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RADIATION AND CHEMISTRY IN THE STRATOSPHERE: SENSITIVITY TO O_2 ABSORPTION CROSS SECTIONS IN THE HERZBERG CONTINUUM

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Abstract. We propose that a significant overestimate of the molecular oxygen absorption cross sections in the important spectral window from 200-220 nm is in large part responsible for the discrepancy between observed and modeled vertical profiles of some halocarbons ($CFCl_3$ in particular), as well as for the long-standing problem of simultaneously fitting N_2O, CH_4, CF_2Cl_2 and $CFCl_3$ profiles with a single eddy diffusion model. Recent measurements of the direct solar flux in the stratosphere by J.R. Herman and co-workers seem to support this idea. Replacing our current O_2 cross sections in the 200-220 nm range by values in better agreement with the results of the above group leads to a reduction in N_2O, CF_2Cl_2 and $CFCl_3$ concentrations (by factors of 0.70, 0.62 and 0.19, respectively, at 30 km), while CH_4, H_2 and CO profiles are essentially unchanged. Moreover, the predicted concentration of HNO_3 above 30 km is reduced by $\sim 50\%$, yielding better agreement with observations. The reduction in O_2 cross sections produces a 10-20% decrease in ozone above about 35 km, but a fairly large increase ($\sim 30\%$) near the peak around 20-25 km. The changes in other stratospheric species are also briefly discussed.

Introduction

The present general understanding of stratospheric chemistry and comparisons between models and observations have recently been conveniently summarized by Hudson et al. (1982), in the latest WMO summary report. One persistent problem that still remains, both in 1–D and 2–D models, is the inability to produce a satisfactory fit to the altitude distributions of all long-lived source species that diffuse upwards from the troposphere and undergo relatively simple chemistry in the stratosphere. In particular, it has been difficult to produce good simultaneous fits to N_2O, CH_4, CF_2Cl_2(FC12) and $CFCl_3$(FC11) profiles above 20 km. The calculated mixing ratios near 30 km for FC12 and FC11 are generally overestimated by a factor of about two and five or more, respectively, given a model that is in reasonable agreement with N_2O and CH_4. This general discrepancy holds for 1–D and 2–D models alike and seems to be fairly independent of latitude or season (see Hudson et al., 1982; Miller et al., 1981). Possible solutions including either transport, unknown chlorofluorocarbon sinks or inaccurate solar radiation calculations in the Schumann-Runge bands have been suggested. In this paper, we discuss in detail the most plausible solution, which involves the uncertainty in the photodissociation rate of some stratospheric molecules (such as N_2O, FC11 and FC12) due to uncertainties in molecular oxygen absorption cross sections near 200 nm. We briefly discuss the uncertainty in the O_2 cross sections and the importance of the spectral region from ~ 195 to 220 nm for the photolysis of certain stratospheric species. The sensitivity of N_2O, CH_4, FC11, FC12, HNO_3, O_3 and other trace gases to the O_2 absorption near 200 nm is then presented and available mid-latitude observations are compared to theoretical profiles from a complete one-dimensional model.

Photolysis of Stratospheric Gases in the 190-220 nm Spectral Region

Photodissociation of various molecules plays a major role in stratospheric chemistry and the solar flux provides the driving term for many chemical interactions. Nicolet (1980,1981) has published recent reviews on the subject, with some emphasis on molecular oxygen and ozone absorption; it certainly seems that the O_2 cross sections in the Herzberg continuum (200-242 nm) are uncertain by at least 25%. Moreover, the solar flux at the top of the atmosphere is not known to much better than 15% in this spectral region (see Hudson et al., 1982). However, molecules that dissociate near 200 nm, where O_2 is the main opacity source, will be more sensitive to the O_2 cross sections $\sigma_\lambda(O_2)$ than to the solar flux, since $\sigma_\lambda(O_2)$ enters as an exponential factor in the photodissociation rate (J_λ) calculations. Indeed, $\Delta J_\lambda / J_\lambda = -\Delta\tau_\lambda = -\tau_\lambda(\Delta\tau_\lambda/\tau_\lambda)$, which implies that a small percentage change in total optical depth τ_λ can lead to a larger relative change in J_λ, if τ_λ is larger than unity (below about 35 km in this case).

