

UC Irvine

UC Irvine Previously Published Works

Title

Photodissociation of isotopically heavy O₂ as a source of atmospheric O₃

Permalink

<https://escholarship.org/uc/item/9dj381qm>

Journal

Geophysical Research Letters, 7(4)

ISSN

0094-8276

Authors

Cicerone, RJ
McCrumb, JL

Publication Date

1980-04-01

DOI

10.1029/gl007i004p00251

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

PHOTODISSOCIATION OF ISOTOPICALLY HEAVY O_2 AS A SOURCE OF ATMOSPHERIC O_3

R. J. Cicerone and J. L. McCrumb*

 University of California, San Diego
 Scripps Institution of Oceanography
 La Jolla, California 92093

Abstract. $^{18}O^{16}O$ is the sixth most abundant gas in the atmosphere after $^{14}N^{14}N$, $^{16}O^{16}O$, Ar, $^{15}N^{14}N$ and H_2O . From available data on line positions in the Schumann-Runge (S-R) bands ($175 < \lambda < 205$ nm) of $^{18}O^{16}O$ we estimate its atmospheric photodissociation rates. In the high stratosphere and mesosphere this proposed source of O and O_3 could be significant compared to photodissociation of $^{16}O^{16}O$ although our estimates are subject to several uncertainties that are discussed. We calculate the transmission of solar radiation through the S-R bands of $^{18}O^{16}O$ and $^{16}O^{16}O$ with transmission functions averaged over individual S-R bands. Line-by-line calculations will be needed to refine our estimates but certain spectroscopic data are not yet available.

Description of the Problem

Photodissociation of O_2 is the dominant source of upper atmospheric O_3 . It is necessary to understand this source as well as possible because of the important role of O_3 in the absorption of biologically harmful ultraviolet (UV) sunlight and the potential climatic importance of atmospheric O_3 (Manabe and Strickler, 1964; Ramanathan and Dickinson, 1979). Further, UV photolysis of O_3 ($\lambda < 310$ nm) yields $O(^1D)$ which in turn generates key radicals, e.g., OH, HO_2 and NO from CH_4 , H_2O , H_2 and N_2O . These radicals along with O are central to all of atmospheric chemistry. Above 90 km altitude O_2 is photolyzed primarily by Lyman alpha (121.6 nm) and Schumann-Runge continuum ($\lambda < 175$ nm) radiation. Although the solar photon fluxes are difficult to measure at these wavelengths the photodissociation rates of O_2 are easily calculated (see e.g., Banks and Kockarts, 1973) from the solar fluxes.

In the mesosphere and stratosphere the primary sources of odd oxygen involve Schumann-Runge band ($175 < \lambda < 205$ nm) and Herzberg continuum ($205 < \lambda < 242$ nm) absorption by O_2 ; photochemical smog reactions can produce O_3 in the low stratosphere and troposphere (see e.g., Crutzen, 1973; Johnston and Whitten, 1975). The quantitative calculation of the photodissociation of atmospheric O_2 in the Schumann-Runge (S-R) bands is very difficult: transmission measurements show that Beer's Law is not followed, each of the 18 absorption bands (2-0, 3-0, . . . 19-0) consists of many rotational lines (Hudson and Carter, 1968, Ackerman et al., 1970), the absorption is temperature-dependent, pre-dissociation linewidths are not known completely (Frederick and Hudson, 1979a) and line overlapping occurs to some extent. For these reasons and for expediency, line-by-line calculations are not used when the photodissociation rate, J, is needed. Instead, a more tractable but still involved computation is made from measured absorption or transmission averaged over the separate S-R absorption bands. (See e.g., Hudson and Mahle, 1972; Park, 1974; Nicolet and Peetermans, 1980.) In this paper we extend the treatment to estimate $J(^{18}O^{16}O)$, the photodissociation rate of the second most common isotopic form of O_2 and we estimate its significance as an odd-oxygen source.

