Absorption of Solar Radiation by O₂: 
Implications for O₃ and Lifetimes of N₂O, CFC₁₃, and CF₂Cl₂
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An accurate line-by-line model is used to evaluate effects of absorption in the Schumann-Runge bands of O₂ on transmission of ultraviolet radiation. Allowing also for absorption in the Herzberg continuum, the model is shown to provide a reliable simulation of observed transmission in the spectral interval 192 to 200 nm. The model is used to evaluate rates for photolysis of N₂O, CFC₁₃, and CF₂Cl₂, and to infer global loss rates (1.22x10¹⁰ kg N yr⁻¹, 7.21x10⁷ and 3.04x10⁷ kg Cl yr⁻¹, respectively) and instantaneous lifetimes (123, 44, and 116 years, respectively) appropriate for 1980. A parameterized version of the line-by-line model enabling rapid evaluation of transmission in the Schumann-Runge region is described. Photochemical calculations employing the parameterization and constrained by data from the Atmospheric Trace Molecule Spectroscopy experiment are used to examine the budget of odd oxygen. Consistent with previous studies, it is shown that photochemical loss of odd oxygen exceeds production by photolysis of O₂ for altitudes above 40 km. The imbalance between production and loss is shown to be consistent with a source of odd oxygen proportional to the product of the mixing ratio and photolysis rate of ozone, which suggests that processes involving vibrationally excited O₂ may play an important role in production of odd oxygen.

1. INTRODUCTION

Photodissociation of molecular oxygen in the optically allowed Schumann-Runge (S-R) bands and in the optically forbidden Herzberg continuum provides the dominant source of odd oxygen (Oₓ = O₂ + O) in the stratosphere and mesosphere. The Schumann-Runge bands represent the most important source of opacity for the spectral interval 175 to 200 nm, while the Herzberg continuum, extending from its threshold at 242 nm, makes a significant contribution to the opacity of the atmosphere at longer wavelengths.

Absorption in the S-R bands results in predissociation of the oxygen molecule; discrete absorption from the X³Σg⁻ ground state to the bound B²Σu⁺ state is followed by a nonradiative transition to either of the repulsive 1Πₓ, 3Πₓ, 5Πₓ, or 1Σu⁺ states, resulting in production of two ground state atoms. Uncertainties relating to the complexity of spectral features in the S-R bands have persisted for the past two decades in treatments of the transmission of solar radiation in the 175- to 200-nm range [Kockarts, 1971; Hudson and Mahale, 1972; Park, 1974; Fang et al., 1974; Frederick and Hudson, 1980; Nicolet and Pepperman, 1980; Simon and Brassey, 1983; World Meteorological Organization, 1986], with implications for production of Oₓ and for lifetimes of N₂O, CFC₁₃, and CF₂Cl₂. The problem is associated with the paucity of laboratory data for S-R band absorption [Brix and Herzberg, 1954; Hudson and Carter, 1968; Ackerman et al., 1970]. The situation has improved more recently with values for S-R band spectral parameters based on laboratory studies by Yoshino et al. [1983, 1987] and Lewis et al. [1986a, b]. These data were used by Murtagh [1988] and Nicolet and Kennes [1989] to obtain revised values of rates of photolysis in the S-R bands for the upper stratosphere and mesosphere.

The Herzberg continuum extends over the spectral interval 185 to 242 nm and is associated with the optically forbidden X³Σg⁻ → A¹Σu⁺ transition in O₂. The unbound part of the A¹Σu⁺ potential is accessed for wavelengths below 242 nm; absorption of solar radiation in the Herzberg continuum leads to dissociation of the O₂ molecule. There has been a downward trend in values of cross sections reported for the Herzberg continuum over the past 20 years. In situ measurements of solar irradiance in the stratosphere performed in the early 1980s [Frederick and Mentall, 1982; Herman and Mentall, 1982; Anderson and Hall, 1983] suggested that Herzberg cross sections in use at that time [e.g., Hasson and Nicholls, 1971; Shardenan and Prasad Rao, 1977] were too large by about 50%. The lower cross sections implied by the in situ data were confirmed subsequently by laboratory measurements [Johnston et al., 1984; Cheung et al., 1986b; Jenouvrier et al., 1986a,b]. The smaller cross sections obtained in the laboratory resulted from more careful analyses of the pressure dependence of absorption by O₂ in the Herzberg continuum [e.g., Cheung et al., 1986b]. Rates for photolysis of O₂ calculated using the new data for this spectral interval were presented by Nicolet and Kennes [1986].

Cross sections for absorption in the Herzberg continuum at shorter wavelengths, between 180 and 195 nm, were measured by Yoshino et al. [1992]; their data suggest that the cross section for the Herzberg continuum underlying the S-R bands is significantly less than expected on the basis of earlier data. Opacity contributed by the underlying Herzberg continuum affects the magnitude and height profile of the source for Oₓ and has, further, a critical influence on rates for photolysis of a variety of species, including N₂O, HNO₃, and the longer lived chlorofluorocarbon molecules [Froidevaux and Yung, 1982].

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Concentrations of O₃ calculated on the basis of photochemical models are sensitive to uncertainties in rates for photodissociation of O₂ [Froidevaux et al., 1989], especially between 40 and 80 km where ozone is thought to be in photochemical steady state. The failure of current models to correctly reproduce measurements of O₃ from 40 to 80 km is well documented: calculated concentrations of ozone are lower than observed values by 30 to 60% at 50 km and the deficit grows to 40 to 80% at 80 km [Solomon et al., 1983; Froidevaux et al., 1985; Jackman et al., 1986; Natarajan et al., 1986; McElroy and Salawitch, 1989b]. The wide latitude assigned to cross sections for O₂ absorption (~40% uncertainty in the S-R bands and ~30% for the Herzberg continuum [DeMore et al., 1991]) has led to suggestions that the discrepancy could be resolved, at least partly, by adjustments in O₂ cross sections [Solomon et al., 1983; Clancy et al., 1987; Froidevaux et al., 1989; Allen and Delitsky, 1991]. Allen and Delitsky [1991] specifically targeted the uncertainty for photolysis in the S-R band and Herzberg continuum regions to account for the disagreement between calculated concentrations of ozone and values inferred from the ATMOS (Atmospheric Trace Molecule Spectroscopy) experiment. They found good agreement with observations when cross sections for absorption by O₂ were increased by 40% in both the O₂ bands and Herzberg continuum. However, Clancy et al. [1987] concluded that adjustments in O₂ cross sections alone were insufficient to explain observations of ozone by the Solar Mesosphere Explorer.

Here we describe calculations for transmission of ultraviolet radiation based on a line-by-line representation of S-R band cross sections [Minschwaner et al., 1992]. Calculated O₂ cross sections in the S-R bands and stratospheric transmittances in the 192- to 200-nm wavelength range are presented in section 2. Comparisons between the calculations and laboratory [Yoshino et al., 1983] and in situ measurements [Anderson and Hall, 1986] establish that the S-R band description and values for Herzberg continuum cross section adopted here are appropriate for applications to the atmosphere. Rates for photolysis of N₂O, CFC₁₃, and CF₂Cl₂ are calculated in section 3, with resulting estimates for global loss rates and lifetimes for these gases. Photochemical calculations incorporating the new O₂ cross sections are discussed in section 4. Results are presented for the O₂ budget of the stratosphere obtained from the Harvard photochemical model [Logan et al., 1978], updated according to the S-R band parameterization described in the appendix and constrained by ATMOS measurements of radical and source gases [Farmer et al., 1987]. The calculations do not support the hypothesis that the discrepancy in the O₂ budget may be attributed to uncertainties associated with the absorption cross section of O₂ in the 175- to 242-nm wavelength range. The height profile for the missing source of O₂ is, however, consistent with production of O₂ due to photolysis at longer wavelengths of vibrationally excited O₂, as postulated by Slanger et al. [1988].

