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**Implication for stratospheric composition of a reduced
absorption cross section in the Herzberg continuum of
molecular oxygen**

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G. BRASSEUR, A. DE RUDDER and P.C. SIMON

B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

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FOREWORD

This paper will appear in Geophysical Research Letters.

AVANT-PROPOS

Cet article paraîtra dans "Geophysical Research Letters".

VOORWOORD

Deze tekst zal verschijnen in "Geophysical Research Letters".

VORWORT

Dieses Artikel wird in "Geophysical Research Letters" herausgegeben werden.

IMPLICATION FOR STRATOSPHERIC COMPOSITION OF A REDUCED

ABSORPTION CROSS SECTION IN THE HERZBERG CONTINUUM OF

MOLECULAR OXYGEN

by

G. BRASSEUR, A. DE RUDDER and P.C. SIMON

Abstract

Recent determinations of O₂ absorption cross sections in the Herzberg continuum, obtained from in situ solar irradiance measurements, have shown that the corresponding laboratory values might be overestimated by 30 to 50 percent. The change in the stratospheric composition due to such a reduction in these cross sections has been calculated by means of a steady state one dimensional chemical model. An accurate determination of the O₂ absorption spectrum in the 200-220 nm range is required since the distribution of several trace species is very sensitive to the atmospheric transmissivity in this wavelength region.

Résumé

La section efficace d'absorption de l'oxygène moléculaire, dans le domaine spectral du continuum de Herzberg, a été déterminée à partir de la mesure de l'éclairement solaire, à deux altitudes connues. Ces observations indiquent que les valeurs obtenues au laboratoire seraient de 30 à 50 pourcent trop élevées.

Les conséquences d'une réduction de la valeur des sections efficaces sur la composition chimique de l'atmosphère ont été étudiées à l'aide d'un modèle mathématique unidimensionnel. Comme la distribution verticale des composés minoritaires est très sensible à la transmission du rayonnement entre 200 et 220 nm, une détermination précise de la section efficace d'absorption de O_2 dans ce domaine spectral est requise.

Samenvatting

Recente bepalingen van de werkzame absorptiedoorsneden van O_2 in het Herzberg continuüm bekomen door in situ metingen van de zonnestraling hebben aangetoond dat de overeenkomstige laboratoriumwaarden waarschijnlijk overschat zijn met 30 tot 50 percent. De verandering in de stratosferische samenstelling te wijten aan een dergelijke vermindering in deze werkzame absorptiedoorsneden werd berekend door middel van één dimensioneel chemisch model van het steady state type. Een nauwkeurige bepaling van het absorptiespectrum van O_2 in het 200-220 nm interval is vereist door de verdeling van verschillende sporelementen uiterst gevoelig is aan de atmosferische transmissiviteit in dit golflengtegebied.

Zusammenfassung

Die neue Bestimmungen des O_2 absorption Durchschnittmesser in das Herzberg Continuum, haben gezeigt dass die Laboratorium Messungen wahrscheinlich von 30% bis 50% zu gross sind.

Die Änderungen in der stratosphärischen Zusammensetzung einer solchen Reduktion sind abgeschätzt worden für ein Eindimensionales chemisches Modell.

Ein genaue Bestimmung des O_2 absorption Durchschnittmesser zwischen 200 und 220 nm is notwendig, denn die minoritäre Bestandteile der Stratosphäre hängen merklich von die Transmittivität der, Sonnenstrahlen in diesem Wellenlänge Bereich, ab.

1. INTRODUCTION

The photodissociation of molecular oxygen in the stratosphere, which is the starting process of the ozone formation, is primarily due to the action of solar radiation between the wavelength of 200 and 240 nm. In this spectral range, called the Herzberg continuum, the absorption by O_2 is very weak and an accurate value of the corresponding cross section ($< 10^{-23} \text{ cm}^2$) is 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 O_2 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 wavelength 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 (1982) have suggested changes in the O_2 absorption cross section in order to explain the observed attenuation of the solar irradiance between two different heights located in the range of 30 to 40 km. The observations have been performed by a balloon borne Fastie-Ebert double monochromator flying over Palestine, Texas.