The Molecular Data

^{18}O comprises .204% of atmospheric oxygen (Nier, 1950). Thus, $^{18}O^{16}O$ is .408% of atmospheric O_2 and is well-mixed below 100 km. Spectroscopically, the non-identical nuclei of $^{18}O^{16}O$ lead to twice as many absorption lines as appear for $^{16}O^{16}O$ (Herzberg, p. 141, 1963); alternate rotational lines are absent in the S-R bands of $^{16}O^{16}O$. For various reasons including the expense and difficulty of preparing oxygen enriched in $^{18}O^{16}O$ there are few data available on line positions and intensities in the S-R bands of $^{18}O^{16}O$. Hecht et al. (1975) have measured and analyzed the S-R absorption in $^{18}O^{16}O$, $^{17}O^{16}O$, $^{18}O^{18}O$ and $^{16}O^{16}O$. Although they observed spectra from the 3-0 band to the 21-0 band they presented data on individual lines only from $v' = 5$ to 13 with $v'' = 0$, i.e., 5-0, 6-0, . . . 13-0. Their band origins for $^{16}O^{16}O$ were located within about 0.15 cm^{-1} of those of Ackerman and Biaume (1970). Individual line locations for $^{16}O^{16}O$ were similarly close. For $^{18}O^{16}O$ Hecht et al. (1975) tabulated positions of 88 lines in the 6-0, 7-0, 8-0, 9-0 and 10-0 S-R bands. We find that only 5 of these 88 lines are within $\pm 1 \text{ cm}^{-1}$ of the 520 line positions given by Ackerman and Biaume (1970) for the 2-0 through 13-0 bands of $^{16}O^{16}O$, 12 of the 88 lines of Hecht et al. are within $\pm 2 \text{ cm}^{-1}$ of any line listed by Ackerman and Biaume. Although these data are incomplete they indicate that solar radiation at wavelengths between the lines in the S-R bands of $^{16}O^{16}O$ might leak through to be absorbed by lines of $^{18}O^{16}O$ and $^{17}O^{16}O$. Even without direct overlapping of the absorption lines of $^{16}O^{16}O$ and $^{18}O^{16}O$ there is still substantial absorption by $^{16}O^{16}O$ in the wings of its lines. In the calculations described below we estimate this absorption with a band-averaged pseudo-continuum absorption cross section.

The Calculations

The goal of the calculations was to compute the photodissociation rate, J_{34} , of $^{18}O^{16}O$ from available data and to compare it with the corresponding rate, J_{32} , for $^{16}O^{16}O$ at every altitude and zenith angle. Our approach was to begin at the top of the atmosphere (120 km) where $J_{34}(\text{S-R}, 120) = 2J_{32}(\text{S-R}, 120)$ because $^{18}O^{16}O$ has twice as many absorption lines (assumed equally intense) as $^{16}O^{16}O$. The contributions of S-R continuum, Lyman alpha and Herzberg continuum radiation were neglected in calculations of J_{34} because they amount to only .004 times that for $^{16}O^{16}O$. Given $J_{34}(\text{S-R}, 120)$ we calculated $J_{34}(\lambda, \chi, z)$ from

$$J_{34}(\lambda, \chi, z) = J_{34}(\lambda, \chi, 120)T(\lambda, \chi, z) \quad (1)$$

where the cascaded transmission function

$$T(\lambda, \chi, z) = T_w T_c T_o T_{pc} T_{34} \quad (2)$$

T_w , T_c and T_o are the transmissivities of H_2O , CO_2 and O_3 , respectively, given by

$$T_k(\lambda, \chi, z) = \exp[-\sigma_k(\lambda) \sec \chi \int_z^{\infty} [k] dh] \quad (3)$$

where k represents H_2O , CO_2 or O_3 .

T_{pc} is the transmission resulting from pseudo-continuum absorption by overlapping wings of $^{16}O^{16}O$ lines in the S-R bands

*also affiliated with Max Planck Institute for Nuclear Physics, Heidelberg

$$T_{pc}(\lambda, \chi, z) = \exp\left[-\sigma_{pc} \int_z^{\infty} \sec\chi [^{16}O^{16}O] dh\right]. \quad (4)$$

In Eqn's (3) and (4) $[x]$ is the concentration (cm^{-3}) of species x at each altitude.

