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# O<sub>2</sub> Absorption Cross Sections (187-225 nm) From Stratospheric Solar Flux Measurements

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The absorption cross sections of molecular oxygen are calculated in the wavelength range from 187 to 230 nm from solar flux measurements obtained within the stratosphere. Within the Herzberg continuum wavelength region the molecular oxygen cross sections are found to be about 30% smaller than the laboratory results of Shardanand and Rao (1977) from 200 to 210 nm and about 50% smaller than those of Hasson and Nicholls (1971). At wavelengths longer than 210 nm the cross sections agree with those of Shardanand and Rao. The effective absorption cross sections of O<sub>2</sub> in the Schumann-Runge band region from 187 to 200 nm are calculated and compared to the empirical fit given by Allen and Frederick (1982). The calculated cross sections indicate that the transmissivity of the atmosphere may be underestimated by the use of the Allen and Frederick cross sections between 195 and 200 nm. The ozone column content between 30 and 40 km and the relative ozone cross sections are determined from the same solar flux data set. The calculated ozone absorption cross sections agree with those of Inn and Tanaka (1959) and Bass and Paur (1981) to within 3%.

## INTRODUCTION

Laboratory measurements of the O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) dissociation cross sections in the wavelength range from 200 to 240 nm (Herzberg continuum) are complicated by the pressure dependence of the total observed absorption and by the small size of the cross section (<10<sup>-23</sup> cm<sup>2</sup>). This problem is typically dealt with by making absorption measurements at a series of relatively high pressures and then extrapolating to the low-pressure limit by using the assumption that the absorption has a known functional dependence on the O<sub>2</sub> density. The various laboratory results are well summarized in a recent paper by Shardanand and Rao [1977].

This paper presents the calculation of the O<sub>2</sub> and O<sub>3</sub> absorption cross sections from an analysis of solar flux measurements obtained within the stratosphere between 20 and 40 km altitude. The ozone column content is determined from the ratios of the attenuated solar flux over the wavelength range from 280 to 300 nm. Using this result and the simultaneously measured pressure and temperature, the absorption cross sections are determined for O<sub>2</sub> from 187 to 230 nm and the relative absorption cross sections for O<sub>3</sub> from 210 to 310 nm. The calculated ozone cross sections are shown to agree with those obtained by Inn and Tanaka [1959] and Bass and Paur [1981]. The molecular oxygen cross sections are 30% smaller than those obtained by Shardanand and Rao [1977] and 50% smaller than the values obtained by Hasson and Nicholls [1971] in the 200-210 nm range. At wavelengths longer than 210 nm the cross sections agree quite closely with those of Shardanand and Rao [1977]. In the Schumann-Runge band region of O<sub>2</sub> the calculated cross sections are shown to roughly follow the empirical fit of Allen and Frederick [1982]. However, the atmospheric transmissivity is greater than that indicated by the use of the Allen and Frederick results between 195 and 200 nm.

In order to calculate the molecular oxygen absorption cross sections from the measured solar flux data the following points must be established.

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1. The value of the ozone column density, N(O<sub>3</sub>), between the highest altitude spectrum at 38.15 km and the top of the atmosphere must be determined to an accuracy of better than 10% so that its contribution to the error in N(O<sub>3</sub>) calculated at lower altitudes (e.g., 33.11 km) is less than 5%.

2. When the column content of ozone is calculated at altitudes below 38.15 km from the solar flux data, the values obtained must be independent of the wavelength to an accuracy of better than 3%. This shows internal consistency between the ratios of the measured solar fluxes at two different altitudes as a function of wavelength and the assumed laboratory absorption cross sections used in the analysis.

3. The relative values of the ozone absorption cross sections, σ(O<sub>3</sub>), must be determined accurately over the 187-300 nm wavelength range so that the absolute accuracy of the products N(O<sub>3</sub>) σ(O<sub>3</sub>) is sufficient to permit a meaningful calculation of σ(O<sub>2</sub>). In this paper it is shown that an error in σ(O<sub>3</sub>) of 3% leads to less than a 10% error in σ(O<sub>2</sub>) between 200 and 215 nm but to much larger errors at wavelengths longer than 215 nm.

## EXPERIMENT AND DATA BASE DESCRIPTION

Solar ultraviolet flux data were obtained using a 0.125-m Fastie-Ebert double monochromator carried on a balloon-borne gondola over Palestine, Texas on April 15, 1981. This instrument was previously flown on SABE-1 (Solar Absorption Balloon Experiment 1) and on a rocket payload which obtained the solar irradiance above the atmosphere. A detailed description of this instrument is given by Mentall *et al.* [1981] and Herman and Mentall [1982]. Calibrations of the spectrometer were obtained using a combination of standard lamps. At wavelengths below 250 nm a deuterium lamp was used. Above 250 nm both the deuterium lamp and a quartz-halogen lamp were used. From the quoted accuracies of the lamp calibrations and an observed 3% repeatability, it is estimated that the absolute error is ±8%. The relative error in the calibration is estimated to be less than ±5%. On the SABE-3 flight (Solar Atmospheric Balloon Experiment 3) the spectrometer scanned alternately in wavelength from 180 to 330 nm and then from 330 to 180 nm in a time of 70 s per scan with a spectral resolution of 0.12 nm. During the

TABLE 1. Pertinent Data for Scans

Time	Altitude, km	Pressure, mbar	Zenith, degrees	N(O <sub>3</sub> ), cm <sup>-2</sup>
1440:26	38.15	3.90	55.71	3.445 (17)*
1430:28	37.30	4.37	57.79	4.253 (17)
1423:00	36.17	5.11	59.36	5.192 (17)
1418:02	35.01	5.95	60.41	6.738 (17)
1413:03	34.20	6.66	61.46	8.046 (17)
1410:34	33.71	7.14	61.99	8.627 (17)
1408:04	33.11	7.73	62.52	9.618 (17)
1405:35	32.63	8.28	63.05	1.097 (18)
1403:06	32.18	8.20	63.57	1.194 (18)

All quantities refer to the start of each scan at 180 nm.