Frederick and Mentall (1982), have deduced from their observations on September 15, 1980, that, in the 200-210 nm range, the Hasson and Nicholls cross sections should be multiplied by factors in

the range of 0.52 to 0.68. and the Shardanand and Prasad Rao (1977) values by factors in the range of 0.85 to 0.93. It should be noted however that, when applied to the two sets of laboratory data, these factors do not lead to exactly the same value of the corrected cross sections. This discrepancy results probably from the scatter in the data. The reduction factors 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 (1982) have derived with the same instrument on April 15, 1980, absorption cross sections which are about 30 percent smaller than the laboratory results of Shardanand and Prasad Rao (1977) from 200 to 210 nm and about 50 percent 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).

In fact, the large scatter in the balloon data does not allow to derive accurate values for the O₂ absorption cross sections. The observation of the solar irradiance at two different atmospheric levels only suggests that a reduction has to be applied to the laboratory data. Therefore, the absolute values of the O₂ cross section determined by Herman and Mentall are characterized by an error of ± 10 percent from 120 to 215 nm, ± 20 percent at 220 nm and ± 40 percent at 225 nm. More laboratory as well as in situ measurements are thus required.

Figure 1 shows that the dispersion in the available data is quite important and leads to significant uncertainties in the photodissociation rate of several trace species. The reduction of the O₂ cross section suggested by the observations in the stratosphere should obviously modify the stratospheric composition.