2. O₂ CROSS SECTIONS AND ATMOSPHERIC TRANSMISSION

Absorption of solar radiation in the spectral interval 175 to 200 nm is dominated by the S-R bands of O₂. High-resolution laboratory data for absorption cross sections have been obtained for temperatures of 79 and 300 K [Yoshino et al., 1983, 1987]. However, these cross sections are not directly applicable to studies of the stratosphere. We developed a full line-by-line representation of the S-R band system to allow computation of cross sections at stratospheric temperatures. Details of the line-by-line model are presented elsewhere [Minschwaner et al., 1992]; only key features will be outlined here.

The line-by-line model employs the best available data for molecular constants, band oscillator strengths and predissociation line widths [Cheung et al., 1986a, 1990; Yoshino et al., 1983, 1987, 1990; Lewis et al., 1986a, b]. It accounts for the triplet components of the principal R and P branches, allowing, in addition, for six satellite and two forbidden transitions. Principal branches of isotopically heavy oxygen are included [Cheung et al., 1989; Yoshino et al., 1989; Chiu et al., 1990]. Rotational lines corresponding to N" = 1 to 51 are considered for vibrational bands spanning the range 0-0 to 2-19. Populations of rotational and vibrational levels were evaluated assuming they can be represented by a Boltzmann distribution defined by the local temperature. Line shapes were calculated using Voigt profiles. Cross sections were determined by summing contributions from all absorption lines in a 500 cm⁻¹ window. Additional contributions to the absorption from the underlying S-R continuum were calculated by summing over Boltzmann-weighted partial cross sections [Allison et al., 1971; Lewis et al., 1985a, b].

Cross sections calculated in this manner are compared in Figure 1 with the measurements at 300 K by Yoshino et al. [1983]. The agreement is excellent and typical of that observed for the entire spectral range covered by the measurements (roughly 49,750 to 55,750 cm⁻¹, or 179 to 201 nm). Applications to the atmosphere require values for the absorption cross section over a range of tempera-

![Fig. 1. Observed O₂ absorption cross section (dotted curve) [Yoshino et al., 1983] and cross section calculated with the line-by-line model (solid curve) for a temperature of 300 K.](image)
tures. We found in practice that significant computational savings could be realized by evaluating cross sections at a number of discrete temperatures, using these data to define a polynomial fit applicable for a range of atmospheric conditions. Cross sections obtained in this fashion were shown to accurately reproduce results of explicit line-by-line calculations at 0.5 cm⁻¹ resolution over the temperature range 130 to 500 K [Minschwaner et al., 1992].

Figure 2 presents a comparison of calculated values of spectrally averaged transmission of solar radiation with measurements by Anderson and Hall [1986]. The data refer to the wavelength intervals 192.3-194.2, 194.2-196.1, 196.1-198.0, and 198.0-200.0 nm. The observational data were adjusted to account for absorption by O₃ and for Rayleigh scattering [Anderson and Hall, 1986]; thus the residual transmission indicated in Figure 2 should be due exclusively to effects of O₂. The model results were obtained assuming the temperature structure given by the U.S. Standard Atmosphere (1976). Values for the O₂ cross section in the Herzberg continuum were evaluated using the fit derived by A. Hall [Yoshino et al., 1988] to the experimental data of Cheung et al. [1986b] and Jenouvrier et al. [1986a, b]. The good agreement between calculated and observed transmittances is consistent with simulations of transmission observed at high resolution, as reported earlier [Minschwaner et al., 1992]. Calculations were also carried out using cross sections for the Herzberg continuum presented by Yoshino et al. [1992]. Agreement with the balloon observations was significantly poorer in this case; calculated transmittances were too large. We interpret the discrepancy to indicate that the choice of cross sections for the Herzberg continuum by Yoshino et al. [1992], a function of the procedure used to describe absorption in the far wings of S-R lines, is inconsistent with the formulation adopted here for the S-R bands.

Figure 2 also includes values for transmittances determined according to data for the S-R bands and Herzberg continuum from the World Meteorological Organization (WMO) [1986] Assessment. The disagreement between the balloon measurements and transmittances from WMO [1986], noted previously by Anderson and Hall [1986], suggests that cross sections for either the S-R bands or Herzberg continuum, or both, must be too large in the WMO [1986] Assessment. To investigate this matter further, we performed a separate set of calculations involving absorption by the S-R bands alone. We found a persistent tendency for greater transmittance (lower S-R cross sections) in our calculations as compared to those based on the WMO data. The higher transmission calculated according to our S-R band cross sections, at least in three of the spectral intervals, is sufficient to account for between 30 and 40% of the disagreement shown in Figure 2. The remaining difference can be ascribed, most likely, to the lower values of cross sections employed for the Herzberg continuum in the present study (the value at 200 nm from Yoshino et al. [1988] is about 16% lower than the WMO [1986] recommendation).

The transmittances shown here agree closely with those calculated by Logan et al. [1978], using the formulation of Fang et al. [1974] updated with Herzberg continuum cross sections from Cheung et al. [1984]. This result is consistent with the findings of the intercomparison for O₂ and N₂O photolysis rates shown in Figures 12-8 and 12-9 of WMO [1986]. In that study, the Harvard model [Logan et al., 1978] indicated deeper penetration of solar radiation in the S-R band region in comparison to other models [WMO, 1986].

The portion of the spectrum covered in Figure 2 includes the 2-0, 3-0, and 4-0 bands of the S-R system. In the absence of a high-resolution comparison, it is unclear whether the discrepancies in transmittance noted here result from differences in S-R cross sections for absorption lines or for the window regions between lines. Transmittances obtained by Murtagh [1988] were also lower than values recommended by WMO [1986]. He attributed the discrepancy in part to line widths in his calculation that were narrower than those employed by WMO [1986]. However, tables defining transmittance in the S-R bands presented by WMO [1986] are based on oscillator strengths and predissociation widths given by Frederick and Hudson [1979]; line widths recommended by these authors for the 2-0 band are 70% narrower than those employed here [Cheung et al., 1990], while line widths for the 3-0 and 4-0 bands are only 3% and 8% larger (see Table II [Cheung et al., 1990]). With the exception of the 2-0 band, there are no significant differences between the oscillator strengths presented by Frederick and Hudson [1979] and the values adopted for the present calculation (see Table 2 [Yoshino et al., 1983]). It is possible that the discrepancy may reflect differences in the treatment of the hot bands (4-1, 5-1 and 6-1).
The detailed treatment of the S-R bands described above allows for a quantitative assessment of rates for photolysis of atmospheric constituents that dissociate primarily in the 175- to 210-nm wavelength range. The spectral interval 190 to 210 nm, located at the tail of the S-R band absorption and at the head of the Hartley absorption band of O₃, is particularly important for photolysis of N₂O, CFC₁₃ (CFC-11) and CF₂Cl₂ (CFC-12). Penetration of solar ultraviolet radiation for the spectral interval 175 to 240 nm is confined largely to a window centered at about 200 nm, as indicated in Figure 3. The influence of the S-R bands for wavelengths below 205 nm is evident in Figure 3, even with the moderately coarse resolution (1 nm) employed here. The importance of penetration in narrow spectral windows between individual S-R band absorption lines is more evident at higher resolution. Transmission calculated for a resolution of 0.002 nm is shown in Figure 4. Significant penetration is confined to spectral windows with widths typically as small as 0.2 nm. Transmission to lower altitudes is determined by: the cross section from absorption by O₂ in the wings of S-R absorption lines; the magnitude of the cross section for the underlying Herzberg continuum; and the contribution from the head of the Hartley band of O₃.