\*3.445 (17) =  $3.445 \times 10^{17} \pm 5\%$ .

balloon ascent from 20 to 40 km, each scan covered an altitude range of about 0.3 km. The solar zenith angle changed from 75° to 55° during the 1-hour portion of the ascent data used in this paper. Table 1 summarizes the pertinent data for each spectral scan: the UT time, the altitude calculated from the measured pressure and the 1976 U.S. Standard Atmosphere tables, the measured pressure, the solar zenith angle, and the calculated ozone equivalent vertical column content between the spectrometer and the top of the atmosphere, N(O<sub>3</sub>).

In order to calculate the ozone column content at the highest altitude of 38.15 km, a reference solar flux spectrum obtained above the atmosphere [Mentall *et al.*, 1981] was used. This particular reference spectrum has a wavelength resolution that is nearly identical to that obtained during the SABE-3 flight. The ozone absorption cross sections were taken from Inn and Tanaka [1959] and Vigroux [1953] as tabulated in the Handbook of Geophysics [Howard *et al.*, 1960]. The temperature dependence given by Vigroux was compared to the more recent data obtained by Bass and Paur [1981] to assess the sensitivity of the present calculations to errors in the ozone cross sections. The small

differences between the two ozone cross section data sets were not significant in the wavelength range used to calculate N(O<sub>3</sub>). The remaining data set was a combination of an empirical fit to the effective molecular oxygen Schumann-Runge band cross sections obtained by Allen and Frederick [1982] from 180 to 200 nm, and the Herzberg continuum region from 200 to 240 nm tabulated by Shardanand and Rao [1977].

#### OZONE COLUMN CONTENT

The column content of ozone or any other strongly absorbing material above the solar viewing spectrometer can be determined from the observed amount of solar flux attenuation relative to a reference flux. For wavelength regions of strong ozone absorption, the contribution of scattering in the altitude range of 30 to 40 km to the attenuation of the solar flux can be neglected. For these conditions the flux attenuation for a single wavelength at altitude *Z* is given by the simple relation

$$F_Z = F_\infty \exp [-\text{Ch}(X)(\sigma_{\text{O}_2}N_Z(\text{O}_2) + \sigma_{\text{O}_3}N_Z(\text{O}_3))] \quad (1)$$

where  $F_\infty$  is the solar flux above the atmosphere,  $\text{Ch}(X)$  is the Chapman function of the solar zenith angle *X* [McCartney, 1976],  $\sigma_{\text{O}_2}$  and  $\sigma_{\text{O}_3}$  are the O<sub>2</sub> and O<sub>3</sub> absorption cross sections, and  $N_Z(s)$  is the column content for species *s* between the altitude *Z* and the top of the atmosphere. In wavelength regions where ozone is the only significant absorbing material, (1) can be solved for  $N_Z(s)$  unambiguously.

Figure 1 shows the results of such a calculation using the SABE-3 solar flux spectrum from 38.15 km and the reference spectrum from Mentall *et al.* [1981] and also that of Heath and Park [1982] obtained from Nimbus 7 satellite data. The Heath and Park spectrum is at a much coarser wavelength resolution (1 nm) than the SABE-3 spectra, and leads to the same N(O<sub>3</sub>) but with a higher random noise component than

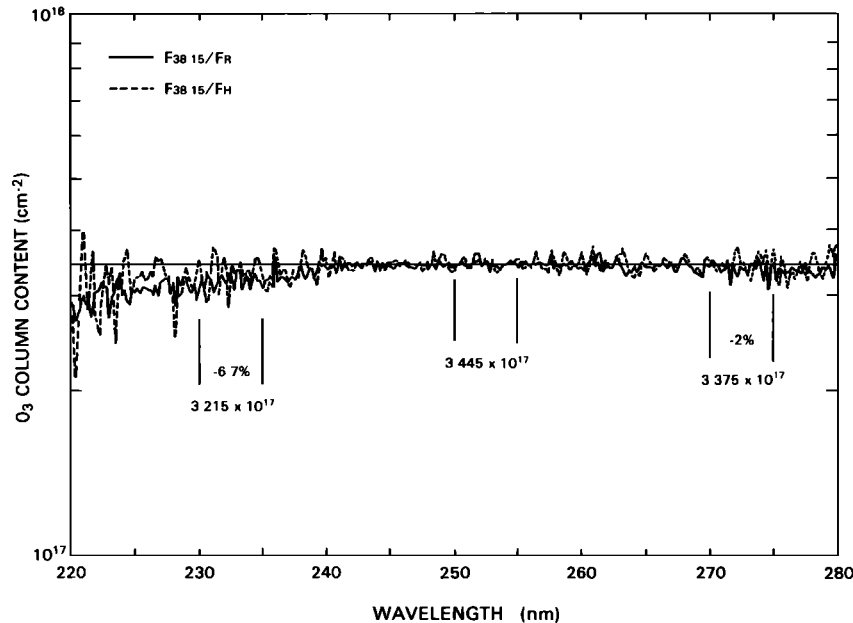


Fig. 1. The ozone column content calculated as a function of the wavelength for two reference solar fluxes obtained above the atmosphere.  $F_R$  is the solar flux obtained during a high altitude rocket flight [Mentall *et al.*, 1981],  $F_H$  is from the spectrometer on the Nimbus 7 satellite [Heath and Park, 1982], and  $F_{38.15}$  is the solar flux from the SABE-3 spectrometer taken at 38.15 km. There is excessive local variation in the calculated values of N(O<sub>3</sub>) between 220 and 240 nm, where the amount of absorption is small and the resolution of the reference flux  $F_H$  does not match  $F_{38.15}$ .