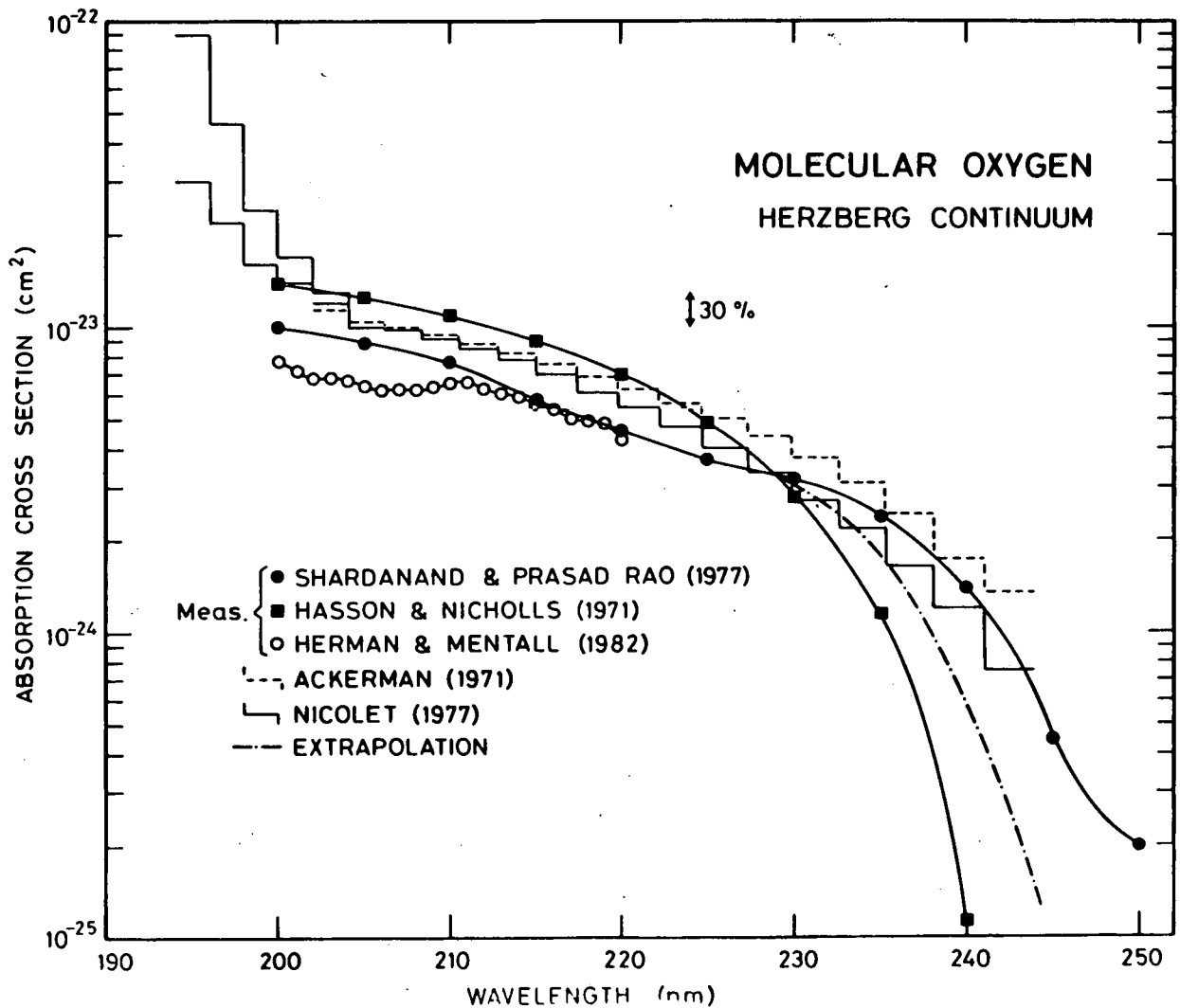


Fig. 1.- Absorption cross section of molecular oxygen in the Herzberg continuum. The dash-dotted line represents the adopted extrapolation for the Herman and Mentall values.

2. REDUCED O₂ CROSS SECTION AND ATMOSPHERIC OPACITY

In order to analyze the implication of a reduction in the absorption coefficients, different model calculations have been performed. The widely used cross sections of O₂ compiled by Ackerman (1971) have been used as the reference case. The values derived by Herman and Mentall (1982), with an extrapolation towards the long wavelengths have been considered for comparison calculations. The change in the transmission factor beyond 200 nm can be seen in figure 2. It clearly appears that the modification introduced by the in situ measurements appears essentially at wavelength shorter than 220 nm with a most pronounced effect at the lowest altitudes. Beyond 230 nm, the absorption is due essentially to ozone and an accurate value of the O₂ cross section is not anymore required. This allows us to use an extrapolation in the spectral range where no in situ measurements are available.

Since the irradiance in the stratosphere is increased with the new values of the absorption cross section, the photodissociation frequency of the species whose absorption spectrum is located around 200 nm (e.g. CFC₁₃, CF₂Cl₂, N₂O, HNO₃,....), is enhanced especially at the lower levels (figure 3). In the case of molecular oxygen, the photodissociation coefficient and consequently the ozone production rate is increased below 28 km but is reduced in the upper part of the stratosphere. The photolysis frequency of O₂ is indeed the product of the absorption cross section and the transmission factor which vary in the opposite direction.

Since the reduction in the O₂ cross section modifies the ozone distribution and consequently the opacity between 200 and 300 nm, the predicted change in the trace species photodissociation rate and concentration arises not only from the reduced O₂ cross section but also from the consequent change in the calculated ozone profile.

