

This work was written as part of one of the author's official duties as an Employee of the United States Government and is therefore a work of the United States Government. In accordance with 17 U.S.C. 105, no copyright protection is available for such works under U.S. Law.

Public Domain Mark 1.0

<https://creativecommons.org/publicdomain/mark/1.0/>

Access to this work was provided by the University of Maryland, Baltimore County (UMBC) ScholarWorks@UMBC digital repository on the Maryland Shared Open Access (MD-SOAR) platform.

Please provide feedback

Please support the ScholarWorks@UMBC repository by emailing scholarworks-group@umbc.edu and telling us what having access to this work means to you and why it's important to you. Thank you.

PHOTOLYSIS RATES BASED ON SCHUMANN-RUNGE BAND APPROXIMATIONS AND IRRADIANCE MEASUREMENTS

J. R. Herman and J. E. Mentall

Laboratory for Atmospheres, NASA/Goddard Space Flight Center Greenbelt, MD 20771

Abstract. The photolysis rate (J_3) for CF_2Cl_2 (F-12) in the stratosphere has been computed for three altitudes using measured solar fluxes from a balloon borne spectrometer. The rate is compared with that obtained by computing the attenuated flux using effective cross sections appropriate for the Schumann-Runge bands (J_1) [Allen and Frederick, 1982]. The result shows that the error in the F-12 photolysis rate caused by using the Allen and Frederick approximation is about 10% ($J_1 < J_3$) for altitudes between 32 and 38 km with solar zenith angles less than about 62 degrees. For species other than O_2 , this implies that the discrepancy in photolysis rates associated with the Schumann-Runge band approximations are not likely to be important. Within the Schumann-Runge band region the computed errors for F-12 photolysis are about 10.5% at 38.13 km and increase with decreasing altitude. If this error applies to O_2 photolysis, there may be the possibility of an incorrect calculation of net odd oxygen production in photochemical models.

Introduction

Calculations of the ozone density above 30 km based on photochemical modelling [Herman, 1979, Herman and McQuillan, 1985, Cicerone et al., 1983] show a persistent underestimate compared to measurements [Krueger and Minzner, 1976]. In this region of the atmosphere, the ozone density is almost completely determined from a simple chemical balance equation with negligible transport effects [Herman and McQuillan, 1985]. For given total atmospheric density and temperature profiles, the amount of ozone is predominantly controlled by the ratio of molecular oxygen photolysis to ozone photolysis with corrections for the presence of other minor constituents in the atmosphere. The uncertainties in the size of the minor constituent corrections to Chapman chemistry are sufficient to remove the disagreement between theory and measurements if the corrections to the HO_x cycle reaction rates and the rates for $\text{O} + \text{O}_2 + \text{M}$ and $\text{O} + \text{O}_3$ are all in the direction to maximize $[\text{O}_x]$ [Rusch et al., 1984]. The greatest uncertainty in the calculation of the photolysis rates leading to ozone production and loss occurs in the wavelength range between 180 and 220 nm corresponding to the O_2 Schumann-Runge bands and Herzberg continuum.

A recent series of papers have attempted to refine our knowledge of the absorption properties of molecular oxygen in the 180 to 220 nm wavelength region. In the wavelength range from 200 to 220 nm these include the deter-

mination of the O_2 Herzberg continuum cross sections from spectroscopic measurements within the stratosphere [Herman and Mentall, 1982b, Frederick and Mentall, 1982] and their laboratory confirmation [Johnston et al., 1984]. In the Schumann-Runge band region there have been determinations of the transmissivity within the atmosphere for a wide variety of conditions [Anderson and Hall, 1983, Frederick and Hudson, 1979a,b and 1980a,b, Nicolet and Cieslik, 1980, and Nicolet and Peetermans, 1980]. Because of the complexity of determining the atmospheric transmissivity and photolysis rates within the Schumann-Runge band wavelengths, various approximation algorithms have been proposed that are useful for stratospheric photochemical modelling calculations [Park, 1974, Nicolet and Cieslik, 1980, and Allen and Frederick, 1982]. The most thoroughly tested of these is that of Allen and Frederick based on the data obtained from the SABE 1 and SABE 3 (Solar Atmospheric Balloon Experiment) balloon flights [Frederick et al., 1981, Herman and Mentall, 1982b]. These last two papers were cited by Allen and Frederick (1982) to show that the approximate transmissivities agree with measured values from SABE 1 at 40 km altitude and small zenith angle (34-42 degrees) to better than 10% and are in "good" agreement with the SABE 3 data at lower altitudes and larger zenith angles. The possible existence of errors in the cross sections used in stratospheric modelling does not arise from the approximations of Allen and Frederick, but rather from the underlying transmissivity data. The error limits on the calculated transmissivities increase with decreasing altitude [Frederick and Hudson, 1980a,b].