Cross sections for absorption of radiation by N₂O, CFC₁₃, and CF₂Cl₂ vary slowly with wavelength compared with the extreme variability indicated for the S-R bands of O₂. As discussed in the appendix, photolysis frequencies can be evaluated to an accuracy of better than 10% using band transmittances. We choose, for present purposes, to use the line-by-line approach, accounting explicitly for the variation of temperature with altitude. We are able in this manner to minimize unnecessary numerical errors associated with evaluation of photolysis frequencies and lifetimes for the gases of interest here.

Cross sections for photodissociation of N₂O, CFC₁₃, and CF₂Cl₂ were taken from DeMore et al. [1990]. Solar irradiances were specified according to measurements obtained by the Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) [VanHoosier et al., 1988], on board Spacelab 2 in 1985. Values for the solar irradiance in the SUSIM data set are quoted at 0.05-nm spectral intervals with a stated photometric error of 5% [VanHoosier et al., 1988]. The SUSIM measurements indicate values for the solar irradiance that are about 15% larger than the WMO [1986] recommendations in the spectral region of the S-R bands, and about 3% higher in the Herzberg continuum [Nicolet and Kennes, 1988]. Altitude, latitude, and seasonal distributions of N₂O, CFC₁₃, and CF₂Cl₂ were constructed using a combination of satellite and in situ data. Examples of profiles adopted for this purpose are illustrated in Figures 5, 6, and 7. Most of the measurements used to develop these climatologies were taken in the late 1970s and early 1980s. Concentrations of CFC₁₃ and CF₂Cl₂ were scaled to represent conditions in 1980. Lifetimes and loss rates presented below are therefore appropriate for 1980.

Model profiles for N₂O were constrained to agree with balloon and aircraft measurements below about 35 km [Goldan et al., 1980, 1981; Farmer et al., 1980; Fabian et al., 1981; Vedder et al., 1981; Gallagher et al., 1983; Gunson et al., 1990], as indicated in Figures 5a and 5b. In the absence of in situ data, we used satellite observations from the Stratospheric and Mesospheric Sounder
Fig. 5a. Vertical profiles of N₂O for the tropics, equinox. Circle denote balloon-borne measurements at 9°N and 5°S [Goldan et al., 1980, 1981]; squares represent aircraft measurements between 1.6°S and 9.9°N [Vedder et al., 1981]. The dashed curve refers to the average of SAMS satellite measurements at 5°N, equinox, between 1979 and 1981. The dotted curve indicates the vertical profile used here to estimate the lifetime of N₂O.

Fig. 5b. Vertical profiles of N₂O for mid-latitudes, equinox. Balloon-borne measurements at 41°N [Goldan et al., 1980, 1981] and 45°N [Gallagher et al., 1983] are denoted by circles and triangles, respectively. The dashed curve refers to the average of SAMS satellite measurements at 45°N, equinox, between 1979 and 1981. The dotted curve indicates the vertical profile used in this study for 45°N, equinox.

Fig. 6a. Vertical profiles for CFC-11, tropics. Balloon-borne measurements at 9°N and 5°S [Goldan et al., 1980, 1981] and 9°N [Gallagher et al., 1983] are denoted by circles and triangles, respectively; squares represent aircraft measurements between 1.6°S and 9.9°N [Vedder et al., 1981]. Observations have been scaled to values appropriate for 1980 by assuming a growth rate (independent of height) of 5.7% yr⁻¹. The solid curve refers to the vertical profile used in this study.

Fig. 6b. Vertical profiles for CFC-11, mid-latitudes. Same as Fig. 6a, except for a latitude of 45°N. Circles denote balloon-borne measurements at 41°N [Goldan et al., 1980, 1981].

emphasized the balloon and aircraft data below altitudes of 25 to 30 km, with a smooth merge to SAMS observations above 35 km. As will be seen later, the global loss of N₂O occurs mainly at latitudes equatorward of 30°. Discrepancies between balloon and satellite data at higher latitudes are not expected to introduce significant error in our estimates for the global lifetime of N₂O. Climatological distributions formulated for CFC-11 and CF₂Cl₂ were developed based on a combination of balloon and aircraft measurements by Heidt et al. [1975], Goldan et al. [1980], Fabian et al. [1981], Vedder et al.
The variation of photolysis rates with wavelength for \( N_2O \), CFC13, and CF2Cl2 is shown in Figures 8, 9, and 10, respectively. Photolysis rates for \( N_2O \) are largest at wavelengths between 195 and 205 nm over an altitude range of 25 to 35 km. There are significant contributions to the photolysis rate associated with windows in the S-R band spectrum between 188 and 195 nm. Photolysis of CFC13 is important over approximately the same wavelength range as for \( N_2O \), but the peak is shifted to lower altitudes by about 8 km. Photolysis of CF2Cl2 emphasizes shorter wavelengths than \( N_2O \), but occurs in roughly the same altitude regime.

Photolysis represents the most important loss process for \( N_2O \), CFC13, and CF2Cl2 [World Meteorological Organization, 1982]. Additional loss of \( N_2O \) arises as a consequence of reaction with \( O(1D) \),

\[
\begin{align*}
N_2O + O(1D) & \rightarrow NO + NO \quad (1) \\
N_2O + O(1D) & \rightarrow N_2 + O_2 \quad (2)
\end{align*}
\]

Reaction (1) provides, in addition, the dominant source of nitrogen radicals (NO\(_y\) = NO + NO\(_2\) + NO\(_3\) +...
Absorption of solar radiation by \( \text{O}_2 \) is calculated by the absorption cross section \( \sigma_i(\lambda) \) for species \( i \) at wavelength \( \lambda \). The photodissociation frequency, or \( J \) value, for species \( i \) is given by

\[
J_i(z) = \int I(\lambda, z, \chi) \sigma_i(\lambda) d\lambda
\]

where \( I(\lambda, z, \chi) \) is the solar irradiance at wavelength \( \lambda \), altitude \( z \), and solar zenith angle \( \chi \); \( \sigma_i(\lambda) \) is the absorption cross section for species \( i \); the integral is extended over the relevant wavelength range \( \Delta \lambda \). The diurnally averaged \( J \) value was obtained by integrating equation (3) over a range of solar zenith angles appropriate for each latitude and season. Height, latitudinal, and seasonal profiles for pressure, temperature, and \( \text{O}_3 \) were taken from Anderson et al. [1986]. Concentrations of \( \text{O}(^1\text{D}) \) were evaluated using the Harvard photochemical model [Logan et al., 1978], updated to account for recent information on reaction rates [DeMore et al., 1990].