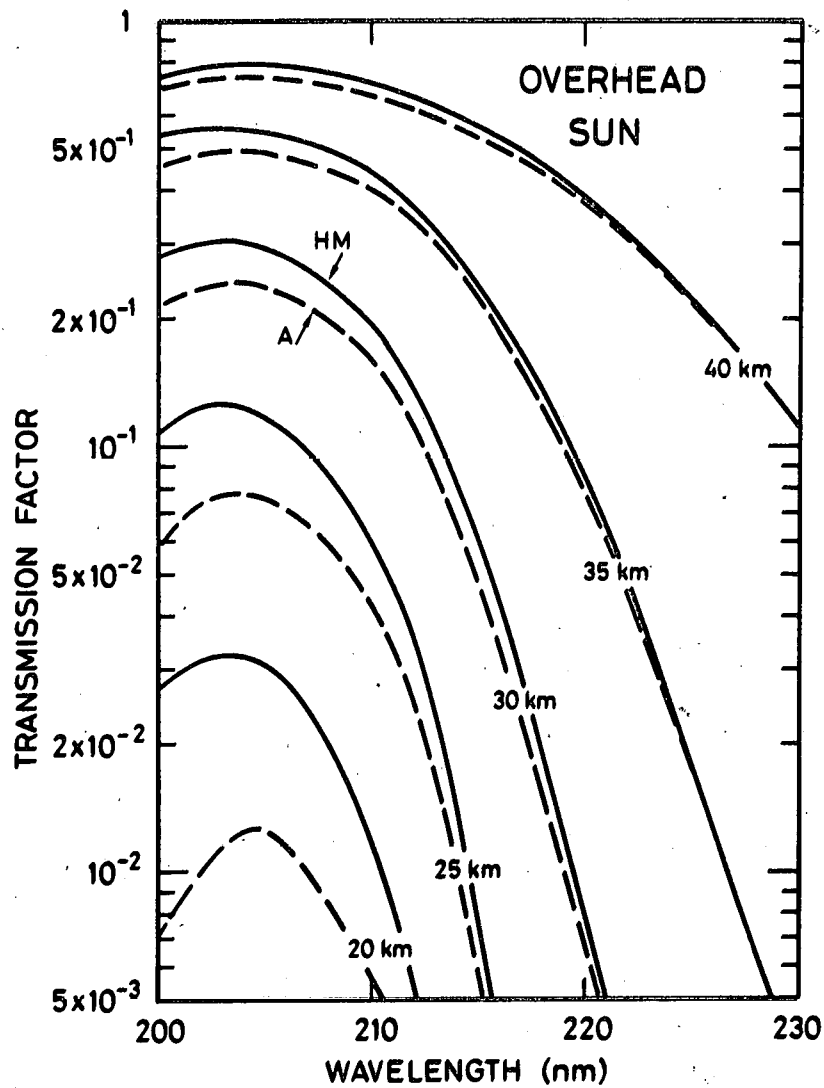


Fig. 2.- Transmittivity of the atmosphere between 200 and 230 nm calculated with the cross section values derived by Herman and Mentall (1982) (full lines) and compiled by Ackerman (1971) (dashed lines) - overhead sun.

