the past three cycles: 19, 20 and 21. Out of the 21 cycles observed since 1755, cycle 19 attained the highest Wolf number: 190 in 1957 and 180 in 1958, the highest monthly mean (R = 254 in October 1957) and the highest daily maximum (R = 371 on December 24-25, 1957). The highest values of solar radio flux at 10.7 cm were 233 and 232 in 1957 and 1958, respectively, 281 in October 1957 and 371 on December 23, 1957. The annual mean values during cycle 20 were only average; the maxima for the years 1968, 1969 and 1970, respectively, were 106, 105 and 104 for the Wolf number, and 149, 152 and 156 for the 10.7-cm solar radio flux. Cycle 20 was 10th in importance among the 21 cycles of the past 200 yr, and hence can be regarded as the average cycle. However, cycle 21 is one of the most important from the point of view of activity; its average maximum Wolf number in 1979 and 1980 was 150, while the maximum 10.7-cm fluxes for these years were 192 and 198. It is clear that long-term variations in the level of solar activity must be estimated in terms of sufficiently reliable indices such as the Wolf number or the solar flux at 10.7 cm. It is not possible to use directly all the various observations that have been made in space since 1957 because the accuracy required for long-term studies has not yet been attained. However, the variations in activity associated with the 27-day cycles are valuable because, especially during periods of high activity, the absolute accuracy has a less important role in the analysis than the precision of short-term changes.

As an example, Figure 1 shows the variations in Lyman-α during the past cycle. There is a lack of homogeneity, and a scatter of the values which correspond to changes in flux of a factor of 5: i.e., from 2×10^{11} photons cm^{-2} s^{-1} at minimum activity to 10^{12} photons cm^{-2} s^{-1} at the maximum. A first attempt to make all the observations internally consistent, or consistent with each other, was made by Bossy and Nicolet (1981) (see also Nicolet, 1981). First, it was found that the absolute value at minimum activity could not be determined with sufficient accuracy. Writing for a quiet sun:

$$F(\text{Lyman-}\alpha) = (2.75 \pm 0.75) \times 10^{11} \text{ photons cm}^{-2} \text{ s}^{-1} \qquad (14)$$

it is implied that the absolute calibration leads to errors of between 25 and 30%. In fact, such limits include almost all the observations made at very low solar activity, and at the present time there is no possibility of determining the absolute value of the Lyman-α flux without recourse to artificial techniques. A value of 3×10^{11} photons cm^{-2} s^{-1} is just as appropriate as any higher or lower value (e.g., Rottman, 1981).

The process of improving the internal consistency of the observational data must be carried out by a simple method that can be controlled. It can be based on a solar activity index, such as the 10.7-cm flux which is known to about $\pm 5\%$ for at least the past three cycles. Almost all the adjusted values of the Lyman-α flux can be represented, with a dispersion of $\pm 10\%$, by an expression of the form:

$$F(\text{Lyman-}\alpha) = 3 \times 10^{11} \left[1 + 0.2 \frac{F_{10.7} - 65}{100} \right] \text{photons cm}^{-2} \text{s}^{-1}. \qquad (15)$$
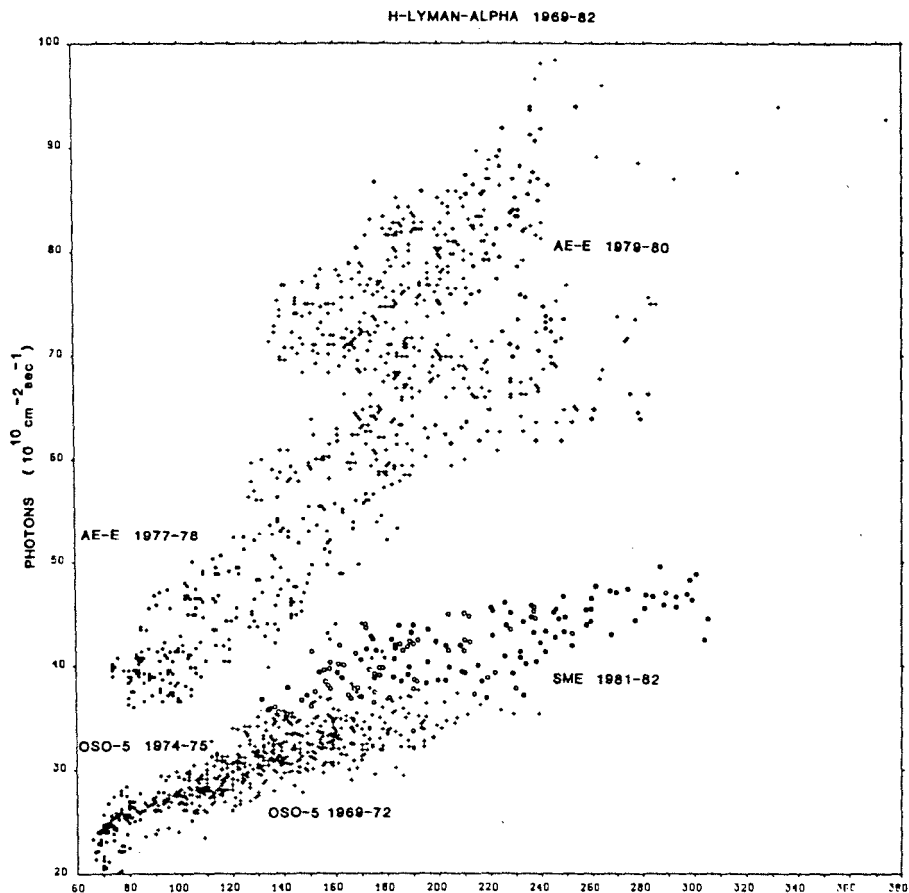
H-LYMAN-ALPHA 1969-82