Frederick and Hudson (1979a) report that a cross section, σ_{pc} , of order $10^{-22} cm^2$ accounts for this pseudo-continuum absorption. It is clear, however that $\sigma_{pc} = 10^{-22} cm^2$ can apply only very far from line centers, i.e., for frequencies ν such that $(\nu - \nu_0)^2 \gg (\Delta L)^2$. Here, ν_0 is a line center position and ΔL is a line width (half width at half maximum). To estimate σ_{pc} and thus the ability of wings of $^{16}O^{16}O$ lines to attenuate solar radiation, consider the Lorentzian line-shape factor $f(\nu; \Delta L)$

$$f(\nu; \Delta L) = K\Delta L / [(\nu - \nu_0)^2 + \Delta L^2]; \quad (5)$$

If there is a rotational line of $^{16}O^{16}O$ at ν_0 with predissociation linewidth ΔL , Eqn (5) can be used to compute the ratio of the line absorption cross section at ν to that at line center, ν_0 . One can compute, for example, the value of ν at which the absorption cross section in a wing of an $^{16}O^{16}O$ line is .004 times that at line center. At this ν , the local atmospheric absorption due to a line center of $^{18}O^{16}O$ would equal the absorption in a line wing of $^{16}O^{16}O$, for $\Delta L = 1 cm^{-1}$ ($\nu - \nu_0$) would be $16 cm^{-1}$. For $f(\nu; \Delta L)$ to be .01 of its maximum value ($\nu - \nu_0$) = $10 cm^{-1}$ if $\Delta L = 1 cm^{-1}$ and ($\nu - \nu_0$) = $2 cm^{-1}$ when $\Delta L = 0.2 cm^{-1}$. In our calculations we have taken $\sigma_{pc} = 10^{-22} cm^2$ (from Frederick and Hudson, 1979a) as CASE 1 which will be seen to yield upper limit estimates of J_{34} from Eqns. (1)-(4), and for CASE 2, the values of σ_{pc} listed in Table 1. The band-averaged σ_{pc} values were calculated as follows. First, the average spacing between the rotational lines of $^{16}O^{16}O$ was found from Ackerman and Biaueme (1970) for each of their bands. Then, with ΔL values from Frederick and Hudson (1980) and peak cross sections for each band from Ackerman et al. (1970) Eqn. (5) was employed to compute the cross section at $(\nu - \nu_0) = 0.3$ times the average

Table 1

Band (n-0)	B_n/N_n (cm^{-1})	ΔL (cm^{-1})	σ_{pc} (cm^2)	J_n (sec^{-1}) at 70, 50 km
2	16	.12	7(-25)	5.3(-11), 5.3(-11)
3	18	.92	8(-23)	3.8(-11), 2.9(-11)
4	14	2.09	1(-21)	9.7(-11), 3.4(-12)
5	17	1.17	1(-21)	2.9(-10), 1.0(-11)
6	18	.56	9(-22)	9.7(-10), 4.7(-11)
7	18	.85	2(-21)	1.3(-9), 1.6(-12)
8	19	.72	3(-21)	1.9(-9), 8.0(-14)
9	19	.38	2(-21)	4.1(-9), 4.5(-12)
10	24	.21	4(-22)	8.3(-9), 1.8(-9)
11	17	.64	8(-21)	2.1(-9), 3.8(-21)
12	17	.41	4(-21)	1.1(-8), 1.1(-14)
13	16	.07	3(-22)	1.9(-8), 2.8(-9)
14	15 ?	.03	7(-23)	2.3(-8), 8.4(-9)
15	15 ?	.10	7(-22)	2.3(-8), 1.1(-9)
16	12 ?	.13	1.2(-21)	2.0(-8), 2.1(-10)
17	12 ?	.20	3(-21)	1.1(-8), 0
18	12 ?	.20	2(-21)	1.3(-8), 0
19	15 ?	.20	1(-21)	3.5(-8), 0

Table 1. B_n/N_n is the bandwidth divided by the number of lines in the n-0 band of $^{16}O^{16}O$ and is an approximate average spacing (cm^{-1}) between rotational lines in each Schumann-Runge band. For 9-0 and higher bands the spacings are between triplet centers. Predissociation linewidths, ΔL , are from Frederick and Hudson (1980), σ_{pc} values were calculated here as described in the text and J values are for overhead sun.