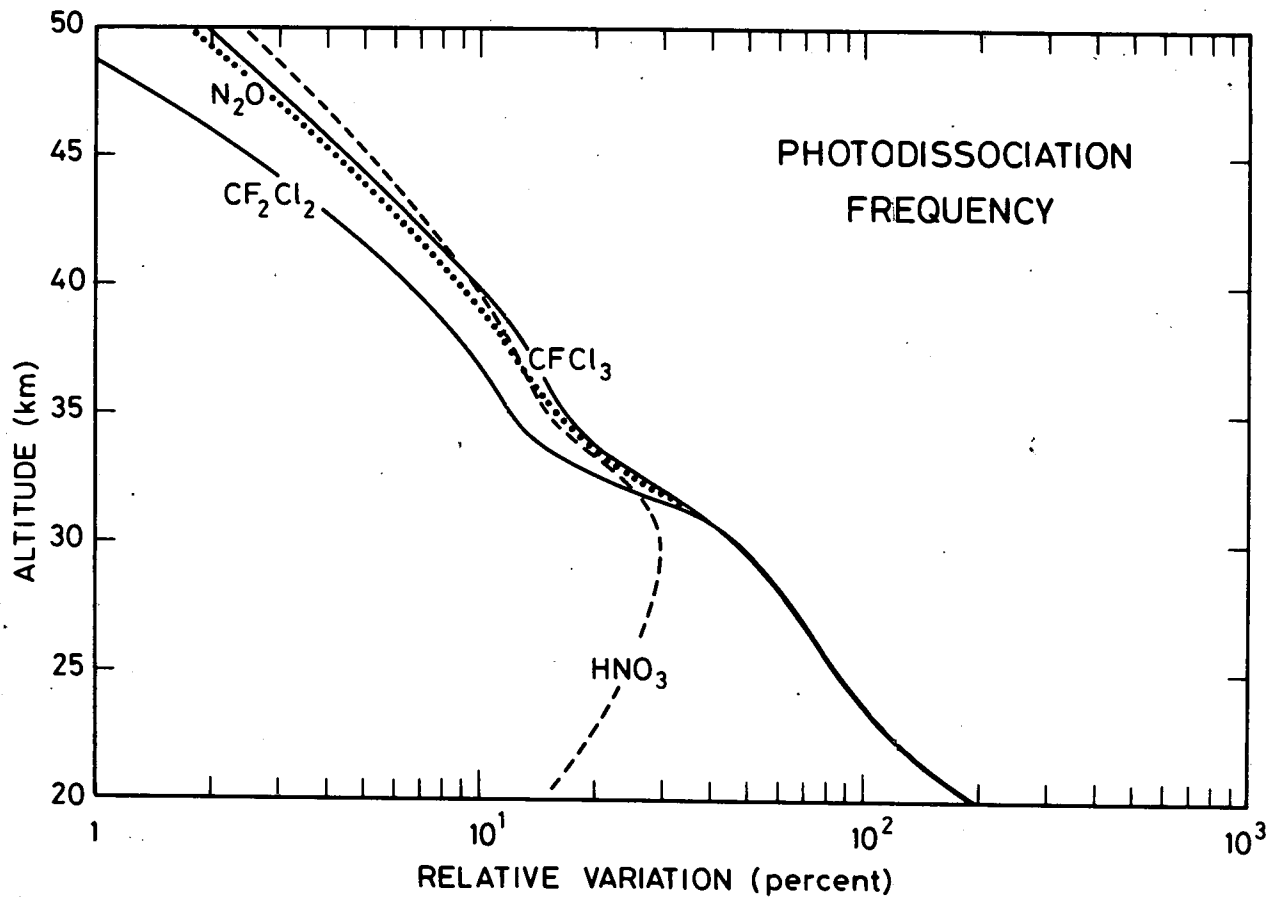


Fig. 3. - Relative variation in the 24 hours average photodissociation coefficient when the absorption cross sections are taken from Herman and Mentall (1982) instead of Ackerman (1971).

3. REDUCED O₂ CROSS SECTION AND TRACE SPECIES CONCENTRATION

The modification of the photodissociation rates arising from the reduction of the O₂ absorption in the Herzberg continuum leads to changes in the distribution of most minor constituents. This effect which has been recently considered by Froidevaux and Yung (1982) is investigated by means of the one-dimensional model which has been described by Brasseur et al. (1982). This steady state model derives the concentration of the most important middle atmosphere species belonging to the oxygen, hydrogen, nitrogen and chlorine families. The reaction rates recommended by WMO (1982) are adopted. The photodissociation frequencies are calculated assuming a 24 hour average solar illumination at the equinox. The solar irradiance is taken from Brasseur and Simon (1981) and is very similar to the values recommended by WMO (1982). The net vertical transport is parametrized by means of an exchange coefficient whose value at all altitudes is taken from Massie and Hunten (1982).

The temperature profile is prescribed and kept constant. Since the temperature/ozone coupling introduces a negative feedback, the present calculation with a fixed temperature profile provides upper limits in the calculated variations.