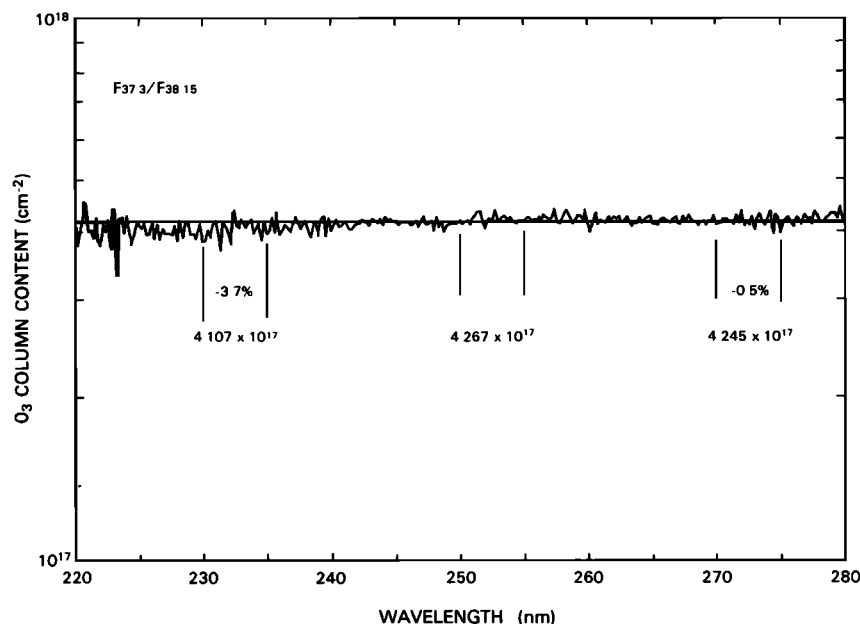


Fig. 2. The ozone column content calculated as a function of wavelength for two measured solar fluxes obtained from the SABE-3 spectrometer at 37.3 and 38.15 km.

does a similar analysis using the more nearly matched spectrum of *Mentall et al.* [1981]. The good agreement using the two independent reference spectra makes it unlikely that the calculated O<sub>2</sub> cross sections will depend on the choice of reference spectrum. The higher random noise component is not especially important for the determination of the ozone column content but would seriously degrade the calculation of the molecular oxygen cross sections discussed later.

Ideally,  $N_Z(O_3)$  should be independent of the wavelength used in the calculation. Using the region from 250 to 255 nm for a reference ozone value of  $3.445(17) \text{ cm}^{-2}$ , there is a  $-2\%$  change from 270 to 275 nm and a  $-6.7\%$  change between 230 and 235 nm. As is shown below, the  $-2\%$  change is mostly due to calibration differences between spectra obtained from two independent spectrometers and to a lesser degree to the errors in the assumed ozone absorption cross section at 270 nm relative to that at 250 nm. The most likely source of the cross section error would arise from the small degree of temperature dependence not included in the present analysis. The larger  $-6.7\%$  change arises mostly from spectrometer calibration differences and to a lesser extent from the uncertainties in the assumed ozone and molecular oxygen absorption cross sections.

Although the same spectrometer was used to obtain the reference spectrum and the SABE-3 spectra, there are known calibration differences between the two experiments. Because of these calibration differences, the reference spectrum can be used only to determine  $N(O_3)$  between 38.15 km and the top of the atmosphere. The calibration technique [Mentall et al., 1981] for wavelengths longer than 250 nm was more accurate and reproducible than that for wavelengths shorter than 250 nm. Using the wavelength range from 250 to 255 nm, the value of  $N(O_3)$  at 38.15 km is  $3.445(17) \text{ cm}^{-2} \pm 5\%$ , and that from 37.3 km is  $4.253(17) \text{ cm}^{-2} \pm 5\%$ . It should be noted that a similar analysis of the spectral data from an earlier balloon flight, SABE-1, using the same spectrometer, did not show the calibration problems at short wavelengths. Both the SABE-1 and SABE-3

results are within the stated absolute calibration accuracy [Mentall et al., 1981].

At altitudes below 37.3 km, possible absolute calibration error effects are minimized by forming the ratios of SABE-3 solar flux spectra taken at various altitudes to the spectrum obtained at 37.3 km. For two different altitudes, Z1 and Z2, the ratio of measured solar fluxes  $R_{12} = F_{Z1}/F_{Z2}$  obtained at different solar zenith angles,  $X_1$  and  $X_2$  is given by

$$R_{12} = \exp [\sigma_{O_2}(S_2 N_2(O_2) - S_1 N_1(O_2)) + \sigma_{O_3}(S_2 N_2(O_3) - S_1 N_1(O_3))] \quad (2)$$

where  $\text{Ch}(X_1) = S_1$  and  $\text{Ch}(X_2) = S_2$ . Solving for the ozone column content gives

$$N_2(O_3) = \frac{\ln R_{12} + \sigma_{O_2}[S_1 N_1(O_2) - S_2 N_2(O_2)] + \sigma_{O_3} S_1 N_1(O_3)}{S_2 \sigma_{O_3}} \quad (3)$$

The resulting values of  $N(O_3)$  are independent of wavelength to within 1% from 240 to 280 nm, as shown in Figure 2. For wavelengths shorter than 240 nm the effects of possible calibration errors have been removed, reducing the 6.7% change shown in Figure 1 to 3.7%. It is important to note that the change is nearly constant from 190 to 235 nm, while the change shown in Figure 1 increases with decreasing wavelength. The increasing error shown in Figure 1 would prevent the calculation of the molecular oxygen absorption cross sections using the reference solar flux above the atmosphere. Included in the calculation of  $N(O_3)$  are the O<sub>2</sub> cross sections of *Shardanand and Rao* [1977] and the single scattering approximation to the Rayleigh scattering effect. The molecular oxygen column content,  $N(O_2) = 0.2095 N(T)$ , is obtained from the total atmospheric pressure data corresponding to the time at which the spectra were obtained. From the hydrostatic pressure balance the total density column content is  $N(T) = P/(MG)$ , where  $P$  is the