Figure 1 illustrates the importance of the 190-220 nm region for N_2O, HNO_3, CF_2Cl_2 and $CFCl_3$, for which J_λ peaks in the center of this spectral range; however, the total photolysis rate of HNO_3 also depends on the flux longward of 300 nm and actually peaks at ~ 310 nm below about 20 km. Rates in Figure 1 were calculated with O_2 and O_3 profiles from the *U.S. Standard Atmosphere 1976* and 24 hr diurnally-averaged transmission. The optical depths $\tau_\lambda(O_2)$ and $\tau_\lambda(O_3)$ in the 200-220 nm range are shown in Figure 2. O_2 and O_3 contribute roughly equally to the total opacity in this region, and it is clear that this model yields total τ_λ values of order 1 to 10 between 20 and 30 km. The cross sections used in the above figures are generally averaged over 5 nm bins, as are the solar flux values, taken from Mount and Rottman (1981). The O_2 cross sections above 207.5 nm follow the recommendation of the 1979 NASA Report (Hudson and Reed, 1979) and the O_3 values are from Ackerman (1971). Below 207.5 nm, effective O_2 cross sections, depending on height and zenith angle, are calculated according to the work of Allen and Frederick (1982). Above 197.5 nm, the contribution from the bands should be about 5% or less, most of the absorption being due to the continuum (Hudson and Mahle, 1972). Shardanand and Prasad Rao (1977) have obtained the latest (and smallest) measurements of O_2 cross sections in the Herzberg continuum and have described the problems associated with the laboratory experiments. The reader is referred to their work for a summary of previous measurements (some of which differ by 50% or more).

If our model cross sections (average values of 14.5, 11.5, 8.85, 7.43 and 5.75, in units of 10^{-24} cm^2, for 200, 205, 210, 215 and 220 nm, respectively) are reduced by a factor of about 0.6, we find some fairly significant changes in relevant stratospheric profiles. Some of our preliminary sensitivity tests were presented by Y. Yung at the Chemical Manufacturers Association Meeting (Steed et al., 1982). During that month, related work from the NASA/Goddard Space Flight Center became available to us, with quite timely and direct implications for the Herzberg continuum absorption of O_2. Frederick and Mentall (1982) discuss some of the direct solar flux measurements within the stratosphere (30-40 km) and conclude that the atmospheric transmission in the 200-210 nm range is larger than expected from laboratory data on O_2 and O_3 cross sections. Herman and Mentall (1982) give a more expanded analysis of the transmitted radiation from 190 to 320 nm, from which they derive some constraints on the absorption characteristics of O_2 and O_3. They find that the O_3 cross sections seem to agree within a few percent with the laboratory data, whereas the O_2 cross sections seem to have been overestimated by 30% or more by all laboratory measurements, in agreement with our own suggestion based on more indirect modeling tests of N_2O, HNO_3 and chlorofluorocarbon profiles.

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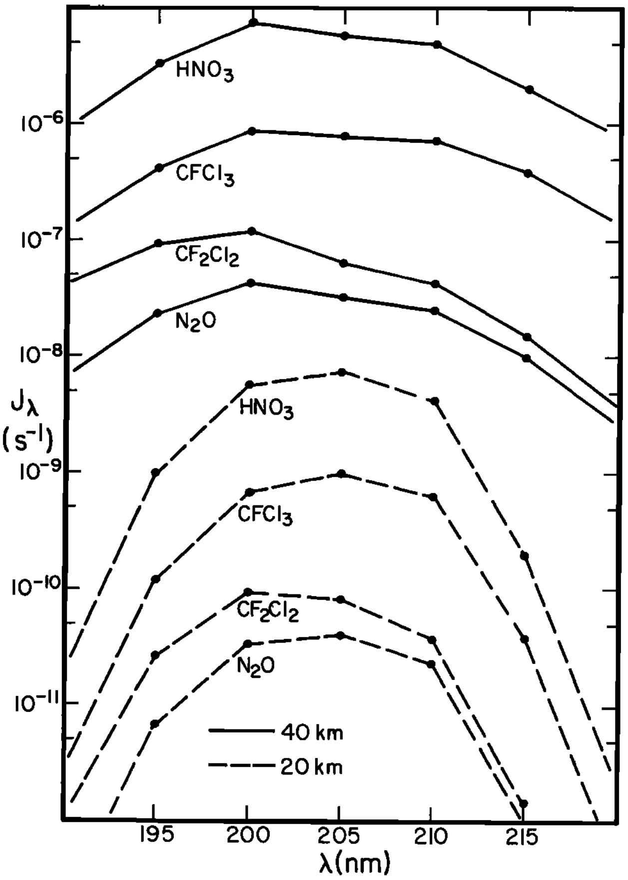

Fig. 1. Diurnally-averaged photodissociation rates (J_λ) for HNO_3, $CFCl_3$, CF_2Cl_2 and N_2O at 40 and 20 km, in the O_2—O_3 spectral window near 200 nm.