Species such as CFCI₃, CF₂Cl₂ and N₂O which are produced at ground level and destroyed in the stratosphere by photodissociation, will be affected by the reduction in the O₂ absorption cross section. As shown by figure 4, the concentration at 25 km altitude is reduced by 36 percent in the case of CFCI₃, by 8 percent in the case of CF₂Cl₂ and N₂O. At 30 km the mixing ratios computed with the cross sections values suggested by Ackerman should be multiplied by 0.86, 0.86 and 0.45 in the case of N₂O, CF₂Cl₂ and CFCI₃ respectively. The corresponding factors determined by Froidevaux and Yung (1982) are

0.70, 0.62 and 0.19. The difference should be attributed mainly to the fact that the reduced O_2 cross sections have been applied only above 200 nm in the present paper and down to 196.1 nm in the study by Froidevaux and Yung (1982). Moreover, the value of the eddy diffusion coefficient adopted by Froidevaux and Yung (1982) (Model K_2) is somewhat smaller than the value adopted in this work, which makes the trace species distribution more sensitive to the photochemical conditions. These changes bring closer together the observed and calculated values but nevertheless the disagreement which appears in all stratospheric models is not completely suppressed. For example, the observed mixing ratio of $CFCl_3$ at 25 km at mid-latitude lies between 3 and 5 pptv (Schmidt et al., 1980) while the model gives 31 pptv for Ackerman's cross sections and 19.7 pptv when the data by Herman and Mentall are adopted. Similarly, the calculated mixing ratios of CF_2Cl_2 at 30 km are respectively 53.1 pptv and 45.6 pptv for the two absorption coefficients of O_2 while the observation suggests only a relative concentration of 9 to 30 pptv (Schmidt et al., 1980). The concentration of total odd chlorine in the upper stratosphere (2.46 pptv) is unchanged. A further reduction of the calculated concentration of chlorofluorocarbons could be obtained with an increased penetration of the solar irradiance in the Schumann-Runge bands. Herman and Mentall (1982) claim that the transmissivity directly observed in the atmosphere between 195 and 200 nm is larger than the one which is calculated with the cross sections given by Allen and Frederick (1982). This discrepancy should be attributed to a reduction in the Herzberg continuum which lies beneath the bands between 180 et 200 nm (Frederick et al., 1981) and to a possible reduction in the widths of the different spectral lines. In the present model, because of the lack of data, no change has been applied to the absorption coefficients below 200 nm. It should be emphasized that the calculated concentration values are very sensitive to the adopted eddy diffusion profile and that a recalibration of this coefficient should change considerably the vertical distribution of all long-lived species.

The distribution of nitric acid is also modified with the lower values of the Herzberg continuum cross sections. The model suggests a 13 percent reduction at 35 km (see fig. 4) but again a much larger decrease (about a factor of 2) is required to reproduce most of the observations.

The relative change in the ozone distribution is shown in figure 5. The adoption of smaller absorption cross sections leads, in the upper atmosphere, to less ozone production and consequently to a decrease in the concentration of about 18 percent between 40 and 50 km. The new ozone concentration at 50 km is now equal to $4.7 \times 10^{10} \text{ cm}^{-3}$ instead of $5.7 \times 10^{10} \text{ cm}^{-3}$. The number obtained with the Herman and Mentall cross sections is lower than the US Standard Atmosphere (1976) mid-latitude value ($(6.6 \pm 1.1) \times 10^{10} \text{ cm}^{-3}$). The observations of the O_3 concentration in the vicinity of the stratopause are however still sparse and therefore rather uncertain. Nevertheless the newly calculated concentration seems smaller than most available data and the discrepancy has probably to be attributed to an incorrect determination of the solar penetration in the Schumann-Runge bands. As stated by Cieslik (1982), the equivalent O_2 cross section for a large solar penetration is somewhat smaller if the linewidths recently measured by Lewis et al. (1978; 1979) are adopted instead of the values determined previously. In that case the contribution of the Schumann-Runge bands in the photodissociation process should be enhanced near the stratopause. More laboratory data are required before a final statement can be made. In the lower stratosphere (20 km), where most of the ozone is confined, and where the intensity of the solar radiation is enhanced, the O_3 concentration is increased by about 20 percent. These changes in the vertical distribution which are in good agreement with the results of Froidevaux and Yung (1982), lead to an enhancement in the ozone column of 7.6 percent.