Figure 1. Lyman-α solar flux versus the solar radio flux at 10.7 cm. Observations OSO-5 (1974–1975) from Vidal-Madjar (1975), OSO-5 (1969–1972) from Vidal-Madjar and Phissamay (1980), SME 1981–1982 from Rottman (1983 and private comm.), AEE from Hinteregger (1981 and private comm.).

As can be seen, the variability of Lyman-α has differed completely from one cycle to the next during the past three cycles. However, whatever the amplitude of the cycle, this variation is by less than a factor of 2, and does not correspond at all to Figure 1. From this, it is concluded that the flux over the whole of the spectral region responsible for the photodissociation of O_2, and then for the formation of O_3, varies by less than a factor of 2. The results to be published on the Solar Mesosphere Explorer Satellite (Rottman, 1983) will show variations of only a few percentage points near 200 nm, and a maximum of 50% at the shortest wavelengths, over a fairly long period of time.

The problem of the dependence of photodissociation on the variation in the solar flux raises another peculiarity of atmospheric chemistry: namely, the question of the penetration of solar radiation into the atmosphere, especially in the region of the O_2 Herzberg continuum (Figure 2). In their determinations
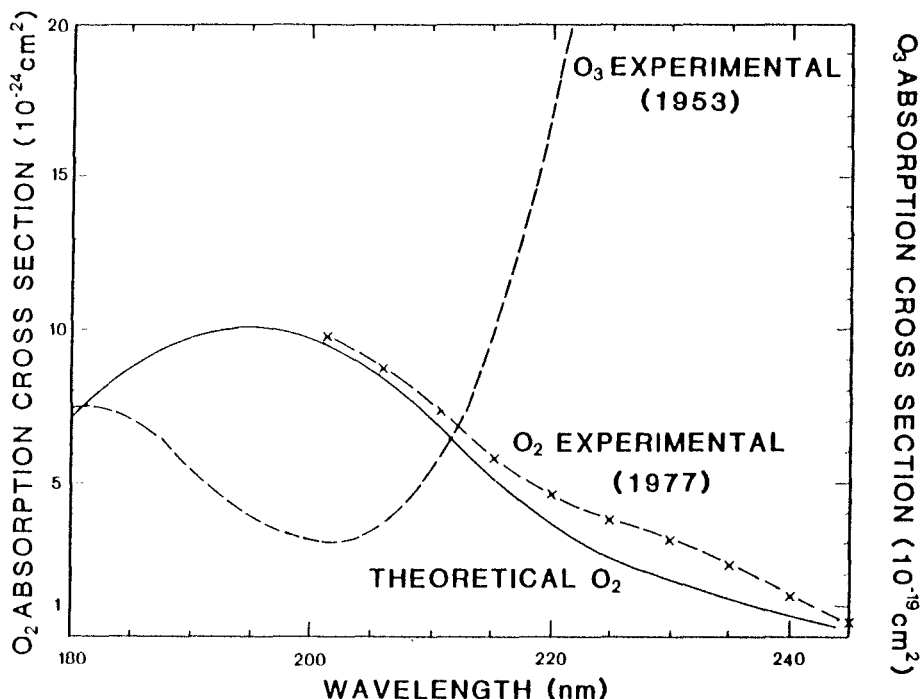
Figure 2. Comparison of the absorption cross-sections of O_2 (10^{-24} to 10^{-23} cm²) in the Herzberg continuum and of O_3 (3×10^{-19} to 2×10^{-18} cm²) between 180 and 240 nm. An O_2 theoretical curve is compared with experimental data as shown in Figure 3.