Modeling of Stratospheric Species and Sensitivity to O_2 Cross Sections

Since Herman and Mentall (1982) have recently estimated that the O_2 cross sections in the Herzberg continuum region (up to 222 nm) should be even lower (by ~30%) than the lowest laboratory values, we adopt average cross sections in agreement with their results. We use reduced values of 5.6, 5.1 and 3.5 (10^{-24} cm^2) at 210, 215 and 220 nm, respectively, keeping in mind that these values have associated error bars of 10-30%. Below 207.5 nm we multiply the effective O_2 cross sections by a factor of 0.55, down to 196.1 nm (spectral interval 5 in Allen and Frederick, 1982). This produces effective average cross sections of about 8.0×10^{-24} cm^2 (200 nm) and 6.3×10^{-24} cm^2 (205 nm) at an altitude where the O_2 absorption effect is maximized.

The 1-D Caltech photochemical model numerically solves the coupled set of continuity equations involving 47 species and over 130 reactions at 2 km intervals between 0 and 80 km. Allen et al. (1981) have described some of the model features, as applied to mesospheric trace species and transport and we have up-dated and expanded this model for stratospheric chemistry. A detailed discussion and comparison with other important species can unfortunately not be presented in this short paper, but a complete description of the model will be found elsewhere (Froidevaux, Allen and Yung, in preparation). Ground albedo and atmospheric Rayleigh scattering effects have been included and 24 hour diurnally-averaged species profiles are sufficient for the present sensitivity study. Transport is described by the standard vertical eddy-diffusion parameterization K(z), which attempts to include all averaged dynamical effects affecting long-lived trace species in the earth's atmosphere. Massie and Hunten (1981) (hereafter MH) recently published a preferred globally-averaged K(z) profile, based on a combined analysis of N_2O, CH_4, O_3 and ^{14}C (time-dependent) tracer data. The diffusion rate of N_2O, CH_4 and halocarbons from the troposphere up into the stratosphere will undoubtedly depend on K(z). FC11 responds more strongly (at a given altitude) than FC12 or N_2O to changes in either K(z) or O_2 opacity due to its faster photolysis rate and sharper fall-off in mixing ratio.

The mid-latitude models presented below are compared to N_2O, CH_4, CF_2Cl_2, $CFCl_3$ and HNO_3 observations graphically summarized in Hudson et al. (1982); the latter report describes in more detail the data base and the relevant references. Most of the observations were taken between 40°N and 50°N, during the summer, and the calculations refer to 45°N latitude and summer solstice solar illumination. Two eddy-diffusion profiles are used (see Table I). Profile K_1 is very similar to the MH composite profile, but joins smoothly with the 70 km value (1.5×10^6 cm^2 s^{-1}) of Allen et al. (1981). Profile K_2 is everywhere lower than the MH composite profile, but is in better agreement with their ^{14}C tracer-inferred profile. Clearly, there is no "ideal" profile in this oversimplified representation of transport processes, but it will be seen that the slower K_2 model will result in better fits with observations near 45°N; indeed there is strong evidence that vertical transport is latitude-dependent and increases towards the tropics. In model A, we use the standard O_2 cross sections and transport profile K_2. Model B differs from A simply by the reduction (factor of ~0.6) in O_2 cross sections described above and Model C is the same as case B, except that the K(z) profile is the faster K_1 model.