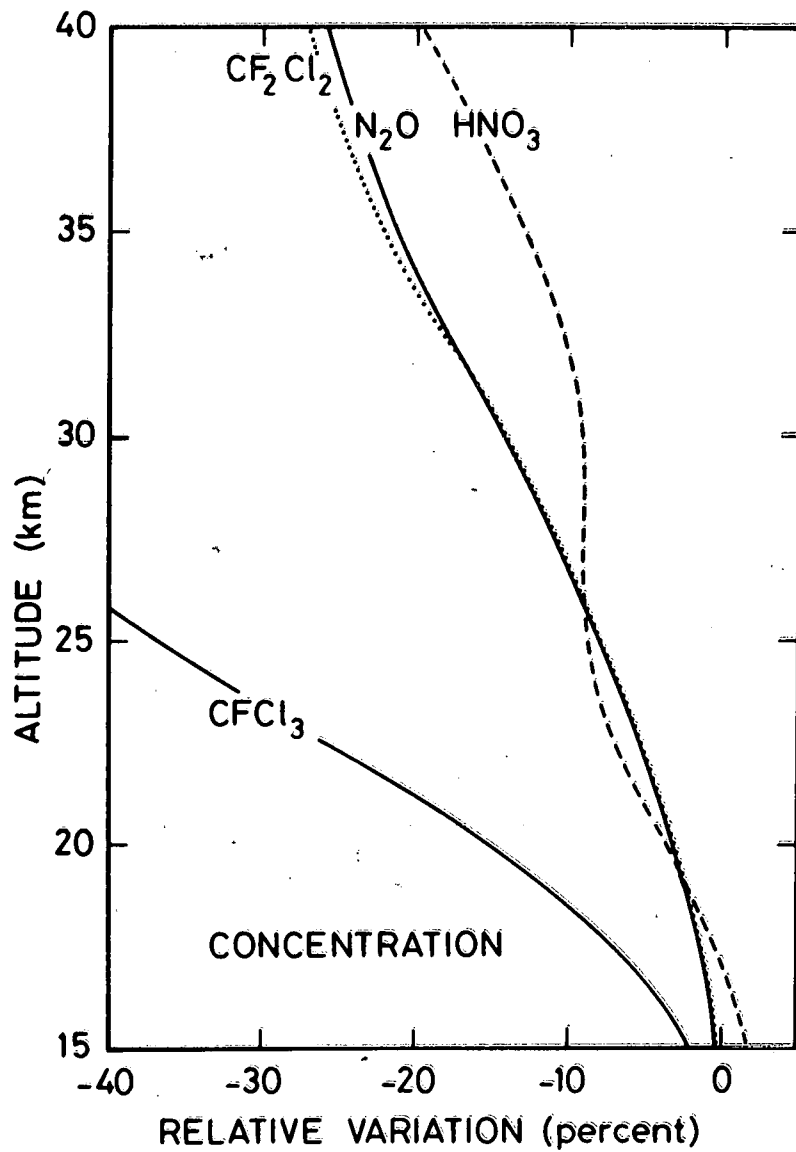


Fig. 4.- Relative variation of the concentration of CFCl_3 , CF_2Cl_2 , N_2O and HNO_3 when the absorption cross sections are taken from Herman and Mentali (1982) instead of Ackerman (1971).

