

IMPLICATION FOR STRATOSPHERIC COMPOSITION OF A REDUCED ABSORPTION CROSS SECTION IN THE HERZBERG CONTINUUM OF MOLECULAR OXYGEN

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Abstract. Recent determinations of O_2 absorption cross sections in the Herzberg₂ 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 O_2 absorption spectrum in the 200-220 nm range₂ is required since the distribution of several trace species is very sensitive to the atmospheric transmissivity in this wavelength region.

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

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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 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 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 O_2 absorption cross sections. The observation of the solar irradiance at two different atmospheric levels only suggests that a reduction has to be

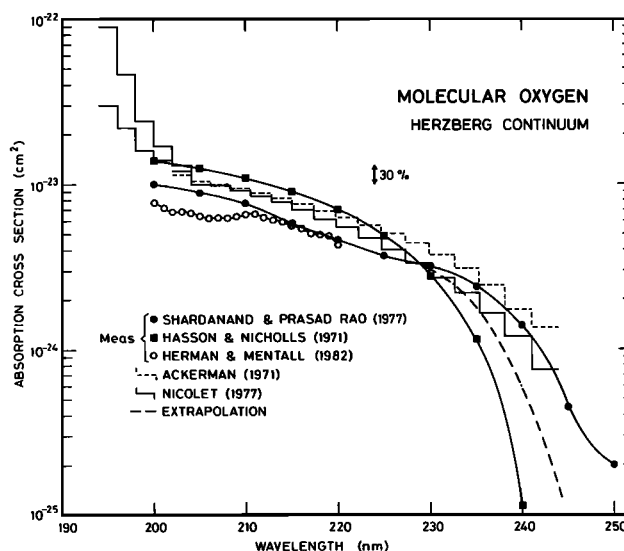


Fig. 1.- Absorption cross section of molecular oxygen in the Herzberg continuum. The dash-dotted line represents the adopted extrapolation for the Herman and Mentall values.

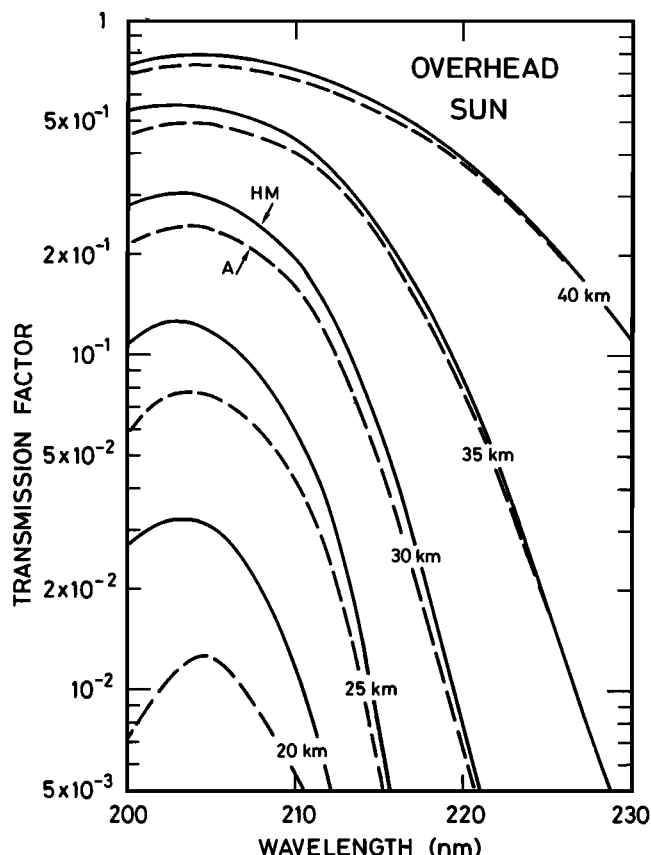


Fig. 2.- Transmittivity of the atmosphere between 200 and 230 nm calculated with the cross section values derived by Herman and Mentall (1982) (full lines) and compiled by Ackerman (1971) (dashed lines) - overhead sun.

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.

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. CFCl₃, 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.