Meridional cross sections of the loss fields for \( \text{N}_2\text{O} \), CFC-11, and CFC-12 at equinox are displayed in Figures 11, 12, and 13. The general pattern of loss for \( \text{N}_2\text{O} \) depicted in Figure 11 is consistent with the studies by Johnston et al. [1979], Crutzen and Schmailzl [1983], and Ko et al. [1991]. As expected on the basis of the results presented in Figures 8-10, loss rates for \( \text{N}_2\text{O} \) and CFC-12 are largest in the 25- to 35-km altitude range (the contribution to the loss rate of \( \text{N}_2\text{O} \) due to reaction with \( \text{O}(^1\text{D}) \) accounts typically for about 10% of the total loss). The maximum in the loss rate for CFC-12 occurs at somewhat lower altitudes, approximately 23 km. For all three constituents, the bulk of the removal is confined to the tropics.
pictures, reflecting larger values for rates of photolysis in this region and, for any given pressure level, higher mixing ratios resulting from upward transport from the troposphere.

The total loss rate, \( L_{\text{NH}}(1980) \) for species "i" in the northern hemisphere in 1980 was obtained by integrating the local loss over latitude (with a resolution of 10° in the tropics, expanding to 15° at higher latitudes) and altitude (from the surface to 80 km), summing contributions for individual seasons (summer, equinox, and winter):

\[
L_{\text{NH}}(1980) = \int dt \int dz \int n_i(\phi, z, t) F_i(\phi, z, t) \cos \phi \, d\phi
\]

where \( n_i(\phi, z, t) \) denotes the concentration (cm\(^{-3}\)) of species "i" at latitude \( \phi \), altitude \( z \), and time \( t \), and \( F_i(\phi, z, t) \) defines the corresponding value of the loss frequency (per second). For species removed solely by photolysis (CFC\(_3\) and CF\(_2\)Cl), \( F_i \) is given by the photolysis frequency defined above:

\[
F_i(\phi, z, t) = J_i(\phi, z, t)
\]

The loss frequency for N\(_2\)O includes a contribution due to reactions (1) and (2) [DeMore et al., 1990]. Global loss rates were calculated assuming equal contributions from the two hemispheres. Errors introduced by this assumption are expected to be small since, as noted above, most of the loss occurs in the lower stratosphere in the tropics where interhemispheric gradients of concentrations are relatively small. Loss rates for N\(_2\)O, CFC\(_3\), and CF\(_2\)Cl are summarized in Table 1.

Global emissions for 1980, obtained by summing values for the annual loss and for the increase in inventory of individual gases, are listed also in Table 1. The increase in inventory for N\(_2\)O during 1980 was estimated based on the observed trend of about 0.2% yr\(^{-1}\) [Weiss, 1981], and implies a source for N\(_2\)O of 1.52 \times 10\(^{12}\) kg N yr\(^{-1}\). The preindustrial abundance of N\(_2\)O was about 5% less than the 1980 value (285 ppb compared with 300 ppb) [Khalil and Rasmussen, 1988]. By scaling the removal rate for N\(_2\)O given in Table 1, we estimate a steady state source for the preindustrial atmosphere of about 1.16 \times 10\(^{12}\) kg N yr\(^{-1}\). Global production of N\(_2\)O appears to have risen by 31% over the past few hundred years. The increase is usually attributed to diverse forms of agricultural activity [McElroy, 1976] but is not well understood.

Increases observed in inventories of CFC\(_3\) and CF\(_2\)Cl in the atmosphere during 1980, 5.7% yr\(^{-1}\) and 6.0% yr\(^{-1}\) [Cunnold et al., 1983a, b], provide the dominant contribution to the global emissions estimated in Table 1. The implied sources for CFC\(_3\) and CF\(_2\)Cl, 2.47 \times 10\(^8\) and 2.41 \times 10\(^8\) kg Cl yr\(^{-1}\), are larger than values quoted by industry for 1980, 2.04 \times 10\(^8\) kg Cl yr\(^{-1}\) for CFC\(_3\) and 2.29 \times 10\(^8\) kg Cl yr\(^{-1}\) for CF\(_2\)Cl [Chemical Manufacturers Association, 1982]. Global emissions estimated by the Chemical Manufacturers Association (CMA) for 1980 include approximate contributions from the former U.S.S.R. and Eastern Europe, amounting to 5% of the total for CFC\(_3\) and 15% for CF\(_2\)Cl. It seems unlikely that the uncertainty associated with this contribution for CFC\(_3\) could account for the disagreement with the value reported here; calculated emissions exceed the CMA estimate by 21%. This discrepancy is, however, consistent with recent simulations using a chemical tracer model (CTM) [Kao et al., 1992]. When initialized with CMA estimates of global emissions for the period 1979 to 1982, the CTM indicated trends in CF\(_2\)Cl approximately 20% lower than observed over the same period.

The instantaneous lifetime of species "i" for 1980, \( \tau_i(1980) \), may be defined as the ratio of its atmospheric inventory to the global removal rate:

\[
\tau_i(1980) = \frac{d \int n_i(\phi, z, 1980) \cos \phi \, d\phi}{2L_{\text{NH}}(1980)}
\]

where the integral over latitude is extended to include both hemispheres. As indicated in Table 1, the instantaneous lifetimes for N\(_2\)O, CFC\(_3\), and CF\(_2\)Cl are calculated to be 123, 44, and 116 years, respectively. The largest contribution to the uncertainty in lifetimes calculated here originates from the climatologies used to describe the distributions of these gases. We estimate uncertainties in the concentrations at latitudes and altitudes where the removal rate is maximum to be 15% for N\(_2\)O, and 20% for CFC\(_3\) and CF\(_2\)Cl. Accounting for uncertainties in the solar flux (5% [VanHoosier et al., 1988]), the absorption cross section for O\(_2\) (15% in the S-R bands [Mischwanner et al., 1992], 10% in the Herzberg continuum [Nicolet and Kennes, 1988]), and the absorption cross section of each gas (20%, 10%, and 10% for N\(_2\)O, CFC\(_3\), and CF\(_2\)Cl, respectively [DeMore et al., 1990]), we estimate associated uncertainties in loss rates and lifetimes to be 25 to 30%.

### Table 1. Summary of Global Loss Rates and Atmospheric Lifetimes for N\(_2\)O, CFC\(_3\), and CF\(_2\)Cl

<table>
<thead>
<tr>
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<th>Inventory (1980)</th>
<th>Annual Removal Rate (1980)</th>
<th>Instantaneous Lifetime, years</th>
<th>Annual Increase in Inventory</th>
<th>Implied Global Source</th>
</tr>
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<tbody>
<tr>
<td>N(_2)O</td>
<td>1.50 \times 10(^{12}) kg N</td>
<td>1.22 \times 10(^{10}) kg N yr(^{-1})</td>
<td>123</td>
<td>3.00 \times 10(^{8}) kg N</td>
<td>1.52 \times 10(^{10}) kg N yr(^{-1})</td>
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<tr>
<td>CFC(_3)</td>
<td>3.07 \times 10(^{8}) kg Cl</td>
<td>7.21 \times 10(^7) kg Cl yr(^{-1})</td>
<td>44</td>
<td>1.75 \times 10(^8) kg Cl</td>
<td>2.47 \times 10(^8) kg Cl yr(^{-1})</td>
</tr>
<tr>
<td>CF(_2)Cl</td>
<td>3.51 \times 10(^8) kg Cl</td>
<td>3.04 \times 10(^7) kg Cl yr(^{-1})</td>
<td>116</td>
<td>2.11 \times 10(^8) kg Cl</td>
<td>2.41 \times 10(^8) kg Cl yr(^{-1})</td>
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</tbody>
</table>
For gases whose concentrations are changing significantly with time, values for instantaneous lifetimes differ from lifetimes in steady state due largely to temporal changes in abundances for the troposphere relative to the stratosphere. Net input to the atmosphere exceeds contemporary loss for $N_2O$, $CFC_13$, and $CF_2Cl_2$. We expect in this case that the instantaneous lifetime should be somewhat longer than the lifetime in steady state; stratospheric abundances lag behind tropospheric levels reflecting the relatively sluggish rate at which air is exchanged between the troposphere and stratosphere [Schmidt and Khedim, 1991]. The distinction between instantaneous and steady state lifetimes is trivial for $N_2O$; increases of 0.2% yr$^{-1}$ in tropospheric concentrations have a negligible influence on the relative abundance between the stratosphere and troposphere [Ko and Sze, 1991; Russell et al., 1988; Rinsland et al., 1989; Gunson et al., 1990; Zander et al., 1990]. Earlier analyses comparing concentrations of $O_3$ observed by ATMOS with values calculated using constraints imposed by ATMOS measurements of radical and source gases concluded that loss of $O_3$ exceeds production over most of the upper stratosphere in both hemispheres [Melnikov and Salawitch, 1989b; Natarajan and Callis, 1989; Allen and Delitsky, 1991]. Our approach here is to use the treatment for $O_3$ photolysis described above to define the pattern of the missing source of odd oxygen implied by the ATMOS observations for altitudes between 30 and 60 km: abundances of $O$ and $O_3$ are controlled mainly by photochemical processes in this region. The missing source of $O_3$ is shown to be consistent with the pattern expected from photodissociation of vibrationally excited $O_2$ [Slanger et al., 1988; Toumi et al., 1991].