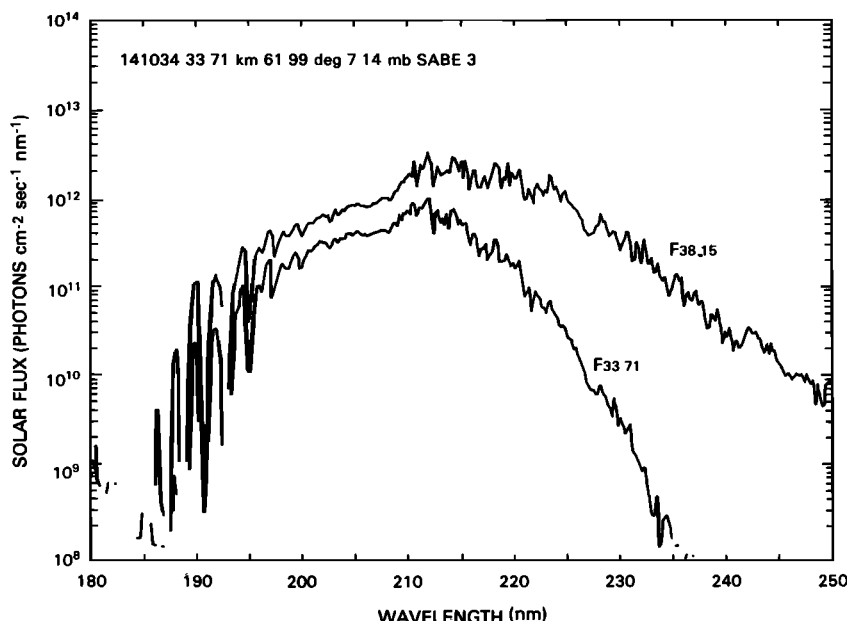


Fig. 3. The SABE-3 spectrum obtained at 38.15 km and one of the spectra used to calculate the O<sub>2</sub> absorption cross sections obtained at 33.71 km. The spectra are shown at a resolution of 0.2 nm and clearly show some of the structure caused by atmospheric absorption within the Schumann-Runge bands of O<sub>2</sub>. Between 200 and 220 nm, most of the absorption is from the O<sub>2</sub> Herzberg continuum, with the increasing O<sub>3</sub> absorption becoming dominant for wavelengths greater than 220 nm.

pressure,  $M$  is the average mass (28.96 amu), and  $G$  is the gravitational acceleration at the balloon altitude. The small errors indicated in Figure 2 are not the total errors but only the relative errors in the procedure once the fluxes and cross sections are specified. The total fractional error in  $N(O_3)$  for ozone absorption alone can be estimated from the terms in the equation

$$\frac{dN(O_3)}{N(O_3)} = \frac{1}{\ln R} \frac{dR}{R} - \frac{d\sigma_{O_3}}{\sigma_{O_3}} \quad (4)$$

where  $R = F_{\infty}/F_z$  from (1). At 250 nm and 38.15 km,  $R = 858$ ,  $\ln(R) = 6.75$ , and  $dR/R < 0.1$ , so that the percent error in the column ozone due to errors in the flux measurement is about 2%. This error decreases with decreasing altitude between 40 and 30 km. At lower altitudes (less than 30 km) only the longer wavelength portion of the spectrum from 290 to 330 nm is within the sensitivity range of the spectrometer. In this wavelength range the cross sections are relatively small and more temperature dependent. At the longest wavelength used to calculate  $N(O_3)$ , 290 nm, the cross section error is less than 5% [Bass and Paur, 1981]. The ozone cross section in the vicinity of 250 nm is known to within 2%, so that the total ozone column content error should be less than 5% over a wide range of wavelengths and altitudes.

The above discussion of errors in the calculation of the ozone column content establishes the basis for being able to meaningfully calculate the much smaller molecular oxygen cross section from the 200 to 240 nm region of the spectra. The spectra used in this calculation were obtained at altitudes from 32 to 34 km where the strength of the solar flux in the 240 to 270 nm region is below the sensitivity of the spectrometer. Therefore the ozone column content is calculated near 280 nm, and then applied to the 200–240 nm region after altitude corrections are made for the 70-s scan time. The procedure is acceptable, since we have established that

the measured solar flux and the ozone absorption cross sections are consistent over the entire wavelength range. When calculating the O<sub>2</sub> absorption cross-section errors, the absolute error of the product  $N(O_3)\sigma_{O_3}$  is the relevant quantity. This means that only the relative error in the O<sub>3</sub> cross section enters into the O<sub>2</sub> cross section calculation. Figure 2 shows that this error is much less than 5%.

#### MOLECULAR OXYGEN ABSORPTION CROSS SECTIONS

Once the ozone column content is known from the portion of the solar flux absorption data that is not dependent on O<sub>2</sub> absorption, (3) with the addition of Rayleigh scattering can be used to obtain the O<sub>2</sub> absorption cross sections between 190 and 240 nm. Solving for  $\sigma_{O_2}$ , (3) becomes

$$\sigma_{O_2} = \{\ln R_{12} - \sigma_{O_3}[S_2N_2(O_3) - S_1N_1(O_3)] - \sigma_R[S_2N_2(T) - S_1N_1(T)]\} [S_2N_2(O_2) - S_1N_1(O_2)]^{-1} \quad (5)$$

where  $\sigma_R$  is the Rayleigh scattering cross sections and  $N(T)$  is the total density.

Formation of the indicated solar flux ratios  $R_{12}$  by using the SABE-3 spectrometer data from 37.3 km as the reference flux  $F_{z1}$  and the spectra taken from 34.2 to 32.18 km, successively, as  $F_{z2}$ , yields the O<sub>2</sub> absorption cross sections. In order to eliminate the small structure arising from slight wavelength misalignments in the individual spectra, a nine-point running average (1.8 nm) was used after the cross sections were obtained. For the most part the structure in the spectra between 200 and 240 nm are not atmospheric features but are in the original solar spectrum above the atmosphere. An example of measured spectra at three different altitudes, 58, 44, and 39 km, showing these features is given in Figure 3 of Herman and Mentall [1982], and at the altitudes of 38.15 and 33.71 km in Figure 3 of this paper. Once the smoothed cross sections are obtained, the results from the several altitudes are averaged together to yield the