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

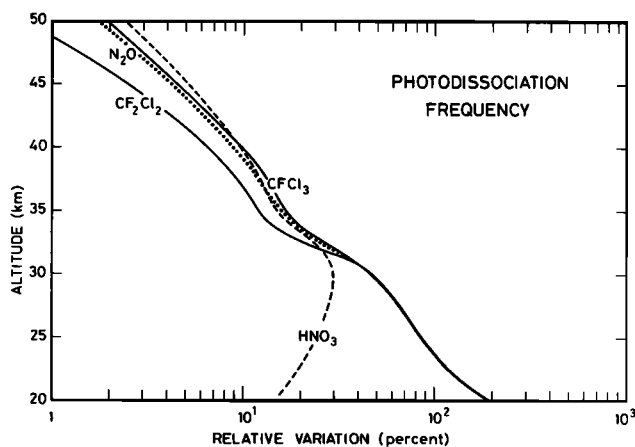


Fig. 3.- Relative variation in the 24 hours average photodissociation coefficient when the absorption cross sections are taken from Herman and Mentall (1982) instead of Ackerman (1971).

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 CFCl₃, 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 CFCl₃, 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 CFCl₃ 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 O₂ cross sections have been applied only above

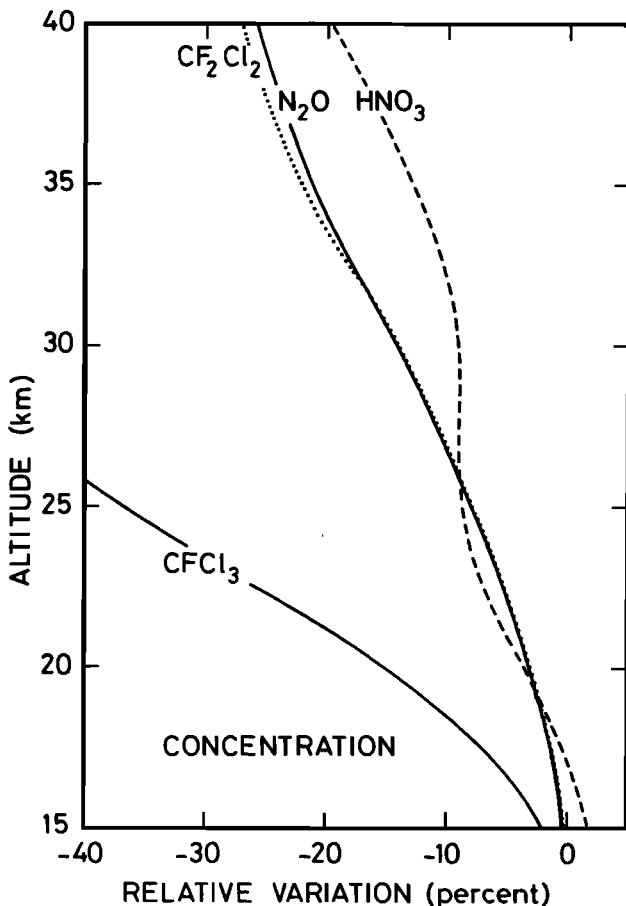


Fig. 4.- Relative variation of the concentration of CFCl₃, CF₂Cl₂, N₂O and HNO₃ when the absorption cross sections are taken from Herman and Mentall (1982) instead of Ackerman (1971).

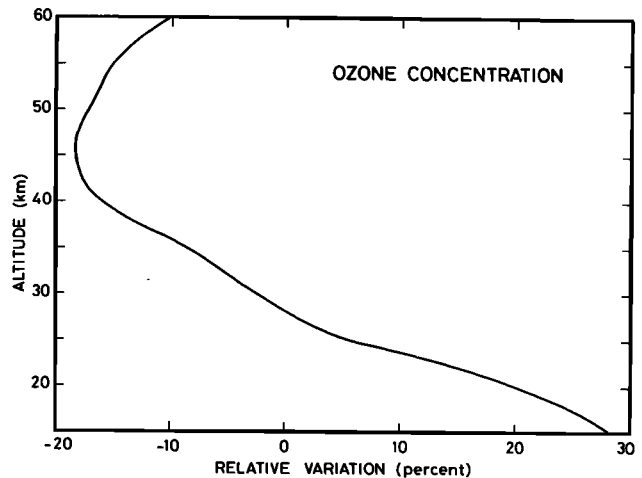


Fig. 5.- Same as fig. 4 but for ozone.