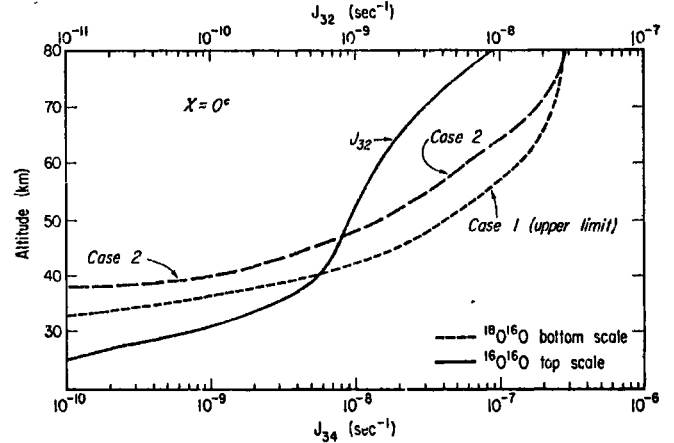


Figure 1. Calculated photodissociation rates of $^{16}O^{16}O$ (top scale) and $^{18}O^{16}O$ (bottom scale), each for overhead sun ($\chi=0$). For $^{16}O^{16}O$ contributions to J_{32} from all wavelengths ($121 < \lambda < 242 nm$) are included; in the S-R bands the transmittances of Hudson and Mahle were used. For $^{18}O^{16}O$ only the contribution of the S-R bands is shown. J_{34} was calculated from Eqn's (1)-(4) as described in the text as are the conditions of CASE 1 and CASE 2.

line spacing. This procedure should give at least a rough estimate of effective band-averaged σ_{pc} values. The only line-by-line calculations with which we can compare are for the 5-0 and 9-0 bands by Frederick and Hudson (1979b and 1980), respectively. Our σ_{pc} values (Table 1) for those bands are comparable to Frederick and Hudson's at about $5 cm^{-1}$ off line center. Thus, Eqn. (4) provided two estimates of T_{pc} : CASE 1 with $\sigma_{pc} = 10^{-22} cm^2$ and CASE 2 with σ_{pc} from Table 1.

Alternatively, one might use the $\bar{\sigma}$ values of Park (1974) which are generally but not uniformly larger than our σ_{pc} .

The final term in (2), the transmission T_{34} due to self-absorption by $^{18}O^{16}O$ was evaluated from the tabulated $^{16}O^{16}O$ transmissions, T_{32} , of Hudson and Mahle (1972) and formulas for T_{32} from Nicolet and Peetermans (1980). The transmissions, T_{32} , of Hudson and Mahle are averaged over entire S-R bands; thus a key assumption is that the S-R bands of $^{18}O^{16}O$, while containing twice as many lines as those of $^{16}O^{16}O$, occupy the same wavelength intervals. From Hecht et al. (1975) and Ackerman and Biaueme (1970) we saw that the heads of the 6-0, 7-0, 8-0, 9-0 and 10-0 S-R bands of $^{18}O^{16}O$ are shifted by -80 to -100 cm^{-1} from those of $^{16}O^{16}O$ but only two of the 88 $^{18}O^{16}O$ line positions fall at frequencies that correspond to lower ν' values in $^{16}O^{16}O$. Specifically, a $\nu' = 10$, $J = 21$ line in $^{18}O^{16}O$ appears at 54622.6 cm^{-1} in the 9-0 band of $^{16}O^{16}O$ and the $\nu' = 9$, $J = 21$ line in $^{18}O^{16}O$ spills into the 8-0 band of $^{16}O^{16}O$.

We calculated T_{34} in two ways: i) by taking $T_{34} = T_{32}(.008C)$, where $T_{32}(.008C)$ is the Hudson and Mahle transmission through a column, C , of $^{16}O^{16}O$ (at each altitude $C_{34} = .004C_{32}$ and there are twice as many absorption lines in $^{18}O^{16}O$), and ii) by taking $T_{34} = 1 - 2A_{32}$ where $A_{32} = 1 - T_{32}(.004C)$. In all the results that follow the T_{34} values from method ii) were used; they are smaller than the values of T_{34} from method i). Note that a more accurate calculation of T_{34} would explicitly recognize the transition from a C to a \sqrt{C} functional dependence in the curve of growth (Turco, 1975). Our method ii) does this implicitly. Our calculations with Eqn's (1)-(4) thus used 18 values of λ (the intervals of the 2-0, 3-0, . . . 19-0 S-R bands), altitude intervals of 2 km and solar fluxes from Samain and Simon (1976). O_2 and O_3 concentrations were taken from standard model atmospheres while for H_2O and CO_2 constant mixing ratios of $5 \cdot 10^{-6}$ and $3.25 \cdot 10^{-4}$ were assumed. Before presenting results we should mention that we are neglecting the $\nu'' = 1$ bands of $^{16}O^{16}O$ which appear in the windows