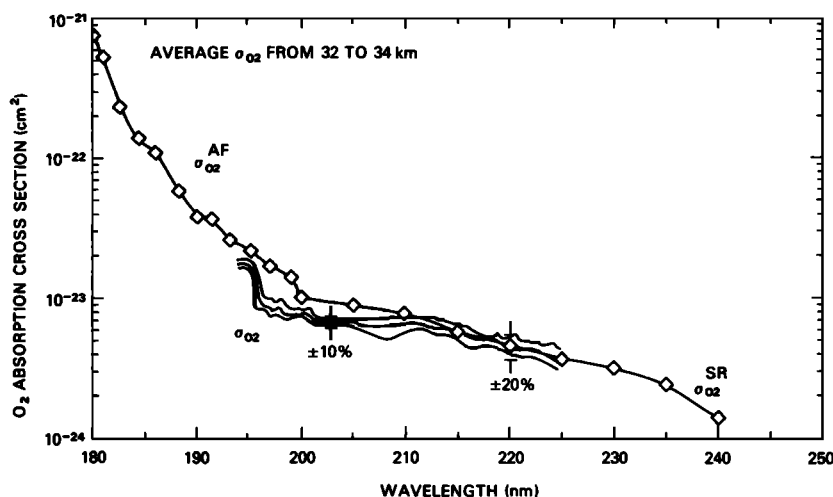


Fig. 4. The molecular oxygen absorption cross sections formed by performing a running average over nine calculated values (1.8 nm) and averaging over the altitude range from 32.18 to 34.2 km. The envelope shown on the figure represents the spread in values from the different altitudes. The formal error bars represent the estimated errors from all sources as discussed in the text. The calculated values of  $\sigma_{O_2}$  are compared with those obtained by Shardanand and Rao [1977],  $\sigma_{O_2}^{SR}$ , and in the Schumann-Runge band region (190–200 nm) to the effective cross sections given by Allen and Frederick [1982],  $\sigma_{O_2}^{AF}$ .

center curve in Figure 4. The two outer curves paralleling  $\sigma_{O_2}$  are the envelope of the cross section determinations from the different altitudes. Formal error bars are included, based on the discussion below.

The calculated O<sub>2</sub> cross sections shown in Figure 4 are tabulated at 1 nm intervals from 200 to 220 nm in Table 2. Spectra outside of the altitude range from 32.18 to 34.2 km were not used for  $F_{22}$  in (5). Because of the strong absorption in the 200 to 230 nm region the amount of solar flux is too small for the spectrometer to measure accurately below 32 km. Above 34.2 km the O<sub>2</sub> column density is not large enough to produce the optimum optical depth of 0.7 to 1 to give useable results from (5). At the altitude of 33.71 and wavelength of 205 nm the optical depth of O<sub>2</sub> is approximately 1 and that of O<sub>3</sub> is about 0.25 for the zenith direction.

Figure 3 shows a portion of the spectrum obtained at 38.15 km and one from 33.71 km used for the calculation of  $\sigma_{O_2}$ . Equation (5) can be applied to the flux ratio of these two spectra when the O<sub>2</sub> absorption is large enough for  $\ln(R_{12})$  to be greater than about 1% of the other terms in the numerator. This limit on  $\ln R_{12}$  and the spectrometer's sensitivity make it impossible to use (5) outside the wavelength range 187–230 nm without causing large errors.

The structure introduced into the partially absorbed solar flux by the presence of the O<sub>2</sub> Schumann-Runge bands clearly appears in the spectra shown in Figure 3. The magnitude of the effective cross sections producing the structure can be estimated by forming the ratio of the solar flux above the atmosphere with the partially absorbed solar flux at various altitudes. The effective cross sections obtained are averages over the 0.2 nm wavelength bins corresponding to the spectral resolution of the spectrometer.

The Beer's law form of (5) is not generally applicable to molecular band spectra except in the weak line approximation [Goody, 1964]. An analysis of the transmissivities of the Schumann-Runge bands of molecular oxygen based on the tables given by Frederick and Hudson [1980] show the full range of behavior between the strong and weak line approximations for the altitude range between 30 and 35 km. The

weak and strong line approximations have a linear and square root dependence on the optical depth, respectively. In a more realistic case the square root dependence is replaced by a power law that usually lies between 0.5 and 1. Plotting the tabulated transmissivities,  $T(N(O_2))$ , of Frederick and Hudson in the form  $\log(\log(T))$  versus  $\log(N)$  shows both the weak and strong line limit regions. For the wavelength range of interest, 187–200 nm, seven of Frederick and Hudson's spectral intervals are appropriate,  $i = 4$  to 10. The results of fitting two forms of a power law dependence on the optical depth are given in Tables 3a and 3b.

Clearly, no single power law in the strong line limit is appropriate for the entire wavelength range. Accordingly,

TABLE 2. O<sub>2</sub> Absorption Cross Sections

$\lambda$ , nm	$\sigma_{HM}$	$\sigma_{SR}$	$\sigma_{HN}$	% $\Delta_{SR}$	% $\Delta_{HN}$
200	7.81	10.10	13.85	29.32	77.34
201	7.32	9.86	13.60	34.70	85.74
202	6.93	9.62	13.34	38.82	92.53
203	6.93	9.38	13.09	35.35	88.86
204	6.80	9.14	12.83	34.41	88.74
205	6.49	8.90	12.58	37.13	93.84
206	6.33	8.66	12.26	36.81	93.62
207	6.33	8.42	11.93	33.02	88.50
208	6.33	8.18	11.61	29.23	83.38
209	6.45	7.94	11.28	23.10	74.95
210	6.66	7.70	10.96	15.62	64.56
211	6.69	7.32	10.59	9.42	58.33
212	6.37	6.94	10.22	8.95	60.50
213	6.15	6.56	9.86	6.67	60.26
214	5.98	6.18	9.49	3.34	58.66
215	5.78	5.80	9.12	0.35	57.79
216	5.45	5.56	8.70	2.02	59.71
217	5.11	5.32	8.29	4.11	62.19
218	5.07	5.08	7.87	0.20	55.27
219	4.89	4.84	7.46	-1.02	52.47
220	4.40	4.60	7.04	4.55	60.00

All measurements but  $\lambda$  in  $10^{-24}$  cm<sup>2</sup>. Values of  $\sigma_{HM}$  are from the present work,  $\sigma_{SR}$  from Shardanand and Rao [1977],  $\sigma_{HN}$  from Hasson and Nicholls [1971]; % $\Delta_{SR} = 100 * (\sigma_{SR} - \sigma_{HM})/\sigma_{HM}$ , % $\Delta_{HN} = 100 * (\sigma_{HN} - \sigma_{HM})/\sigma_{HM}$ . Note that  $\sigma_{HN}$  and  $\sigma_{SR}$  have been interpolated onto 1-nm intervals.