Because of the importance of this spectral region for photochemical modelling of the stratosphere, this paper will compare the photolysis rates computed from the Allen and Frederick approximation with those computed directly from the attenuated solar flux data obtained during the SABE 3 balloon flight.

Calculated Photolysis Rates

Two methods are used to calculate the photolysis rate of a selected molecular species. The first method uses the measured solar flux, $F(\lambda)$, above the atmosphere, the measured column content of O_2 and O_3 , the laboratory values of the O_3 absorption cross sections [Inn and Tanaka, 1959] and the approximate effective O_2 absorption cross sections from Allen and Frederick [1982]. For each SABE 3 spectrum the atmospheric pressure was measured and is approximately related to the O_2 column content, $C(\text{O}_2)$ in cm^{-2} , through the hydrostatic pressure balance equation. The O_3 column content, $C(\text{O}_3)$, corresponding to each spectrum is determined as shown in Table 1 of

This paper is not subject to U.S. copyright. Published in 1985 by the American Geophysical Union.

Paper number 5L6584.

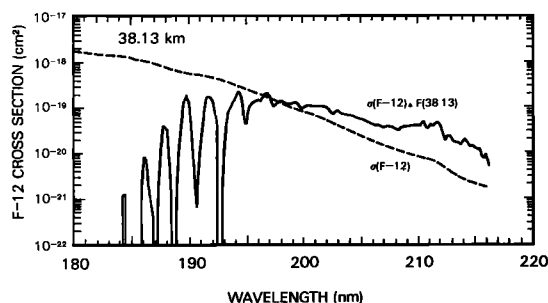


Fig. 1. The dissociation cross section for CF_2Cl_2 (F-12) appropriate for the altitude 38.13 km (dashed line), and the relative contribution of each term in equation 2 to $J(\text{F-12})$ plotted in arbitrary units (solid line).

Herman and Mentall [1982b]. The solar flux above the atmosphere is based on a normalization of the data obtained by Broadfoot [1972] to the data obtained from the Nimbus 7 satellite [Heath, 1980]. The normalization [Herman and Mentall, 1982a] enables the spectral resolution of the SAGE 3 data to be matched while retaining the absolute accuracy of the Nimbus 7 solar flux data. Rayleigh scattering is taken into account by using an approximation formula for the cross sections [Nicolet, 1984]

$$\sigma_R = 4.02 \times 10^{-28} / \lambda (4+r) \quad (1)$$

$$r = 0.389\lambda + 0.09426/\lambda - 0.3228,$$

where λ is the wavelength in μm . The photolysis rate, J in sec^{-1} , is then computed according to

$$J(t, X) = \sum_{\lambda} \sigma_p F(\lambda) \exp[-\text{Ch}(X)t] \quad (2)$$

$$t = \sigma(\text{O}_2) C(\text{O}_2) + \sigma_R C(\text{M}) + \sigma(\text{O}_3) C(\text{O}_3),$$

where $\text{Ch}(X)$ is the Chapman function of the solar zenith angle X , $\sigma(\text{O}_2)$ is the effective O_2 cross section, σ_R is the Rayleigh scattering cross section, $C(\text{M})$ is the total density column content = $C(\text{O}_2)/0.209$, and $\sigma(\text{O}_3)$ is the O_3 absorption cross section. The only other data needed is a suitable photolysis cross section σ for a molecular species.

The second method uses the measured

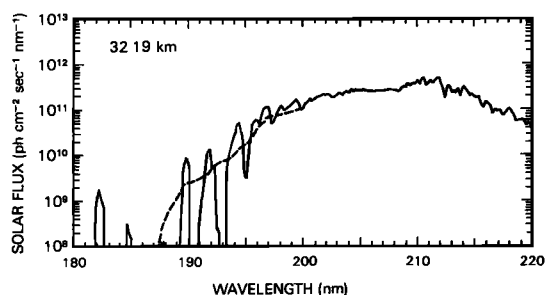


Fig. 2. The attenuated solar flux at 32.19 km from the SAGE 3 balloon flight spectrometer (solid line) and the calculated flux (dashed line) using the Allen and Frederick effective Schumann-Runge band cross sections.