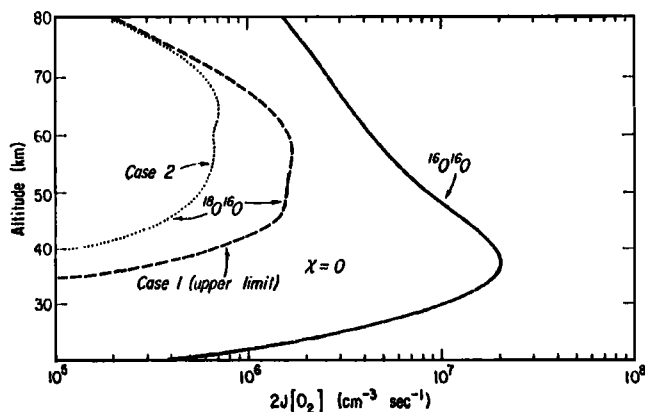


Figure 2. Odd-oxygen production rates, $2J_{34}[^{18}\text{O}^{16}\text{O}]$ and $2J_{32}[^{16}\text{O}^{16}\text{O}]$, as a function of altitude for overhead sun. CASE 1 and CASE 2 are described in the text. A separate contribution from $^{17}\text{O}^{16}\text{O}$ should also be considered.

between lines in the $v'' = 0$ bands of $^{16}\text{O}^{16}\text{O}$ at temperatures near 300° K (Hudson and Carter, 1968); our assumption is justified at mesospheric temperatures but might not be near the stratopause ($T = 250^\circ\text{K}$). Further, the actual underlying continuum absorption ($\sigma \approx 10^{-23}\text{cm}^2$) in the S-R bands deduced by Hudson and Mahle (1972) has been neglected by comparison with σ_{pc} .

Results and Discussion

Figure 1 shows computed photodissociation rates for $^{18}\text{O}^{16}\text{O}$ vs. altitude for overhead sun. Only the S-R band contribution to J_{34} is presented while for J_{32} the contributions from the S-R bands, Lyman alpha, and the S-R and Herzberg continua are presented although only the S-R bands and Herzberg continuum contribute significantly to J_{32} below 65 km. For CASE 1 the ratio J_{34}/J_{32} reaches a maximum of 100 at 65 km and decreases to 10 at 40 km. For CASE 2 J_{34}/J_{32} maximizes at 69 km where it is 57, while at 40 km $J_{34}/J_{32} = 1.6$. The CASE 1 results ($\sigma_{pc} = 10^{-22}\text{cm}^2$ in Eqn (4) would imply that photodissociation of $^{18}\text{O}^{16}\text{O}$ contributes at least 10% as much odd oxygen as does photodissociation of $^{16}\text{O}^{16}\text{O}$ everywhere above 45 km and below 85 km (S-R continuum and Lyman- α cause a rapid increase in J_{32} above 80 km) but CASE 1 surely is a generous upper limit estimate of the $^{18}\text{O}^{16}\text{O}$ effect based on available data. In CASE 2 (σ_{pc} from Table 1) the $^{18}\text{O}^{16}\text{O}$ contribution to O_3 production is over 10% only above 54 km. Figure 2 shows the overhead sun, odd-oxygen production rate, $2J_{34}[^{18}\text{O}^{16}\text{O}]$, for each of these cases and the corresponding rate, $2J_{32}[^{16}\text{O}^{16}\text{O}]$, calculated heretofore. The additional odd-oxygen production due to $^{18}\text{O}^{16}\text{O}$ is evident in the upper stratosphere and mesosphere. Specifically, for CASE 1 $2J_{34}[^{18}\text{O}^{16}\text{O}]/2J_{32}[^{16}\text{O}^{16}\text{O}] = .13, .38, .18$ and $.06$ at 80, 65, 50 and 42 km. For CASE 2 the ratio of $^{18}\text{O}^{16}\text{O}$ to $^{16}\text{O}^{16}\text{O}$ ozone production is less: $.21$ at 65 km, $.06$ at 50 km and $.013$ at 42 km. The contribution due to $^{18}\text{O}^{16}\text{O}$ would be shifted slightly to higher altitudes in a diurnal average calculation because the S-R bands contribute less relative to the Herzberg continuum.