TABLE 3a. Fitting Parameters for  $T = \exp [-(N\sigma)^n]$ 

Range, nm	$i$	$n$	$\sigma(\text{O}_2)$ , cm <sup>2</sup>
198.0–200.0	4	0.993	1.60 (–23)
196.1–198.0	5	0.83	2.08 (–23)
194.2–196.1	6	0.67	4.55 (–23)
192.3–194.2	7	0.56	1.11 (–22)
190.5–192.3	8	0.665	9.80 (–23)
188.7–190.5	9	0.58	1.30 (–22)
186.9–188.7	10	0.60	3.33 (–22)

The values of  $n$  and  $\sigma(\text{O}_2)$  are obtained from the form  $T(N(\text{O}_2)) = \exp [-(N\sigma)^n]$ , where the fit to the transmissivities is made in the strong line region appropriate to the 30 to 40 km region of the atmosphere.

TABLE 3b. Fitting Parameters for  $T = \exp \{-(N\sigma)^n/[1 + (a/N\sigma)^{1-n}]\}$ 

Range, nm	$i$	$n$	$\sigma(\text{O}_2)$ , cm <sup>2</sup>	$a$
198.0–200.0	4	0.99	3.4 (–23)	2.0
196.1–198.0	5	0.6	6.0 (–23)	1.3
194.2–196.1	6	0.49	9.0 (–23)	0.33
192.3–194.2	7	0.40	2.7 (–22)	0.28
190.5–192.3	8	0.53	1.6 (–22)	0.055
188.7–190.5	9	0.48	1.8 (–22)	0.016
186.9–188.7	10	0.5	3.9 (–22)	0.012

The values of  $n$ ,  $\sigma(\text{O}_2)$ , and  $a$  are obtained from a form of the transmissivity that fits the entire range of optical depths for the earth's stratosphere:  $T(N(\text{O}_2)) = \exp \{-(N\sigma)^n/[1 + (a/N\sigma)^{1-n}]\}$ .

the appropriate power  $n$  is used to compute the effective cross sections from the measured solar flux data within each wavelength interval in a manner similar to that implied by (5). The calculated cross sections are shown in Figure 5 for the altitudes 33.1, 35.01, and 37.3 km. The results from different altitudes are in close agreement with one another in the regions of relatively weak absorption due to the overlapping Lorentz wings of the rotational lines within a band and the underlying continuum, and in the regions of strong absorption. For the cases shown in Figure 5 the calculated cross sections roughly follow the trend given by the empirical fit of *Allen and Frederick* [1982]. However, the amount of solar flux between 190 and 200 nm penetrating the atmosphere would be underestimated using the Allen and Frederick representation. No formal error estimates can be given for the effective cross sections except to note that the variance expected in the calculation due to the errors in the measured fluxes and laboratory O<sub>2</sub> cross sections is about 10%.

An important effect of having  $n < 1$  for the calculation of the transmissivity is a smaller growth rate of solar flux

attenuation for a given increase in O<sub>2</sub> column density than for  $n = 1$ . Stratospheric model calculations using estimated effective cross sections and the weak line approximation form  $n = 1$  will systematically underestimate the amount of solar flux penetrating the stratosphere in the Schumann-Runge band region. However, the cross section formulation of *Allen and Frederick* [1982] includes the proper behavior of the cross section with optical depth by forming an elaborate fitting polynomial to the band averages of the detailed transmissivities.

#### DISCUSSION OF ERRORS DUE TO SCATTERING AND OZONE ABSORPTION

The total scattered flux at about 200 nm in the 30–40 km region of the atmosphere can amount to about 10% of the direct solar flux [*Herman and Mentall*, 1982]. Between 200 and 240 nm the Rayleigh scattering cross section goes from 3.5 (–25) to 1.5 (–25) cm<sup>2</sup> [*McCartney*, 1976] where

$$\sigma_R = 1.06 \frac{128\pi^5}{3\lambda^4} \alpha^2(\lambda) \quad (6)$$

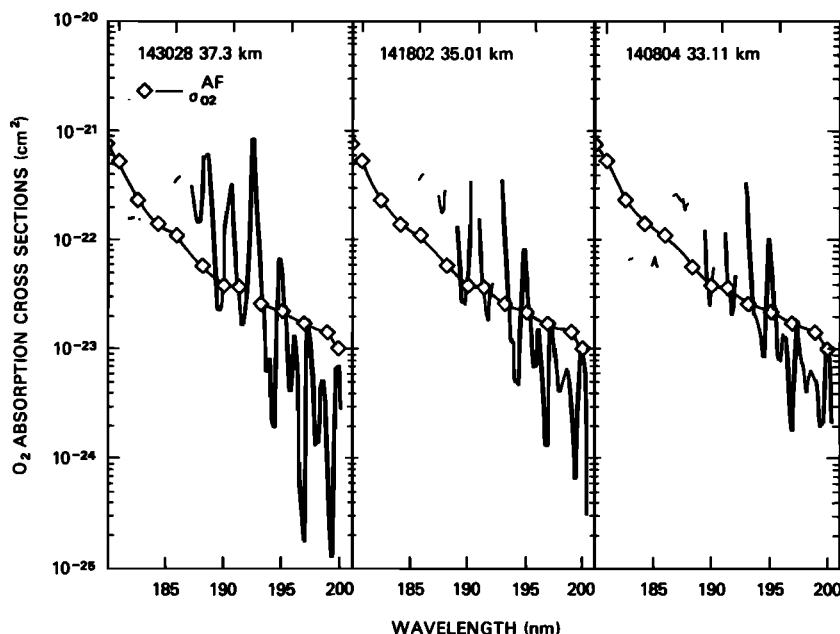


Fig. 5. The molecular oxygen effective absorption cross sections in the Schumann-Runge band region (193–200 nm) for three different altitudes. The calculations are made at a spectral resolution of 0.2 nm. The calculated cross sections based on the strong line approximation of Tables 3a and 3b are compared with the empirical fit to the Schumann-Runge band cross sections given by *Allen and Frederick* [1982].