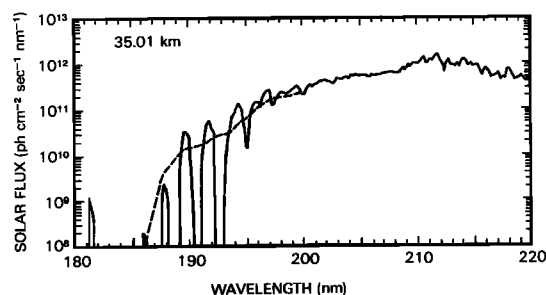


Fig. 3. The same as Figure 2 except at 35.01 km.

attenuated solar flux from SAGE 3 over the same spectral range multiplied at each wavelength by the corresponding molecular photolysis cross section. Unfortunately, the spectral resolution of the SAGE 3 data is not adequate to accurately determine the O_2 absorption cross sections in the Schumann-Runge band region (see figure 5 of Herman and Mentall, 1982b). This means that the photolytic dissociation rate of molecular oxygen cannot be directly calculated from the SAGE 3 data and then be compared with the calculation using the approximate Allen and Frederick cross sections. Instead another species must be used.

Most models of the stratosphere have from about 10 to 30 photolysis processes that are important in the stratosphere between 30 and 40 km. The largest errors involved when using the Allen and Frederick Schumann-Runge bands cross section approximation would arise from a species whose photolytic dissociation rate is determined mostly within the Schumann-Runge band region. From the list of photolytically active species tabulated in the NASA/JPL [1983] report, the wavelength dependence of CF_2Cl_2 (F-12) comes closest to fitting the above requirement. The F-12 dissociation cross sections [NASA/JPL, 1983] and the product $F(\lambda)\sigma$ appropriate for 38.13 km are plotted in Figure 1 for the wavelengths from 180 to 220 nm. The relative contribution of each wavelength interval ($dJ/d\lambda$) within equation 2 to $J(\text{F-12})$ as a function of wavelength (solid line) peaks within the low order Schumann-Runge bands as required for this study.

Figures 2, 3, and 4 show the SAGE 3 direct solar flux at 3 altitudes (32.19, 35.01, and 38.13 km) for the wavelength range from 180 to 220 nm. Also shown is the calculated attenuated solar flux using the Allen and Frederick Schumann-Runge band cross sections corrected for

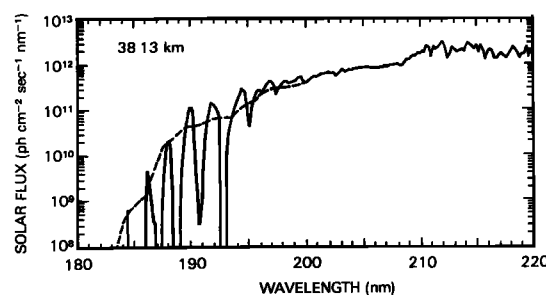


Fig. 4. The same as Figure 2 except at 38.13 km.

TABLE 1. Summary of Data

Alt.	SZA	P	C(O ₃)	J ₁	J ₂	J ₃
km	deg	mb	cm ⁻²	sec ⁻¹	sec ⁻¹	sec ⁻¹
38.13	55.71	3.90	3.4(17)	7.02(-7)	6.91(-7)	7.50(-7)
35.01	60.41	5.95	6.7(17)	3.61(-7)	3.66(-7)	3.90(-7)
32.19	63.57	8.80	1.2(18)	1.42(-7)	1.44(-7)	1.66(-7)

J₁ uses the high resolution computed reduced flux.

J₂ uses the low resolution computed reduced flux.

J₃ uses the high resolution SAGE 3 measured flux.

3.4(17) is to be read as 3.4×10¹⁷

the revised O₂ Herzberg continuum cross sections [Herman and Mentall, 1982b] from 180 to 206 nm. From 206 to 220 nm the calculated flux agrees very well with the measured SAGE 3 flux, but was not used in the comparison of photolysis rates to avoid introducing extraneous small errors.