Data from ATMOS were used to specify vertical profiles for $O_3$, $NO_x$, $Cl$ ($HCl + ClONO_2 + ClO + HOCl + Cl_2 + Cl + 2\times Cl_2O_2$), $H_2O$, $CH_4$, and temperature. Profiles for individual species within the $NO_y$, $Cl_y$, and $HO_x$ (H + OH + HO$_2$ + 2$\times$H$_2$O$_2$) families of gases were obtained by solving the appropriate set of coupled time-dependent equations [Logan et al., 1978; Praher et al., 1984], using reaction rates and cross sections from DeMore et al. [1990]. Transmission of solar radiation and rates for photolysis of $O_3$ were calculated based on the procedure outlined in the appendix. Profiles for $NO_x$ were constrained using ATMOS observations of $NO$, $NO_2$, $CINO_3$, $HNO_3$, and $N_2O_5$ for altitudes below 53.5 km (where data for $CINO_3$, $HNO_3$, or $N_2O_5$ are unavailable from ATMOS, model values for the concentrations of these gases were combined with ATMOS measurements to estimate $NO_x$; adjustments to $NO_x$ from model values never exceeded 10%). The $NO_x$ profile was assumed to be independent of height for altitudes above 53.5 km. Profiles for $Cl_y$ were obtained by combining ATMOS measurements of $HCl$ and $CINO_3$ with model values for the concentrations of $CINO_3$ and $HOCl$ for altitudes below 55 km; at higher altitudes, the mixing ratio of $Cl_y$ was assumed to be constant, equal to the value inferred for 55 km. The value of $Cl_y$ calculated in this fashion was not allowed to exceed 2.8 ppb, the maximum value for 1985 based on measurements of halogenated source gases [WMO, 1986]. Species of the $HO_x$ family were assumed to be in photochemical steady state, and concentrations were calculated using ATMOS measurements of $H_2O$ and $CH_4$ combined with profiles of $O(1D)$ inferred from measurements of $O_3$. Since loss of $O_3$ is dominated by processes involving hydrogen radicals at altitudes greater than 50 km, where ATMOS measurements of $H_2O$, $CH_4$, and $O_3$ are available to allow calculation of the key $HO_x$ species, assumptions concerning $NO_x$ and $Cl_y$ for this region are not critical.

Model results and ATMOS observations for individual $Cl_y$ species at 30øN and 47øS, respectively, are compared in Figures 14a and 14b. The ATMOS data shown for $ClO$ at 30øN represent upper limits. Model results shown

4. PRODUCTION AND LOSS OF ODD OXYGEN

Observations from the ATMOS experiment [Farmer et al., 1987] provide a unique test of the reliability of models for the chemistry of the mid-latitude stratosphere. Simultaneous measurements of profiles for $O_3$, $NO$, $NO_2$, $N_2O_5$, $HNO_3$, $HNO_4$, $CINO_3$, $HCl$, $H_2O$ and $CH_4$ were obtained from April 29 to May 6, 1985 for sunrise at 47øS, and for sunset at 30øN [Raper et al., 1987; Russell et al., 1988; Rinsland et al., 1989; Gunson et al., 1990; Zander et al., 1990]. Earlier analyses comparing concentrations of $O_3$ observed by ATMOS with values calculated using constraints imposed by ATMOS measurements of radical and source gases concluded that loss of $O_3$ exceeds production over most of the upper stratosphere in both hemispheres [McElroy and Salawitch, 1989b; Natarajan and Callis, 1989; Allen and Delitsky, 1991]. Our approach here is to use the treatment for $O_3$ photolysis described above to define the pattern of the missing source of odd oxygen implied by the ATMOS observations for altitudes between 30 and 60 km: abundances of $O$ and $O_3$ are controlled mainly by photochemical processes in this region. The missing source of $O_3$ is shown to be consistent with the pattern expected from photodissociation of vibrationally excited $O_2$ [Slanger et al., 1988; Toumi et al., 1991].

Data from ATMOS were used to specify vertical profiles for $O_3$, $NO_x$, $Cl$ ($HCl + ClONO_2 + ClO + HOCl + Cl_2 + Cl + 2\times Cl_2O_2$), $H_2O$, $CH_4$, and temperature. Profiles for individual species within the $NO_y$, $Cl_y$, and $HO_x$ (H + OH + HO$_2$ + 2$\times$H$_2$O$_2$) families of gases were obtained by solving the appropriate set of coupled time-dependent equations [Logan et al., 1978; Praher et al., 1984], using reaction rates and cross sections from DeMore et al. [1990]. Transmission of solar radiation and rates for photolysis of $O_3$ were calculated based on the procedure outlined in the appendix. Profiles for $NO_x$ were constrained using ATMOS observations of $NO$, $NO_2$, $CINO_3$, $HNO_3$, and $N_2O_5$ for altitudes below 53.5 km (where data for $CINO_3$, $HNO_3$, or $N_2O_5$ are unavailable from ATMOS, model values for the concentrations of these gases were combined with ATMOS measurements to estimate $NO_x$; adjustments to $NO_x$ from model values never exceeded 10%). The $NO_x$ profile was assumed to be independent of height for altitudes above 53.5 km. Profiles for $Cl_y$ were obtained by combining ATMOS measurements of $HCl$ and $CINO_3$ with model values for the concentrations of $CINO_3$ and $HOCl$ for altitudes below 55 km; at higher altitudes, the mixing ratio of $Cl_y$ was assumed to be constant, equal to the value inferred for 55 km. The value of $Cl_y$ calculated in this fashion was not allowed to exceed 2.8 ppb, the maximum value for 1985 based on measurements of halogenated source gases [WMO, 1986]. Species of the $HO_x$ family were assumed to be in photochemical steady state, and concentrations were calculated using ATMOS measurements of $H_2O$ and $CH_4$ combined with profiles of $O(1D)$ inferred from measurements of $O_3$. Since loss of $O_3$ is dominated by processes involving hydrogen radicals at altitudes greater than 50 km, where ATMOS measurements of $H_2O$, $CH_4$, and $O_3$ are available to allow calculation of the key $HO_x$ species, assumptions concerning $NO_x$ and $Cl_y$ for this region are not critical.