Although the calculation method of CASE 2 is rough in that band-averaged pseudo-continuum cross sections, σ_{pc} , are used to account for absorption by wings of $^{16}\text{O}^{16}\text{O}$ lines this method is preferred over the usage of $\sigma_{pc} = 10^{-22}\text{cm}^2$ at all S-R wavelengths (CASE 1). The fact that the CASE 2 σ_{pc} in Table 1 generally exceed 10^{-22}cm^2 implies that values of J_{34} found for CASE 1 are gross upper limits. The effects of larger σ_{pc} values can be seen in Table 1 where J_{34} values for CASE 2 are shown for 70 km and 50 km for each S-R band. For almost every band $T_{pc} \leq T_{34} < T_w < T_O < T_i$ in Eqn (2) with the σ_{pc} of Table 1.

Our calculations, summarized in Figures 1 and 2 and Table 1, point to the possibility of an additional source of O_3 and O in the

atmosphere. Several topics require discussion: uncertainties in our calculations, the compatibility of our suggested source with current theory and atmospheric data and whether ^{18}O and isotopically heavy O_3 can be detected in the atmosphere. The uncertainties in our calculations are due to lack of spectral resolution in our calculations and to lack of spectroscopic data on $^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}$. Ideally, line-by-line calculations are needed to improve on our band-averaged approach. They would be of the type performed by Frederick and Hudson (1979b) for the predissociation of atmospheric NO but would require even more extensive calculations. Several thousand absorption lines of $^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}$ in the S-R bands are involved. Laboratory data on line positions, intensities and linewidths for $^{18}\text{O}^{16}\text{O}$ are very incomplete and difficult to obtain. In lieu of actual data one often turns to theoretical absorption spectra calculations of the kind reported by Julienne and Krauss (1975) and Julienne (1976). It is very doubtful that theoretical calculations can provide all the answers, as there are large quantum mechanical complications in some regimes. Frederick and Hudson (1979a) discuss, for example, interdependences of predissociation linewidth and oscillator strength and note that v' and J become inadequate quantum numbers; only total angular quantum is valid for large J. Thus, there are not adequate data for complete line-by-line calculations at this time. Limited calculations of this type could be very useful in evaluating the accuracy of our band-averaged treatment, however. For example, the $v'' = 1$ bands of $^{16}\text{O}^{16}\text{O}$ and their temperature dependence could be included.

The odd-oxygen production rates in Figure 2 are compatible with present knowledge of the stratosphere and mesosphere. Indeed it has been recognized by several workers that photochemical models predict less O_3 in the high stratosphere and mesosphere than is measured (Rundel et al., 1978). Photodissociation of $\text{O}_2(^1\Delta)$ or its reactions do not appear to be significant O_3 sources. When our O_3 source due to $^{18}\text{O}^{16}\text{O}$ is incorporated in a photochemical model the calculated O_3 increases almost linearly with the added source, $2J_{34}[^{18}\text{O}^{16}\text{O}]$. Where the reaction $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$ is important there is a slight departure from linearity. Also, although there are large uncertainties in our calculations it is doubtful that photodissociation of $^{18}\text{O}^{16}\text{O}$ could influence the lower stratosphere and troposphere. If O of molecular weight 50 were to exist there, interesting isotope effects could appear in the quantum yield of $\text{O}(^1D)$, especially near the 310 nm cut-off, with direct consequences for atmospheric radical concentrations. The possibility of detecting heavy O or O_3 in the atmosphere is limited by the rapidity of the Chapman reactions; they result in isotopic dilution.