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 K₂) 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 CFCl₃ 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 CF₂Cl₂ at 30 km are respectively 53.1 pptv and 45.6 pptv for the two absorption coefficients of O₂ 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 and 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 O₃ 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. In the lower stratosphere (20 km), where most of the ozone is confined, and where the intensity of the solar radiation is enhanced, the O₃ 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.

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 O₂. 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.

References

- ACKERMAN, M., Ultraviolet solar radiation related to mesospheric processes, in *Mesospheric Models and Related Experiment* (G. Fiocco, editor), Reidel Publish. Co, Dordrecht, Holland, 1971.
- ALLEN, M. and J.E. FREDERICK, Effective photodissociation cross sections for molecular oxygen and nitric oxide in the Schumann-Runge bands, *J. Atmos. Sci.*, **39**, 2066-2075, 1982.
- BRASSEUR, G., A. DE RUDDER and A. ROUCOUR, The natural and perturbed ozonosphere, *Proceedings of the International Conference on Environmental Pollution, Thessaloniki, Greece*, to be published, 1982.
- BRASSEUR, G. and P.C. SIMON, Stratospheric Chemical and Thermal Response to long-term Variability in Solar UV irradiance, *J. Geophys. Res.*, **86**, 7343-7362, 1981.
- DITCHEBURN, R.W. and P.A. YOUNG, The absorption of molecular oxygen between 1850 and 2500 Å, *J. Atmos. Terrest. Phys.*, **24**, 127-139, 1962.
- FREDERICK, J.E., R.D. HUDSON and J.E. MENTALL, Stratospheric observation of the attenuated solar irradiance in the Schumann-Runge band absorption region of molecular oxygen, *J. Geophys. Res.*, **86**, 9885-9890, 1981.
- FREDERICK, J.E. and J.E. MENTALL, Solar irradiance in the stratosphere: implications for the Herzberg continuum absorption of O₂, *Geophys. Res. Lett.*, **9**, 461-464, 1982.
- FROIDEVAUX, L. and YUNG, Y.L., Radiation and Chemistry in the stratosphere: Sensitivity to O₂ absorption cross sections in the Herzberg continuum, *Geophys. Res. Lett.*, **9**, 854-857, 1982.
- HASSON, V. and R.W. NICHOLLS, Absolute spectral absorption measurements on molecular oxygen from 2460-1920 Å: II continuum measurements 2430-1920 Å, *J. Phys. B.: Atom. Molec. Phys.*, **4**, 1789-1797, 1971.
- HERMAN, J.R. and J.E. MENTALL, O₂ absorption cross sections (187-225 nm) from stratospheric solar flux measurements, *J. Geophys. Res.*, to be published, 1982.
- HUDSON, R.D. and E.I. REED, editors, *The Stratosphere: Present and Future*, NASA Reference Publication 1049, 432 pp. 1979.
- MASSIE, S.T. and D.M. HUNTEN, Stratospheric eddy diffusion coefficients from tracer data, *J. Geophys. Res.*, **86**, 9859-9868, 1981.
- NICOLET, M., *Etude des réactions chimiques de l'ozone dans la stratosphère*, 536 pp., Institut Royal Météorologique, Bruxelles, Belgique, 1978.
- OGAWA, M., Absorption cross sections of O₂ and CO₂ continua in the Schumann and far UV regions, *J. Chem. Phys.*, **54**, 2550-2556, 1971.
- SCHMIDT, U., J. RUDOPH, F.J. JOHNEN, D.H. EHHALT, A. VOLZ, E.P. ROTH, R. BORCHERS and P. FABIAN, The vertical distribution of CH₃Cl, CFCl₃ and CF₂Cl₂ in the midlatitude stratosphere, *Proc. Quadriennial International Ozone Symposium, Vol. II*, 816-823 (J. London, Editor), 1981.
- SHARDANAND and A.D. PRASAD RAO, Collision-induced absorption of O₂ in the Herzberg continuum, *J. Quant. Spectrosc. Radiat. Transfer*, **17**, 433-439, 1977.
- WMO, *The Stratosphere 1981, Theory and Measurements*, WMO Global Ozone Research and Monitoring Project, Report No. 11, 1982.

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