The N_2O profiles shown in Figure 3 illustrate the fact that both an increase in transport rates and an increase in O_2 cross sections can increase the mixing ratios above 20 km. Methane also shows an increase due to transport (from Model B to C), but is insensitive to the 200-220 nm spectral region and Models A and B yield similar profiles. Nevertheless, the N_2O and CH_4 observations do not provide the most sensitive test of these three models. FC11 and

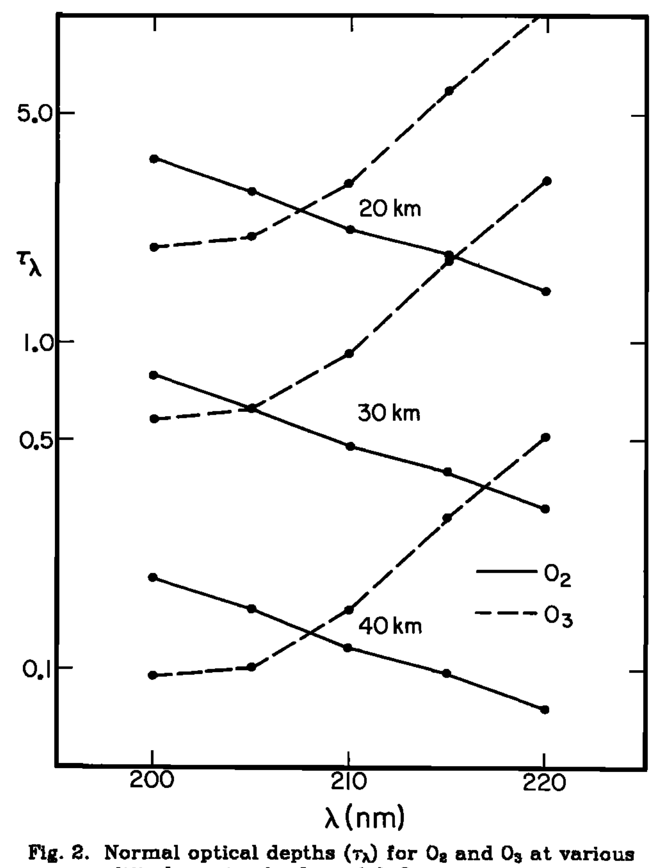

Fig. 2. Normal optical depths (τ_λ) for O_2 and O_3 at various altitudes; standard model O_2 cross sections are used (see text).

Table I. Mid-latitude Model Eddy-diffusion Coefficient K(z)*

Altitude z (km)	Model K_1	Model K_2
$z \leq 8$	As in Massie and Hunten (1981)	As in Massie and Hunten (1981)
$8 \leq z \leq 14$	As in Massie and Hunten (1981)	$K(z) = 1.0 \times 10^5 \exp\{-(z-8)/1.59\}$
$z = 16$; $z = 18$	As in Massie and Hunten (1981)	$K(z) = 2.1 \times 10^3$
$20 \leq z \leq 70$	$K(z) = 4.6 \times 10^3 \exp\{(z-20)/8.64\}$	$K(z) = 2.5 \times 10^3 \exp\{(z-20)/7.82\}$
$z \geq 70$	As in Allen et al. (1981)	As in Allen et al. (1981)

*Units are $cm^2\ s^{-1}$; only 2 significant digits are used in model values.

FC12 show larger reductions in mixing ratios in the middle and upper stratospheres, if Model B is used instead of A (see Figure 4): CF_2Cl_2 is reduced by factors of 0.62 and 0.41 at 30 and 40 km, respectively, whereas $CFCl_3$ is decreased by factors of 0.19 and 0.06 at these altitudes. A much better fit is obtained with Model B; use of the faster transport profile (Model C) increases the mixing ratios back to values similar to Model A. An additional improvement due to Model B is shown in Figure 5. Nitric acid (HNO_3) has always been in strong disagreement with observations above about 30 km. The increase in photolysis between models A and B is translated into a 50% decrease above 30 km, and much smaller changes in the lower stratosphere, where the total photolysis rate becomes insensitive to radiation in the O_2 Herzberg continuum. While some of the HNO_3 data points are in reasonable agreement with model B, there is still over a factor of two discrepancy with the data of Evans et al. (1981) at 35 km. We emphasize that the significant lower stratospheric increase in flux near 200 nm in Model B (flux higher than in Model A by a factor of 2-5) cannot be caused by a 10-20% change in the solar flux at the top of the atmosphere, since the latter uncertainty is not amplified by an exponential factor, as in the case for $\sigma(O_2)$.