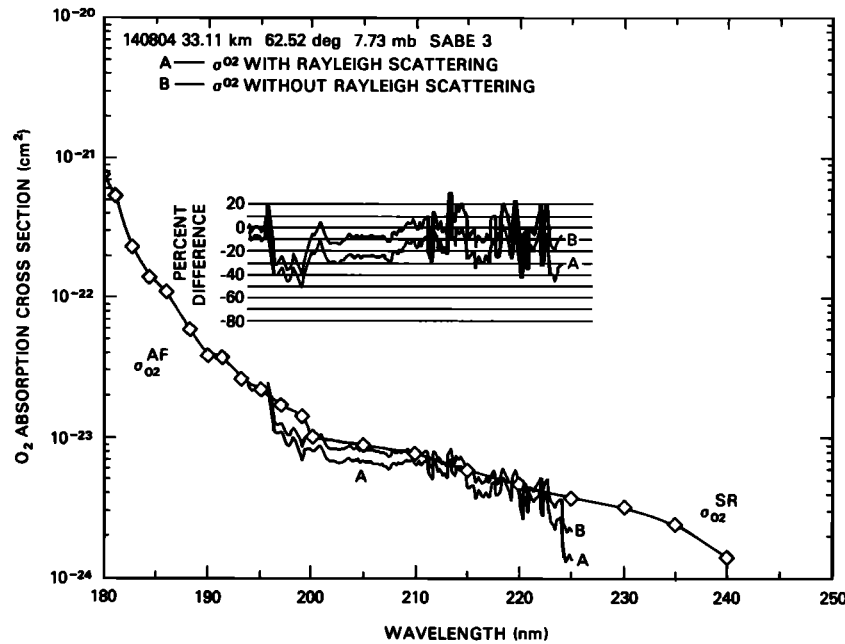


Fig. 6. The molecular oxygen absorption cross sections calculated with (case A) and without (case B) the Rayleigh scattering effect.

$\lambda$  is the wavelength in centimeters,  $\alpha$  is the effective molecular polarizability ( $2.02(-24)$  cm<sup>3</sup> at 200 nm and  $1.90(-24)$  cm<sup>3</sup> at 240 nm), and 1.06 is the correction for molecular anisotropy. The approximate value of  $\sigma_{O_2}$  measured by *Shardanand and Rao* [1977] at 200 nm is  $1.01(-23)$  cm<sup>2</sup>. Since O<sub>2</sub> is about one-fifth of the total atmospheric number density,  $N(T)$ ,  $N(T)\sigma_R/(N(O_2)\sigma_{O_2}) \sim 0.1$ , and therefore cannot be neglected in the calculation of molecular oxygen absorption cross sections. For the altitude range 30–40 km the single scattering approximation indicated in (5) is sufficient.

Omission of the Rayleigh scattering effect can lead to approximately a 20% overestimate of the molecular oxygen absorption cross sections for wavelengths longer than 200 nm, as shown in Figure 6. Multiple scattering at these altitudes contributes at most another 1% reduction in the calculated cross sections.

The largest potential source of error in the calculation of the O<sub>2</sub> cross sections for wavelengths longer than 220 nm arises from the experimental error in the ozone cross section. Between 220 and 225 nm a 3% change in the ozone cross section can produce a 40% change in the calculated O<sub>2</sub>

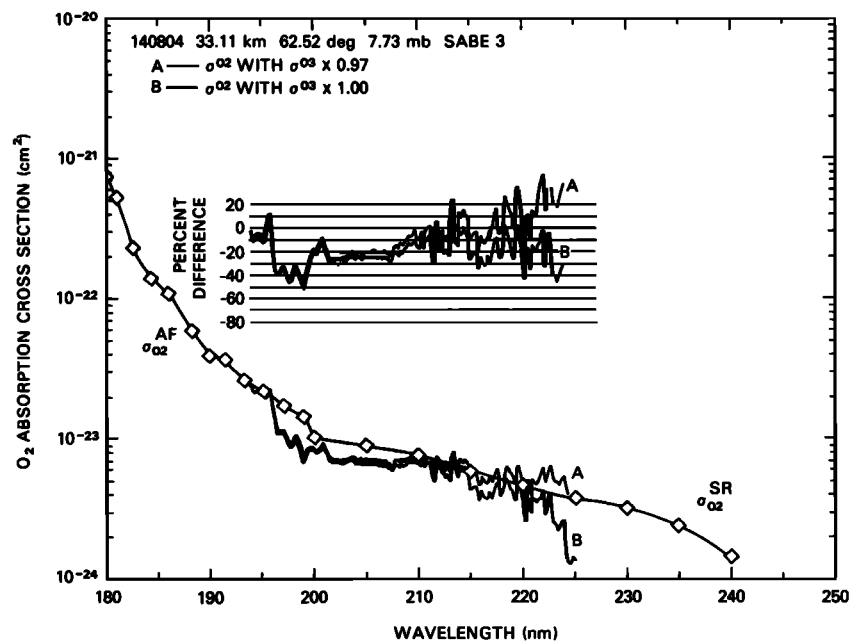


Fig. 7. The molecular oxygen absorption cross sections calculated for an assumed 3% reduction in  $\sigma_{O_3}$  from the values given by *Inn and Tanaka* [1959].



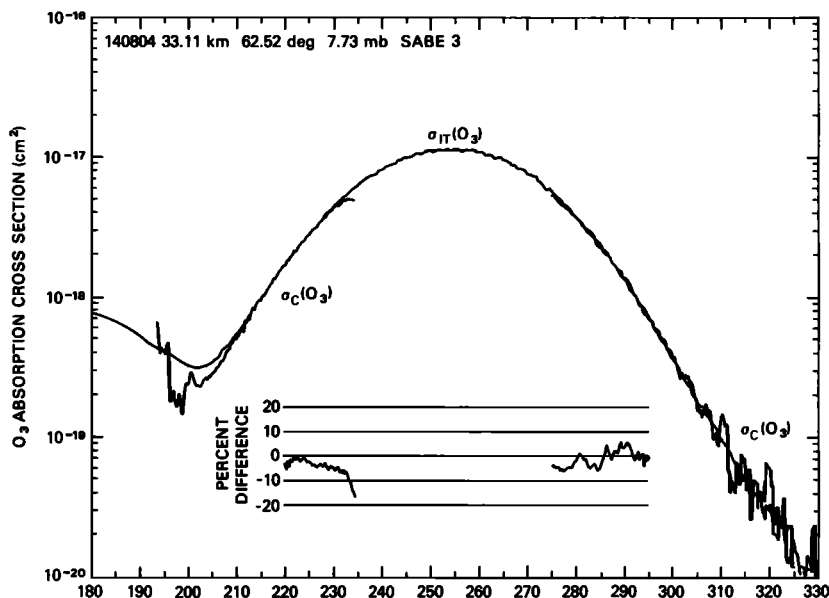


Fig. 8. The ozone absorption cross sections calculated from the ratio of the solar fluxes obtained at 37.3 and 33.11 km. The calculated values  $\sigma_C(O_3)$  are compared with those of *Inn and Tanaka* [1959] and *Tanaka et al.* [1953]. The agreement with  $\sigma_{IT}(O_3)$  is about 3% over the wavelength range, where the solar flux at 33.11 km was within the useable sensitivity range of the spectrometer and where there was significant absorption.