The photolysis rates of F-12, J₁ and J₃ in Table 1, were calculated by performing the sum indicated in equation 2 at 0.2 nm intervals for both the calculated reduced fluxes and the SAGE 3 fluxes. Since coarser wavelength intervals are frequently used in model calculations, the photolysis rates, J₂, were also calculated at the wavelength intervals given by Ackerman [1971]. The results (see Table 1) show that the differences between methods 1 and 3 are 14.1% at 32.19 km, 7.4% at 35.01 km, and 6.4% at 38.13 km. The differences are probably significant since the relative errors between the SAGE 3 fluxes and the attenuated Nimbus 7 fluxes for wavelengths larger than 200 nm are smaller than the percentage differences calculated for the photolysis rates. For the three altitudes considered here, the attenuated Nimbus 7 flux differs from the measured SAGE 3 flux by less than 5% between 200 and 220 nm. The fact that J₃ is systematically about 10% larger than J₂ or J₁ is not significant for most photochemical model calculations at the present time. For the cases considered, the solar zenith angles (SZA) were 63.57, 60.41, and 55.71 degrees, respectively. From the nature of the Schumann-Runge band approximations, the errors should decrease for smaller SZA and increase for larger SZA.

Some of the systematically increasing differences between J₁ and J₃ with decreasing altitude may be due to the errors in the O₂ oscillator strengths and line widths. These errors also increase with decreasing altitude in proportion to C(O₂) [Frederick and Hudson, 1980a] and are automatically built into the approximation polynomials.

If the contribution to J(F-12) is computed entirely within the Schumann-Runge band region, then the disagreement between J₁ and J₃ increases to about 10.5% (J₁ < J₃) at 38.13 km and 25% at 32.19 km. While a 10% error is not significant for F-12 or other species' photolysis rates below 40 km, it is large enough to be significant in the mesosphere. Based on the 10.5% to 25% error in J(F-12) between 180 and 200 nm, there is also the possibility that the

photolysis rate of O₂ may be improperly estimated in the Schumann-Runge band region. This cannot be decided using the present SAGE 3 uv flux data that has insufficient spectral resolution to determine σ(O₂).

The calculated photolysis rates, J₁, presented in Table 1 are sensitive to the measured values of the ozone column content and total pressure. Since J₁ is less than J₃, small reductions in either C(O₃) or C(O₂) tend to improve the agreement between J₁ and J₃. The estimated error in C(O₃) is ±5% and the error in the product σ(O₂)C(O₃) is much less than ±5% [Herman and Mentall, 1982b]. Similarly, the pressure and therefore C(O₂) is known to within ±2%. If C(O₃) and C(O₂) are reduced to their estimated error limits (-5% and -2%), the percent difference between J₁ and J₃ becomes 11.2% at 32.19, 5.2% at 35.01, and 4.9% at 38.13 km. The reduction in C(O₂) and C(O₃) would have to be at least 10% each in order to reduce the disagreement between J₁ and J₃ below the level of significance. The SAGE 3 solar flux data used in these calculations is the same data that was used to determine the O₂ Herzberg continuum cross sections [Herman and Mentall, 1982b]. Since these cross sections have been independently confirmed by laboratory data [Johnston et al., 1984], it is clear in retrospect that the actual errors in C(O₂) and C(O₃) were smaller than the formal errors. However, the ± 8% formal error in the magnitude of the absolute measured flux values still applies. Since the observed differences between J₁ and J₃ increase systematically with decreasing altitude, the errors are likely to be statistically significant.

Summary

The photolysis rates for CF₂Cl₂ (F-12) have been calculated at three different altitudes using the measured solar fluxes from the SAGE 3 spectrometer (J₃) and from the calculated fluxes based on the approximate effective O₂ Schumann-Runge band cross sections given by Allen and Frederick [1982] corrected for the revised O₂ Herzberg cross sections (J₁) [Herman and Mentall, 1982b]. Since the disagreement found was about 10% for F-12 at moderately large zenith angles (J₁ < J₃), the use of the Allen and Frederick effective cross sections in stratospheric modelling problems should be quite adequate. Smaller errors are expected for other

species. Possible errors in the calculated O_2 dissociation rates leading to the production of odd oxygen could not be evaluated with the presently available data. Since the errors in the photolysis rates that could be compared with the SABE 3 calculation within the Schumann-Runge band region are significant (10.5% at 38.13 km), there is the possibility of an incorrect calculation of the net odd oxygen production in the altitude range above 30 km.