Model results and ATMOS observations for individual $Cl_y$ species at 30øN and 47øS, respectively, are compared in Figures 14a and 14b. The ATMOS data shown for $ClO$ at 30øN represent upper limits. Model results shown
here assume a path for reaction of CIO with OH resulting in production of HCl,

$$\text{CIO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2 \quad (8)$$

with the branching ratio taken equal to 0.05, consistent with the upper limit (0.14) quoted by DeMore et al. [1990]. Calculations ignoring this path result in discrepancies for the CINO$_3$ to HCl ratio larger than uncertainties permitted by the observations, as illustrated in Figure 15a and 15b, a point emphasized also by Natarajan and Callis [1991]. The possible importance of (8) was discussed also by McElroy and Salawitch [1989a] who argued that the inclusion of this process would result in improved agreement between calculated and observed profiles for CIO [Weinstock et al., 1981; Brune et al., 1988]. When the HCl path in (8) is included, values of CIO at 40 km are reduced by 20% and 30% for the simulations at 30°N and 47°S, respectively.

Simultaneous measurements of CIO and HCl obtained from thermal emission spectroscopy are consistent with models that allow for the HCl branch in reaction (8) [Stachnik et al., 1992]. Comparison of the observed annual
amplitude of ozone to values calculated with a two-dimensional model provides further support for the HCl branch [Chandra et al., 1993]. Calculated reductions of ozone at 40 km due to the buildup of anthropogenic fluorocarbons are 30% less for models that allow for the HCl path, with branching ratio equal to 0.14–0.15, compared to models that do not allow for HCl production by (8) [Brasseur et al., 1985; Chandra et al., 1993]. These findings underscore the need for further atmospheric and laboratory studies to define the kinetics of the processes that control the partitioning of gases within the Cl family.

Figures 16a and 16b present a comparison of results from the model with ATMOS observations for NOy species at 30°N and 47°S, respectively. Agreement between observed and calculated profiles is excellent for both simulations. The profile for CINO3 is reproduced more accurately when we allow for production of HCl in (8), particularly near 36 km for the simulation at 47°S. The model result for the ratio of NO to NO2 is larger than the measured value by about 30% for the higher altitudes at 30°N, but is nearly equal to the measured value at 47°S. Similar conclusions were reached by Allen and Delitsky [1990]. The measurement uncertainty for NO and NO2 is approximately 30%. It is unclear whether the discrepancy at 30°N indicates a deficiency in the partitioning of NO and NO2, which could reflect in particular an overestimate of the concentration of O, with potentially important implications for the budget of odd oxygen. For altitudes below 30 km, hydrolysis of N2O5 on the background sulfate aerosol alters the partitioning of the NOy species [Cadle et al., 1975] and must be included in order to account for ATMOS observations of NO2 and HNO3, especially for the southern hemisphere [Natarajan and Callis, 1991; McElroy et al., 1992].

Model concentrations for OH are in reasonable agreement with balloon-borne measurements at mid-latitudes [McElroy and Salawitch, 1989a]. Model results for HO2 and HOCI are compared with measurements obtained at 32°N during May 1988 [Chance et al., 1989; Traub et al., 1990] in Figures 17 and 18, lending further support to the validity of the model. Concentrations of OH and HO2 are unaffected by production of HCl by reaction (8), while values of HOCI are reduced by approximately 20% at 40 km altitude when this path is included.

Rates calculated for the production and removal of O, illustrating the relative importance of the dominant catalytic loss processes, are presented in Figures 19a and 19b for the simulations at 30°N and 47°S, respectively. Loss of O is dominated at low altitudes by the catalytic sequence involving oxides of nitrogen,

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2,
\]

and at high altitudes by sequences involving HOx radicals,

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \\
\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2 \\
\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \\
\text{O}_3 + \text{H} \rightarrow \text{OH} + \text{O}_2 \\
\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}.
\]

The catalytic sequence involving chlorine radicals,

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2,
\]

has its largest influence on the O3 budget near an altitude of 40 km; the direct recombination of O and O3 contributes about 10% of the total loss of O3 at all altitudes.
Photolysis of O₂ provides the only source of Oₓ included in these simulations.

The difference between the rates calculated for loss and production of Oₓ is shown in Figures 20a and 20b for the simulations at 30°N and 47°S. Production and loss of Oₓ are nearly equal at an altitude of 40 km for both simulations. Loss of Oₓ exceeds production at higher altitudes, where removal of Oₓ is dominated by processes involving HOₓ radicals. The imbalance of production and loss is larger and more sharply peaked near 50 km for the simulation at 30°N (summer) than for 47°S (winter). The challenge is to account for the pattern of the imbalance in terms of a missing source of Oₓ or a reduction in the rate of the removal processes. The behavior found here is similar to that reported by McElroy and Salawitch [1989b], Natarajan and Callis [1989], and Allen and Delitsky [1991], except for the influence of the HCl path in reaction (8), which is responsible for a reduction of 13% in the loss rate of Oₓ calculated for 47°S at 40 km.

Allen and Delitsky [1991] suggested better agreement between production and loss of Oₓ could be achieved if absorption cross sections in the Herzberg and S-R regions were increased by 40%. We estimate that the uncertainty in the photolysis rate of O₂ calculated here should not exceed 20%, attributable to uncertainties in the absorption cross sections of 10% for the Herzberg region [Nicolet and Kennes, 1988] and 15% for the S-R region [Minschwaner et al., 1992], photometric errors of 5% in solar irradiances [VanHoosier et al., 1988], and maximum errors of 10% associated with the S-R band parameterization (see appendix). Cross sections for O₂ inferred by Anderson and Hall [1986] from measurements of the transmission of solar radiation in the stratosphere verify the recent laboratory measurements of the O₂ cross sections in the Herzberg continuum [Yoshino et al., 1988], as discussed above, and would appear to exclude the adjustments suggested by Allen and Delitsky [1991]. Furthermore, a 40% increase in the absorption cross section of O₂ in both the Herzberg and S-R regions would lead to comparable increases in the production of Oₓ at all altitudes between 40 and 60 km, a pattern inconsistent with that shown in Figure 20a.

Slanger et al. [1988] suggested that photolysis of vibrationally excited O₂ in the ground electronic state X°3Σ⁻ could provide a significant source of Oₓ. They allowed for formation of vibrationally excited O₂ by photolysis of O₃ through the B(1°B²Σ) state, which predissociates leading to production of O₂(X°3Σ⁻) and O(3p). They concluded that significant population of vibrational levels with ν' greater than 15 would be required for this mechanism to provide a significant source of Oₓ.