of the absorption in the Schumann-Runge bands of O_2, all the authors have adopted values for the continuum which are too high; these come from theoretical results for the Herzberg continuum (Jarmain and Nicholls, 1967) calibrated between 200 and 210 nm using the experimental values of Ditchburn and Young (1962). Figure 3 (Nicolet, 1982) illustrates the large scatter in the experimental values of cross-sections (Hasson and Nicholls, 1971; Ogawa, 1971; Shardamand and Prasad Rao, 1977).

The inaccuracy arises from the fact that the absolute value of the cross-section is very low (less than 10^{-23} cm²) and that it must be obtained by extrapolation from values measured at high pressure.

The atmospheric observations studied by Frederick and Mentall (1982) and by Hermann and Mentall (1982) clearly show that the data used up to the present are inadequate. A reduction in the maximum value of the theoretical cross-section at 195 nm from 1.3×10^{-23} to 10^{-23} cm², as shown in Figure 2, results in better agreement with the last experimental values. An overall reduction by a factor of 2, while still bearing in mind the absorption due to Rayleigh scattering (Figure 3), seems to be consistent with these first observational results. Thus it is clear that there is a need for a revision of the method of calculation of the photodissociation in the stratosphere. The calculations of the transmission factor, illustrated in Figure 4 (Nicolet, 1982), show to what extent the Herz-
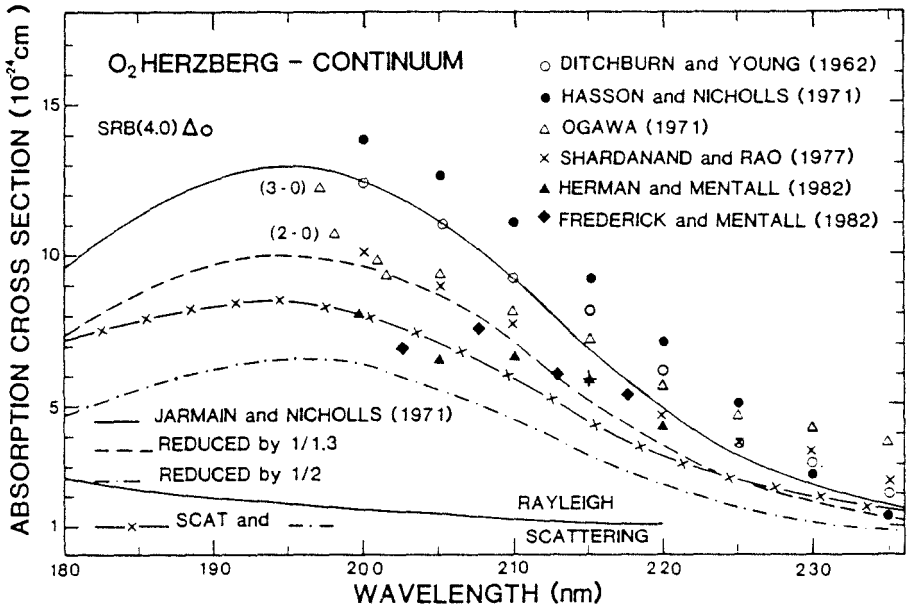
Figure 3. Absorption cross-sections in the Herzberg continuum of O_2. The theoretical curve deduced by Jarmain and Nicholls has been reduced by factors of 1/1.3 (---) and 1/2 (-·-) for comparison with the various experimental values. Rayleigh scattering cannot be neglected since it constitutes at least 10% of the total, and it has been introduced in the derivation of the intermediate curve (x-x). The recent observational data published by Hermann and Mental and Frederick and Mentall are shown.

berg continuum determines the penetration of solar radiation at wavelengths less than 215 nm. A new and more accurate determination of the continuous absorption of O_2 is required, and also a better knowledge of the structure of the Schumann-Runge bands.

To conclude, a better understanding of the influence of solar radiation on the chemistry of the atmosphere demands not only improved experimental data on the absorption of O_2 and O_3, the values of which determine the penetration of UV radiation into the mesosphere and stratosphere, but also information on the irradiance values in the UV that are based on absolute calibrations and are free from errors due to instrumental drifts.