Other stratospheric gases are also affected — directly or indirectly — by a reduction in O_2 cross sections. The main direct effect is an increase in the photodissociation rates of other halocarbons in the middle and upper stratosphere, due to the larger fluxes in the 200-220 nm range. CH_3Cl is destroyed mainly by reaction with OH and is therefore not affected very much by an increase in photolysis (22% decrease in concentration at 30 km); we find reasonably good agreement with the few observations of this compound presented in Hudson et al. (1982). Large reductions in [CCl_4] and [$C_2H_3Cl_3$] are found, however, as for $CFCl_3$ (factor of 0.16 at 30 km). No observations of CCl_4 exist yet, and only tentative measurements (lower limit) of $C_2H_3Cl_3$ are presented by Fabian et al. (1981); these authors find 1 pptv at 23.3 km, which is about an order of magnitude lower than in our model B. More observations of these compounds are needed.

Above 30 km, the net effect of an increase in flux near 200 nm and a (larger) decrease in $\sigma(O_2)$ is a slight (up to 20%) decrease in O_2 photolysis rate. This leads to less ozone production and, along with the slight increase in ozone photolysis, to a 10-20% reduction in [O_3] above 35 km. Our originally somewhat low [O_3] values in the upper stratosphere thus become 20-30% smaller than the lower limits in the *U.S. Standard Atmosphere 1976*, a discrepancy that we cannot explain at this time. Below 30 km, the decrease in the large total opacity leads to a significant increase in flux between 200 and 220 nm, with a net result of ~30% larger O_3 concentrations at the 20-25 km level. This change near the [O_3] peak leads to a 15% increase in total column ozone and brings our model into closer agreement with the *U.S. Standard Atmosphere 1976*. The 70% change in $\sigma(O_2)$ is more important than the 10-20% O_3 reduction above 30 km, which also leads to an increase in flux. Furthermore, the increase in O_3 below 30 km produces a decrease in flux in the lower stratosphere which counteracts the upper stratospheric O_3 reduction effect. To isolate the effect of a change in $\sigma(O_2)$, we have run a case identical to model B, but with the O_3 profile fixed as in the Model A case. We find that the largest part (80-90%) of the reductions in the trace species discussed above is due to the change in $\sigma(O_2)$, not to the subsequent change in the ozone vertical profile. Moreover, if we fix the O_3 profile as in the *U.S. Standard Atmosphere 1976*, we obtain chlorofluorocarbon concentrations close to the Model B values and actually smaller by up to 30% below 30 km. The Standard ozone concentrations are significantly higher than the model values above 35 km, but again, the chlorofluorocarbon profiles are more sensitive to the ozone profile in the lower stratosphere, where

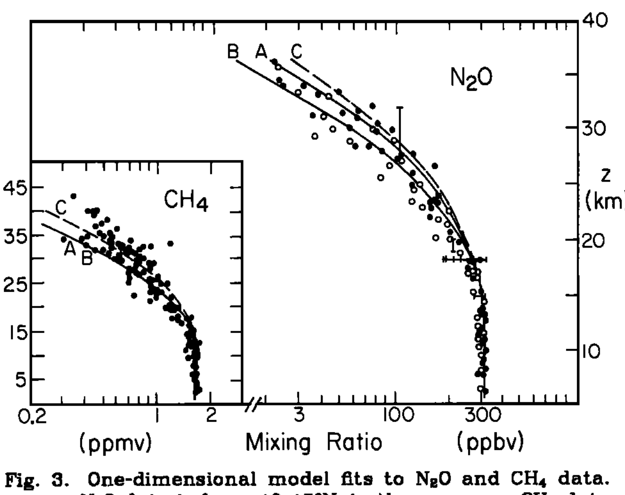

Fig. 3. One-dimensional model fits to N_2O and CH_4 data. N_2O data is from 40-45°N, in the summer. CH_4 data is from 40-60°N at various seasons (see Hudson et al., 1982). Models apply to 45°N, summer (see text for details).