Toumi et al. [1991] estimated that this mechanism could enhance production of Oₓ by up to 60% at altitudes near 60 km. They calculated the concentration of vibrationally excited oxygen, O₂*, in vibrational level ν' by assuming steady state between production by photolysis of ozone (for wavelengths less than 300 nm) and quenching from the level above, and loss by vibration-to-vibration exchange with O₂(ν'=0) and photolysis. With these assumptions, the concentration of O₂* is given by

\[ [O₂°]_{ν'} = \frac{0.13 \phi_{ν'} J_{o₃} [O₃] + k_{ν'-1} [O₂] [O₂]_{ν'-1}}{k_{ν'} [O₂] + J_{ν'}} \]  (13)

where 0.13 represents the quantum yield for production of O₂(X°3Σ⁻) due to photolysis of O₃ in the Hartley region, φ_{ν'} is the quantum yield for production of level ν', J_{o₃} is the photodissociation frequency for O₃ at
wavelengths less than 300 nm, $k_v$ and $k_{v+1}$ are the rate constants for quenching of levels $v$ and $v+1$, respectively, and $J_v$ is the photodissociation frequency for level $v$. Taking $\phi_v$ approximately constant with respect to altitude (as assumed by Tourni et al. [1991]) and noting that photolysis makes a minor contribution to the denominator of (13), the rate for production of $O_x$ due to photolysis of $O_2^+$ is given by

$$\text{Production of } O_x = \sum_{i=1}^{N} J_i [O_2^+]_i \text{ (14)}$$

$$\approx 0.13 J_{O3} [O_3] \sum_{i=1}^{N} \frac{J_i}{k_i} \sum_{j=1}^{N} \phi_j$$

$$\approx C J_{O3} f_{O3}$$

where $f_{O3}$ denotes the mixing ratio of $O_3$. We estimate a value for $C$ of $1.9 \times 10^{14}$ cm$^{-3}$ based on results presented by Tourni et al. [1991].

The variation with altitude of $J_{O3}$ (24-hour average), the mixing ratio of $O_3$, and their product is shown in Figures 21a and 21b for the simulations at 30°N and 47°S, respectively. The value of $J_{O3} \cdot f_{O3}$ decreases at higher...
The mixing ratio of O$_3$ and the 1 sigma estimate of the uncertainty measured by ATMOS at 30°N (circle with error bars) [Gunson et al., 1990], the diurnally averaged photolysis frequency of O$_3$ for wavelengths less than 300 nm for 30°N, May 1 (dashed curve), and the product of the ozone mixing ratio and the photolysis frequency (solid curve).

altitudes due to the drop in the mixing ratio of O$_3$, and at lower altitudes because of the decline in the photolysis rate of O$_3$. The maximum value of $J_{O_3} \cdot f_{O_3}$ occurs at 50 km, the same altitude at which the imbalance between production and loss of O$_3$ is greatest at 30°N. The value of $J_{O_3} \cdot f_{O_3}$ is less for 47°S (winter) than for 30°N (summer), consistent with lower values of the missing source of O$_3$ for this region. The source of O$_3$ from photolysis of O$_2^+$ [equation (14)] is shown by the dotted curve in Figures 20a and 20b. We consider it particularly interesting that a source of O$_x$ proportional to $J_{O_3} \cdot f_{O_3}$ can account for the general trends observed for the quite different insolation conditions in the two hemispheres.

The population of vibrationally excited states depends critically on the vibrational distribution of O$_2$ from photodissociation of ozone and on rates for collisional relaxation. Toumi et al. [1991] used values for $\phi_{v''}$ derived from a study of the photodissociation of O$_3$ at 226 nm [Kinugawa et al., 1990] for all wavelengths less than 300 nm. However, higher vibrational levels ($v'' > 15$) are less likely to be produced by photolysis of O$_3$ at longer wavelengths. Toumi [1992] presented a more detailed account of O$_2^+$ photochemistry including an approximate treatment for the wavelength dependence of $\phi_{v''}$ and allowing for two quanta vibrational transfer in the quenching of O$_2^+$. Production of O$_2$ was found to be significantly smaller than postulated earlier by Toumi et al. [1991], due primarily to the reduction in the generation of higher vibrational levels of O$_2^+$ [Toumi, 1992]. There remain significant uncertainties in several key processes, however, especially the wavelength dependence of $\phi_{v''}$ and rates for collisional relaxation. These uncertainties underscore the need for further laboratory studies to better define the photochemistry of O$_2^+$.

Our results would not exclude additional potential sources of O$_x$ that also depend on O$_2^+$. For example, a source due to reaction of O$_2^+$ with H,

$$
O_2^+ + H \rightarrow OH + O
$$

(15)
could also play a role, since this reaction is exothermic for $v'' \geq 4$. Reaction (15) could also provide a significant source of OH. Additional production of OH appears to be required in order to account for the column measurements of Burnett et al. [1988]. A careful analysis based on experimental data for rates of reaction involving O$_2^+$ is required to complete our understanding of the possible role of excited states of O$_2$ on the chemistry of odd oxygen.

5. CONCLUDING REMARKS

The quantitative description presented for absorption of radiation in the Schumann-Runge bands and Herzberg continuum of O$_2$ was shown to be consistent with both laboratory and in situ atmospheric measurements. Rates for photolysis of N$_2$O, CFC$_3$, and CF$_2$Cl$_2$ exhibit a demonstrable sensitivity to the magnitude and spectral dependence of the attenuation of solar ultraviolet by O$_2$. A high-resolution transmission model was used, in combination with height and latitudinal distributions of N$_2$O, CFC$_3$, and CF$_2$Cl$_2$, to evaluate lifetimes and to infer rates for production of these gases in 1980. Lifetimes calculated here are significantly shorter (123, 44, and 116 years for N$_2$O, CFC$_3$, and CF$_2$Cl$_2$, respectively) and source rates correspondingly higher than values obtained in previous studies. Global emissions of N$_2$O, CFC$_3$, and CF$_2$Cl$_2$ were estimated at 1.52 x 10$^{10}$ kg N yr$^{-1}$, 2.47 x 10$^{10}$ kg Cl yr$^{-1}$, and 2.41 x 10$^{10}$ kg Cl yr$^{-1}$, respectively. It appears that the contemporary source of N$_2$O is larger than the preindustrial value by about 31%. Emission rates estimated for CFC$_3$ and CF$_2$Cl$_2$ in 1980 are about 21% and 5% larger, respectively, than values estimated by industry.

The budget of stratospheric odd oxygen was reexamined using an updated treatment of data from the ATMOS experiment. The photochemical model was shown to provide good agreement with the suite of photochemically reactive species observed in this experiment both for 30°N and 47°S during northern sum-
It was necessary, in order to account for relative abundances observed for CINO3 and HCl, to invoke an additional source of HCl, attributed here to reaction of ClO and OH, equation (8). Careful analysis of rates for production and loss of odd oxygen confirmed the need for an additional source above about 40 km. This is especially important for the simulation at 30°N. The pattern of the missing source, specifically its variation with altitude and the apparent interhemispheric asymmetry, is consistent with production by photolysis of vibrationally excited O2 as discussed by Slanger et al. [1988] and Toumi et al. [1991]. More generally it was shown to be compatible with a rate for production proportional to the product of the ozone mixing ratio and the frequency for photolysis of O3 below 300 nm.

**APPENDIX: OPACITY DISTRIBUTION FUNCTIONS**

The computational expense associated with a line-by-line treatment of S-R band absorption is generally prohibitive for practical use in photochemical models. As a consequence, approximate methods have been devised to calculate O2 photodissociation rates and the transmission of solar radiation in the wavelength range 175 to 200 nm [see Simon and Brasseur, 1983, and references therein]. The Harvard photochemical model [Logan et al., 1978] utilizes opacity distribution functions (ODFs) to perform spectral integrations in wavelength intervals defined by successive S-R band heads [Fang et al., 1974]. The contribution to the photodissociation frequency from a spectral interval, \( \Delta \lambda_i \), is given by

\[
J_{O_2}(z) = \int I(\lambda) T(O_3, \lambda) \sigma(\lambda) e^{-\sigma N(\lambda)} d\lambda
\]  

(A1)

where \( \lambda \) defines wavelength, \( I(\lambda) \) the solar irradiance, \( \sigma(\lambda) \) the S-R cross section, and \( N(\lambda) \) the slant-column abundance of O2 at altitude \( z \). Absorption by O3 is taken into account using a transmission factor, \( T(O_3, \lambda) \). Equation (A1) neglects complications due to variations in temperature over the extent of the absorbing column.