cross section. The change decreases rapidly with decreasing wavelength, so that by 205 nm the change is reduced to 5%, as shown in Figure 7. The 30% difference between the present values of  $\sigma_{O_2}$  and those of *Shardanand and Rao* [1977] between 200 and 210 nm is significant, since the total error is estimated to be less than  $\pm 10\%$ . As the wavelength increases beyond 220 nm,  $\ln R_{12}$  becomes almost equal to the ozone absorption term in (5). This means that small changes in  $\sigma_{O_3}$  lead to large changes in the calculated values of  $\sigma_{O_2}$ . The estimated errors in  $\sigma_{O_2}$  are  $\pm 10\%$  from 190 to 215 nm,  $\pm 20\%$  at 220 nm, and  $\pm 40\%$  at 225 nm.

The relative values as a function of wavelength of the *Inn*

and *Tanaka* [1959] ozone absorption cross sections agree closely with the relative values calculated from the solar flux absorption data. An example of the calculated ozone cross section is shown in Figure 8 for flux ratios taken between the two altitudes 33.11 and 37.3 km. The ozone column content of  $9.618(17) \text{ cm}^{-2}$  was obtained using (3) and averaging the results over the narrow wavelength range from 287 to 290 nm. Equation (5) is then used to solve for  $\sigma_{O_3}$  from 180 to 330 nm using  $\sigma_{O_2}$  from *Shardanand and Rao* [1977]. The agreement with *Inn and Tanaka* [1959] between 210 and 225 nm is better than 3%. For wavelengths shorter than 210 nm, the assumed O<sub>2</sub> absorption cross section gives rise to the large

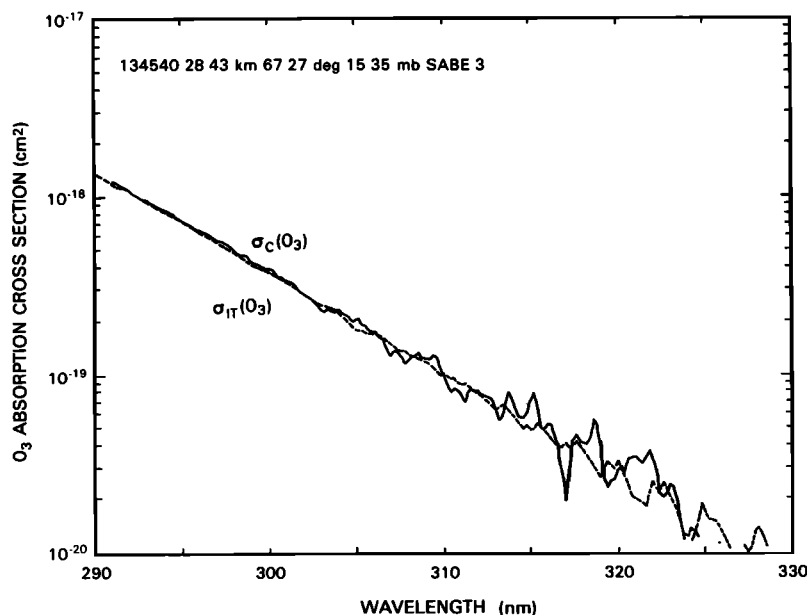


Fig. 9. The ozone absorption cross sections calculated using the solar flux data obtained at 28.43 km. Combining similar calculations from 28 to 38 km gives good agreement with the values of *Inn and Tanaka* [1959] over the wavelength range 210–310 nm.

calculated disagreement with the data from *Inn and Tanaka* [1959] and *Tanaka et al.* [1953] for wavelengths shorter than 200 nm. For wavelengths between 225 and 275 nm the observed solar fluxes were below the useful sensitivity range of the spectrometer at 33.11 km. For wavelengths longer than about 300 nm, the amount of absorption is too small to be used to accurately calculate  $\sigma_{O_2}$ . However, using solar flux data from a lower altitude (28.43 km), the calculation for  $\sigma_{O_2}$  can be extended successfully to about 305 nm, as shown in Figure 9. By combining the results from many different altitudes, good agreement (within 2–3%) is obtained with  $\sigma_{O_2}$  from *Inn and Tanaka* from 210 to 310 nm.

#### CONCLUSION

The absorption cross sections of molecular oxygen have been calculated in the wavelength range from 187 to 230 nm from solar flux measurements obtained within the stratosphere. The ozone column content between 30 and 40 km and the relative ozone cross sections from 210 to 310 nm are determined from the same solar flux data set. The ozone cross sections are shown to agree with the laboratory data of *Inn and Tanaka* [1959] and *Bass and Paur* [1981] to within 3%. By determining the ozone column content from the solar flux data and the ozone absorption cross sections, only the relative errors in  $\sigma_{O_2}$  enter into the calculation of the O<sub>2</sub> absorption cross sections. The molecular oxygen absorption cross sections are found to be about 30% smaller than the laboratory data of *Shardanand and Rao* [1977] and 50% smaller than those of *Hasson and Nicholls* [1971] from 200 to 210 nm. Omission of Rayleigh scattering leads to an overestimate of  $\sigma_{O_2}$  by about 20%. The scattering effect is much smaller in laboratory measurements when pure O<sub>2</sub> is used but not when the O<sub>2</sub> is diluted as part of a mixture of gases. For wavelengths less than 200 nm the calculated O<sub>2</sub> cross section increases sharply because of the presence of the Schumann-Runge bands. The results are in rough agreement with an empirical fit to the O<sub>2</sub> Schumann-Runge effective absorption cross sections appropriate for stratospheric conditions and solar zenith angles during the observation period

[*Allen and Frederick*, 1982]. The calculated cross sections in Figure 5 indicate that the transmissivity of the atmosphere is underestimated by the empirical fit proposed by *Allen and Frederick* [1982] between 195 and 200 nm.

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