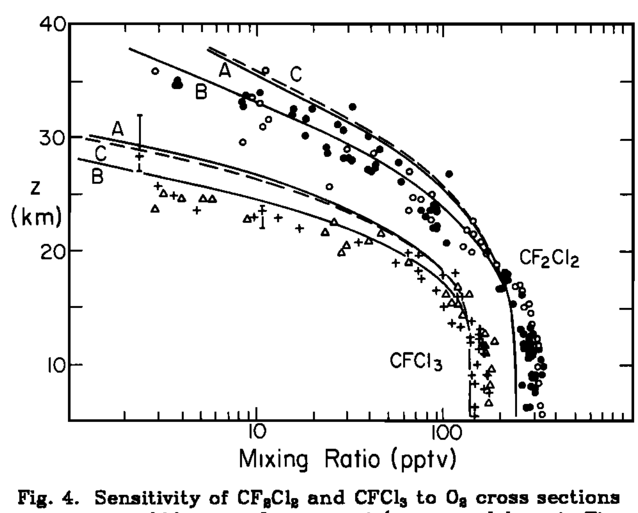

Fig. 4. Sensitivity of CF_2Cl_2 and $CFCl_3$ to O_2 cross sections near 200 nm and transport (same models as in Fig. 3). Data are from 40-45°N, in the summer (see Hudson et al., 1982).

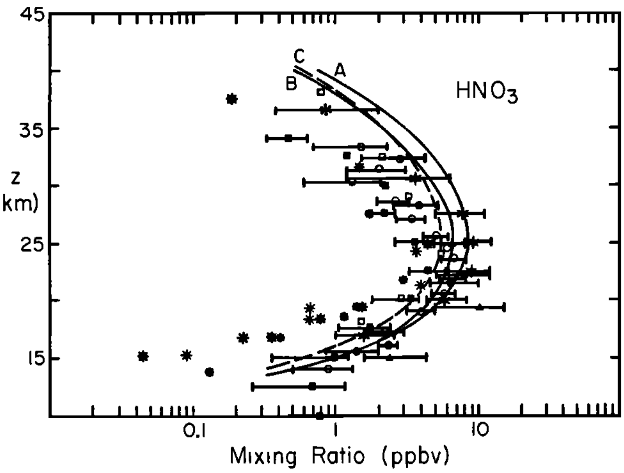

Fig. 5. Same models as for Figs. 3 and 4, but for HNO_3 at mid-latitudes. Data are reproduced from Hudson et al. (1982); see references therein.

the Standard concentrations are somewhat (up to 25%) lower than the Model B values. Uncertainties and variability in $[O_3]$ in the lower stratosphere can therefore also affect halocarbon and other species concentrations and accurate measurements of O_3 should be performed in conjunction with other observations whenever possible. In the upper stratosphere, we also find a reduction in NO_y species (NO, NO_2, NO_3, N_2O_5, HNO_2, HO_2NO_2) by 20-30%, due to the decrease in N_2O (and a small decrease in $O(^1D)$). In the 20-30 km region, the increase in $[O_3]$ and decrease in $[NO]$ lead to a significant shift in the $[ClO]/[Cl]$ and $[HO_2]/[OH]$ ratios, which are both almost linearly related to the $[O_3]/[NO]$ ratio there. $[ClO]$ increases by a factor of 2.3 and $[HO_2]$ by 1.7 at 20 km; $[H_2O_2]$ is increased by a factor of 3 at 20 km, since it depends quadratically on $[HO_2]$. HCl, Cl, and OH show little change (~ 10%) at all altitudes.

Conclusions

It is argued that a significant overestimate in the O_2 Herzberg continuum cross sections may in large part be responsible for the overestimate of model source species concentrations (N_2O, CF_2Cl_2, $CFCl_3$ and other halocarbons) in the middle and upper stratosphere. Accurate simultaneous determinations of source species profiles (as presented by Fabian, 1981) provide constraints on both transport and solar flux penetration; we find better agreement with Fabian's data if the model O_2 cross sections are reduced. Recent measurements of solar fluxes near 200 nm in the middle stratosphere have directly revealed a discrepancy between laboratory experiments and atmospheric observations. It is certainly interesting that over 17 years ago, Brewer and Wilson (1965) had measured the direct solar flux in the lower stratosphere and that these somewhat crude observations had already indicated that the O_2 cross sections were probably overestimated by at least 30% near 210 nm. The present paper demonstrates the sensitivity of many stratospheric species to the radiation field in this spectral range, a feature that should be common to 2-D models as well. Similar conclusions have been arrived at independently by the Goddard group (J.R. Herman, private communication, 1982). Accurate knowledge of the lower stratospheric O_3 profile is also important in determining the attenuated solar flux, but current uncertainties in the solar flux outside the Earth's atmosphere have a much smaller effect on model chlorofluorocarbon profiles than the uncertainties in $\sigma(O_2)$ or $[O_3]$. These results should motivate further refinement of both laboratory and solar flux measurements related to these small, but important, molecular oxygen cross sections.

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