We propose to replace \( I(\lambda) \) by an appropriate mean quantity, \( \bar{I} \), defined with respect to the interval \( \Delta \lambda_i \). A mean transmission factor for ozone can be similarly defined. Employing a statistical analysis of the distribution of \( \sigma(\lambda) \) within the interval \( \Delta \lambda_i \), we evaluate a probability density function \( f(\sigma) \), such that \( f(\sigma) d\sigma \) is the probability that \( \sigma \) lies between \( \sigma \) and \( \sigma + d\sigma \) within the interval \( \Delta \lambda_i \). Equation (A1) can be expressed then in the form

\[
J_{O_2}(z) = \bar{I} \Delta \lambda_i T(O_3) \int_{\sigma_{\text{min}}}^{\sigma_{\text{max}}} \sigma' e^{-\sigma N(\lambda)} f(\sigma') d\sigma'
\]  

(A2)

This can be simplified further with a change of variable from \( \sigma \) to \( g(\sigma) \), the opacity distribution function, given by

\[
g(\sigma') = \int_{\sigma}^{\sigma_{\text{max}}} f(\sigma) d\sigma
\]  

(A3)

The ODF represents a cumulative probability function; \( g(\sigma') \) is the fraction of the spectral interval occupied by cross sections less than \( \sigma' \). From equation (A3) we obtain

\[
dg = f(\sigma') d\sigma'
\]

(A4)

and equation (A2) may be rewritten in the form:

\[
J_{O_2}(z) = \bar{I} \Delta \lambda_i T(O_3) \int g(\sigma) e^{-\sigma N(\lambda)} d\sigma
\]  

(A5)

Equation (A5) involves a reordering of quadrature points into a sequence of monotonically increasing values of \( \sigma \). The economy of this approach is illustrated in Figures A1 and A2, where values of \( \sigma \) are shown as functions of \( \lambda \) and \( g \), respectively, for the 7-0 S-R band at a temperature of 250 K. The number of quadrature points required to evaluate the photodissociation rate for the 7-0 band is reduced from about 1000 using the line-by-line approach to only six in the case of the ODF method of integration.
The six subintervals represented by the histogram in Figure A2 show the integration quadrature employed in the Harvard photochemical model. The values of $o(g)$ shown in the histogram are determined by the median values within each subinterval. We tested the accuracy of this choice of quadrature and found the approach to be robust; results using a 300-point ODF quadrature differed from the six point standard by no more than 1%.

There are two sources of error in applying ODFs to study absorption of ultraviolet radiation by $O_2$: they relate to the use of mean solar irradiances and the temperature dependence of S-R band cross sections. The first is minor provided that the solar irradiance and S-R band cross sections are uncorrelated within a given spectral interval. The second can be more serious if care is not taken to select the appropriate temperature for evaluation of S-R band cross sections. The objective is to minimize errors in transmission of ultraviolet radiation as they may affect rates for photolysis. The total rate for photolysis depends on a sum of contributions from individual spectral intervals. The partial photolysis rate of $O_2$ for a spectral interval $\Delta \lambda_i$ is given by equation (A5).

For the case where the solar irradiance is independent of wavelength, it is easily shown that the contribution to the photodissociation rate is largest when the optical depth, $o_N$, is equal to 1. Therefore for each spectral interval, the temperature chosen to define the ODF corresponds to the altitude at which $o(g)N= 1$, for $g =0.5$, using the U.S. Standard Atmosphere (1976) and a solar zenith angle of 30°. Table A1 gives values for the ODFs calculated in this manner. The appropriate weighting factors, defined by the width of individual subintervals (compare Figure A2), are given at the top of each column.

Using the results in Table A1, the spectrally integrated rate for photodissociation of $O_2$ in the S-R bands at altitude $z$ is given by

![Fig. A3. Calculated photolysis frequencies for $O_2$ integrated over the spectral intervals given in Table A1, using the line-by-line model (solid lines) and the ODF formulation (dotted lines), for the atmospheric structure specified in the U.S. Standard Atmosphere (1976) and a solar zenith angle of 30°. Results are shown for altitudes of 70, 60, 50 and 40 km.](image)

![Fig. A4. Percent difference between photolysis frequencies of $O_2$ found using the ODF method as compared with line-by-line results. The solid, dashed, and dotted curves refer to differences for the photolysis frequencies of $O_2$ using the atmospheric structure of the U.S. Standard Atmosphere (1976), for solar zenith angles ($\chi$) of 0°, 30° and 60°, respectively. The circles and triangles denote differences in the photolysis frequencies of $O_2$ and CFC-11, respectively, for the tropical atmosphere [Anderson et al., 1986] and $\chi = 30°$.](image)


\[ J_{O_2}(z) = \sum_{i=1}^{15} \bar{T}_i \Delta \lambda_i T(O_2) \sum_{j=1}^{6} c_{ij} e^{-\alpha_{ij} N(z)} W_j \]  
(A6)

where \( i \) refers to the individual wavelength interval, and \( W_j \) is the weighting factor for the ODF subinterval \( j \). The mean solar irradiance at level \( z \) for a specific interval, \( i \), is given by

\[ \bar{T}_i(z) = \frac{\bar{T}_i T(O_2)}{\sum_{j=1}^{6} e^{-\alpha_{ij} N(z)} W_j} \]  
(A7)

and is used to compute photodissociation frequencies for minor constituents.

Figure A3 presents a comparison of rates for photolysis of \( O_2 \) calculated using the ODF approach with values obtained using the numerically exact line-by-line standard. Specifically, it illustrates the contribution of individual spectral intervals to the rate for photolysis of \( O_2 \) at altitudes of 40, 50, 60, and 70 km. We allowed for absorption by \( O_3 \) using cross sections from DeMore et al. [1990], with temperatures, densities, and concentrations of ozone taken from the U.S. Standard Atmosphere (1976). Solar irradiances were specified on the basis of SUSIM measurements [VanHoosier et al., 1988]. We employed the full resolution of the SUSIM data (0.15-nm band pass) for line-by-line calculations, while mean values of irradiance were evaluated for individual spectral intervals for the ODF approach. Photolysis rates obtained using the ODF formulation agree with the line-by-line calculations for individual spectral intervals to within 15%, except for isolated cases where the contribution from a particular spectral interval to the total photodissociation rate is too small to be important.

It is apparent from Figure A3 that differences between the line-by-line and ODF results are generally small for intervals where photolysis rates are largest. Errors in total photodissociation rates, presented in Figure A4 for zenith angles of 0°, 30° and 60°, are less than 10% throughout the altitude range 20 to 80 km. Nearly all of the error associated with the use of the ODFs in Table A1 may be attributed to the choice of a single temperature to characterize the S–R cross section in individual spectral intervals. For example, the wavelength interval 190.2 to 192.5 nm is important in determining \( J_{O_2} \) over the entire altitude range from 40 to 80 km (Figure A3); the choice of temperature for the cross section in this interval (265 K, ~ 54 km) represents the best compromise in minimizing systematic errors throughout the altitude range 40 to 80 km. The overall level of agreement between the line-by-line and ODF results is remarkable considering that the ODFs employ only 90 values in total for the cross section compared with almost 14,000 for the line-by-line calculation. The savings in execution time, based on our benchmark tests, is at least a factor of 100.

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