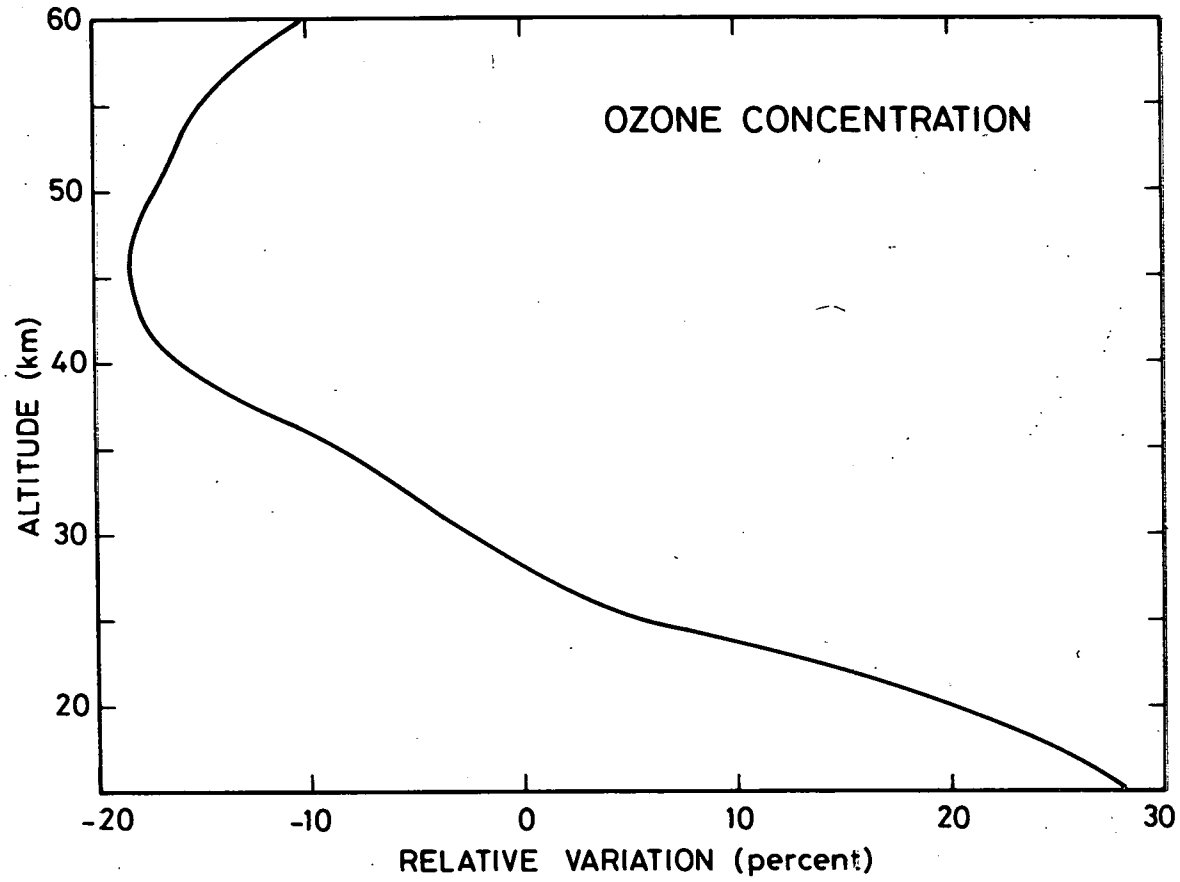


Fig. 5.- Same as fig. 4 but for ozone.

4. CONCLUSIONS AND SUMMARY

A reduction of the absorption cross sections in of the Herzberg continuum which has been suggested from direct observation in the atmosphere, leads to modifications in the calculated distributions of stratospheric minor constituents. The results show the necessity of an accurate determination of the absorption spectrum of O_2 . However, the discrepancies between observed and computed concentrations for several species which are photolysed around 200 nm are only partly reduced. Additional measurements of stratospheric solar irradiance between 30 and 40 km are required to obtain unambiguous values of the absorption cross section in the 200-220 nm range and of the transmission factor in the Schumann Runge bands.

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