References

- Ackerman, M., Ultraviolet solar radiation related to mesospheric processes, in *Mesospheric Models and Related Experiments*, edited by G. Fiocco, Springer-Verlag, New York, 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.
- Anderson, G. P., and L. A. Hall, Attenuation of solar irradiance in the stratosphere: Spectrometer measurements between 191-207 nm, *J. Geophys. Res.*, **88**, 6801-6806, 1983.
- Broadfoot, A. L., The solar spectrum 2100-3200 Å, *Astrophys. J.*, **173**, 681, 1972.
- Cicerone, R. J., S. Walters, and S. C. Liu, Nonlinear response of stratospheric ozone column to chlorine injections, *J. Geophys. Res.*, **88**, 3647-3661, 1983.
- Frederick, J. E., R. D. Hudson, and J. E. Mentall, Stratospheric observations 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 O_2 , *Geophys. Res. Lett.*, **9**, 461-464, 1982.
- Frederick, J. E. and R. D. Hudson, Predissociation of nitric oxide in the mesosphere and stratosphere, *J. Atmos. Sci.*, **36**, 737-745, 1979a.
- Frederick, J. E. and R. D. Hudson, Predissociation line widths and oscillator strengths for the 2-0 to 13-0 Schumann-Runge bands of O_2 , *J. Mol. Spectrosc.*, **74**, 247-258, 1979b.
- Frederick, J. E. and R. D. Hudson, Atmospheric opacity in the Schumann-Runge bands and the aeronomic dissociation of water vapor, *J. Atmos. Sci.*, **37**, 1088-1098, 1980a.
- Frederick, J. E. and R. D. Hudson, Dissociation of molecular oxygen in the Schumann-Runge bands, *J. Atmos. Sci.*, **37**, 1099-1106, 1980b.
- Heath, D. F., Nimbus 7 solar ultraviolet spectra, Private communication, 1980.
- Herman, J. R., The response of stratospheric constituents to a solar eclipse, sunrise, and sunset, *J. Geophys. Res.*, **84**, 3701-3710, 1979.
- Herman, J. R. and C. J. McQuillan, Atmospheric chlorine and stratospheric ozone: nonlinearities and trend detection, *J. Geophys. Res.*, **90**, 1985.
- Herman, J. R. and J. E. Mentall, The direct and scattered solar flux within the stratosphere, *J. Geophys. Res.*, **87**, 1319-1330, 1982a.
- Herman, J. R. and J. E. Mentall, O_2 absorption cross sections (187-225 nm) from stratospheric solar flux measurements, **87**, 8967-8975, 1982b.
- Inn, E.C.Y. and Y. Tanaka, Ozone absorption coefficients in the visible and ultraviolet regions, *Adv. Chem. Ser.*, **21**, 263, 1959.
- Johnston, H. S., M. Paige, and F. Yao, Ozone absorption cross section in the Herzberg continuum between 206 and 327 K, *J. Geophys. Res.*, **89**, 11661-11665, 1984.
- Krueger, A. J., and R. A. Minzner, in U.S. Standard Atmospheres, National Oceanic and Atmospheric Administration S/T 76-1562, 36-39, 1976.
- NASA/Jet Propulsion Laboratory (JPL), Chemical kinetics and photochemical data for use in stratospheric modelling, evaluation No. 6, NASA panel for evaluation, JPL Publ. 83-62, Pasadena, Calif., 1983.
- Nicolet, M., On the molecular scattering in the terrestrial atmosphere: An empirical formula for its calculation in the homosphere, *Planet. Space Sci.*, **32**, 1467-1468, 1984.
- Nicolet, M., and S. Cieslik, The photodissociation of nitric oxide in the mesosphere and stratosphere, *Planet. Space Sci.*, **28**, 105-115, 1980.
- Nicolet, M. and W. Peetermans, Atmospheric absorption in the O_2 Schumann-Runge band spectral range and photodissociation rates in the stratosphere and mesosphere, *Planet. Space Sci.*, **28**, 85-103, 1980.
- Park, J. H., The equivalent mean absorption cross sections for the O_2 Schumann-Runge bands: application to the H_2O and NO photodissociation rates, *J. Atmos. Sci.*, **31**, 1893-1897, 1974.
- Rusch, D. F., R. C. Eckman, T. Clancy, C. A. Barth and S. Solomon, Solar mesosphere explorer measurements of mesospheric ozone and their implications on the odd-oxygen, odd-hydrogen chemistry, *EOS*, **65**, 1029, 1984.

(Received July 24, 1985;
accepted August 7, 1985.)