Acknowledgements

We thank D. L. Albritton, J. E. Frederick, J. Park and R. P. Turco for useful discussions and NASA for Grant NSG 1590 and NSF for Grant ATM78-26728. Computations were performed at the National Center for Atmospheric Research.

References

- Ackerman, M., and F. Biaueme, Structure of the Schumann-Runge bands from the 0-0 to 13-0 band, *J. Molec. Spec.* 35, 73, 1970.
- Ackerman, M., F. Biaueme, and G. Kockarts, Absorption cross sections of the Schumann-Runge bands of molecular oxygen, *Planet. Space Sci.*, 18 1639, 1970.
- Banks, P., and G. Kockarts, *Aeronomy*, Part A, Academic Press, New York, 430 pp., 1973.
- Crutzen, P., A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, *Pure Appl. Geophys.*, 106-108, 1385, 1973.
- Frederick, J., and R. Hudson, Predissociation linewidths and oscillator strengths for the (2-0) to (13-0) Schumann-Runge bands of O_2 , *J. Molec. Spec.*, 74, 247, 1979a.
- Frederick, J., and R. Hudson, Predissociation of nitric oxide in

- the mesosphere and stratosphere, *J. Atmos. Sci.*, *36*, 737, 1979b.
- Frederick, H., and R. Hudson, Dissociation of molecular oxygen in the Schumann-Runge bands, submitted to *J. Atmos. Sci.*, 1980.
- Hecht, H., S. Rabideau, and R. Engelman, Isotope effects in the Schumann-Runge bands of molecular oxygen, Report No. LA-5871-MS, Los Alamos Sci. Lab., New Mexico, 10 pp., 1975.
- Herzberg, G., *Spectra of Diatomic Molecules*, 2nd Edition, Van Nostrand Co., Princeton, 658 pp., 1963.
- Hudson, R., and V. Carter, Absorption of oxygen at elevated temperatures (300 to 900 K) in the Schumann-Runge system, *J. Opt. Soc.*, *58*, 1621, 1968.
- Hudson, R., and S. Mahle, Photodissociation rates of molecular oxygen in the mesosphere and lower thermosphere, *J. Geophys. Res.*, *77*, 2902, 1972.
- Johnston, J. S., and G. Whitten, Chemical reactions in the atmosphere as studied by the method of instantaneous rates, *Int. J. Chem. Kinet.*, *7*, 1, 1975.
- Julienne, P., and M. Krauss, Predissociation of the Schumann-Runge bands of O₂, *J. Molec. Spec.*, *56*, 270, 1975.
- Julienne, P., $^3\Sigma^- - ^3\Sigma^+$ coupling in the O₂b³ Σ_u^- predissociation, *J. Molec. Spec.*, *63*, 60, 1970.
- Manabe, S., and R. Strickler, Thermal equilibrium of the atmosphere with a convective adjustment, *J. Atmos. Sci.*, *21*, 361, 1964.
- Nicolet, M., and W. Peetermans, Atmospheric absorption in the O₂ Schumann-Runge band spectral range and photodissociation rates in the stratosphere and mesosphere, *Planet. Space Sci.*, *28* in press, 1980.
- Nier, A. O., A redetermination of the relative abundances of the isotopes of carbon, nitrogen, oxygen, argon, and potassium, *Phys. Rev.*, *77*, 789, 1950.
- Park, J. H., the equivalent mean absorption cross sections for the O₂ Schumann-Runge bands: application of the H₂O and NO photodissociation rates, *J. Atmos. Sci.*, *31*, 1893, 1974.
- Ramanathan, V., and R. Dickinson, The role of stratospheric ozone in the zonal and seasonal radiative energy balance of the earth-troposphere system, *J. Atmos. Sci.*, *36*, 1084, 1979.
- Rundel, R., D. Butler, and R. Stolarski, Uncertainty propagation in a stratospheric model, 1, development of a concise stratospheric model, *J. Geophys. Res.*, *83*, 3063, 1978.
- Sarnain, D., and P. C. Simon, Solar flux determination in the spectral range 150-210 nm, *Solar Phys.*, *49*, 33, 1976.
- Turco, R. P., Photodissociation rates in the atmosphere below 100 km, *Geophys. Surveys*, *2*, 153, 1975.

(Received September 25, 1979;
accepted December 11, 1979.)