Figure 4. Atmospheric transmission factor at 35 km for standard conditions corresponding to two different solar zenith angles, sec x = 1 and 2. Average experimental cross-sections have been taken as basic values in curves 1 and 2. Curves 1c and 2c correspond to a decrease by 1/1.3 of the theoretical cross-section, and curves 1cc and 2cc to a decrease by 1/2, but with the addition of the Rayleigh scattering absorption.
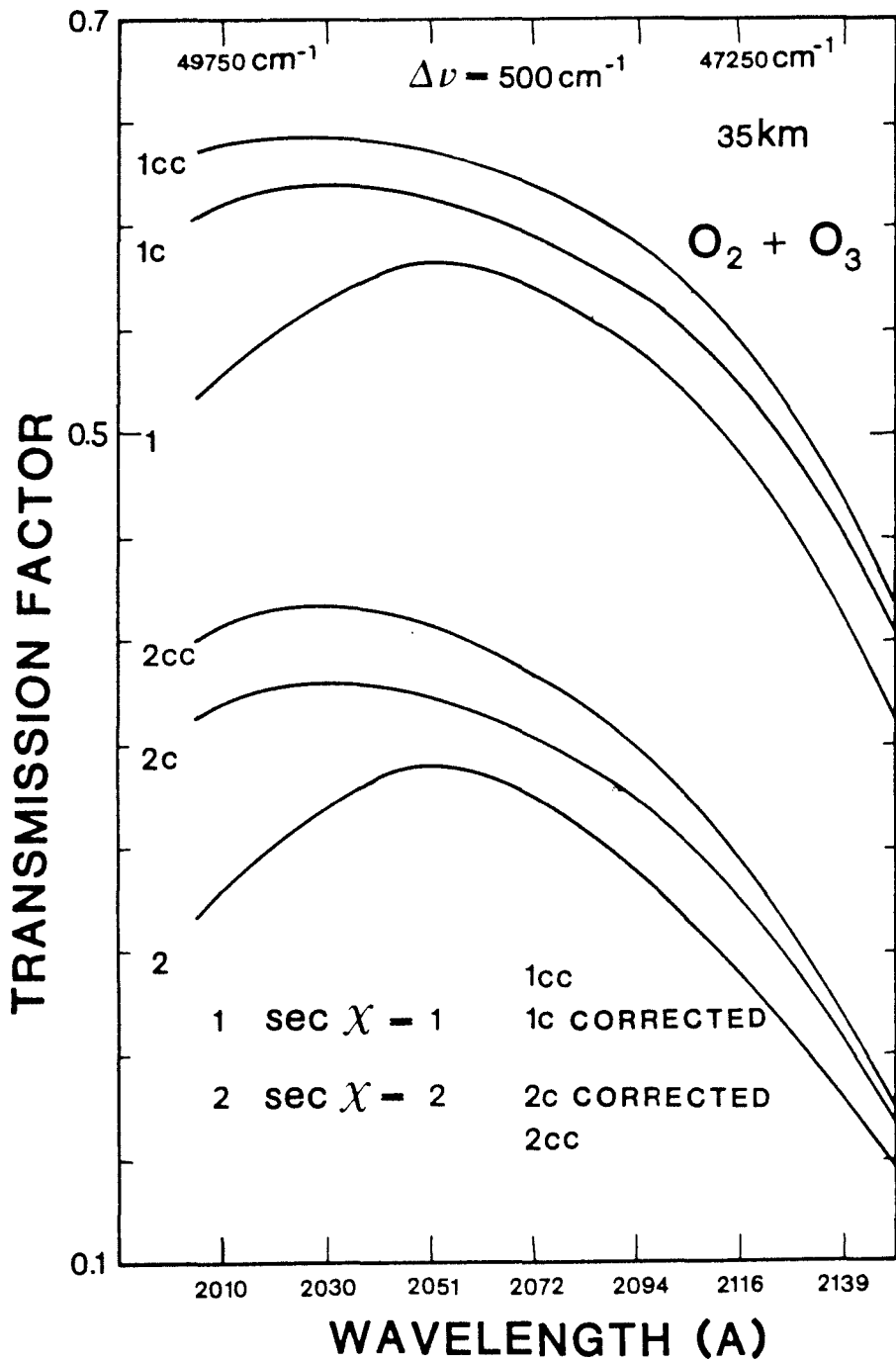
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