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**Authors**
Frederick, John E
Cicerone, Ralph J

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# Dissociation of Metastable $O_2$ as a Potential Source of Atmospheric Odd Oxygen

JOHN E. FREDERICK

*Atmospheric Chemistry and Dynamics Branch, NASA Goddard Space Flight Center, Greenbelt, Maryland*

RALPH J. CICERONE

*National Center for Atmospheric Research, Boulder, Colorado*

An analysis of the possible dissociation of metastable oxygen molecules subject to constraints imposed by selection rules for molecular transitions, airglow observations, and atmospheric chemistry leads to the following conclusions. Dissociation of $O_2(b^1\Sigma_g^+)$ must produce a negligible number of oxygen atoms at all altitudes in the earth's atmosphere. However, if the dissociation cross section of $O_2(a^1\Delta_g)$ has a maximum value in the range $10^{-20}$ cm² to $10^{-19}$ cm², then the process $O_2(a^1\Delta_g) + h\nu \rightarrow O_2(C^3\Delta_u) \rightarrow O(^3P) + O(^3P)$ will constitute a significant, and potentially the major, source of odd oxygen in the uppermost stratosphere and mesosphere.

## INTRODUCTION

In recent years there have been significant revisions in our quantitative knowledge of middle atmospheric odd oxygen sources. These include updated molecular parameters to describe $O_2$ absorption in the Schumann-Runge bands [*Frederick and Hudson*, 1980; *Yoshino et al.*, 1983] and greatly reduced values of the $O_2$ cross section in the Herzberg continuum [*Frederick and Mentall*, 1982; *Johnston et al.*, 1984]. A major consequence of these changes has been the wide realization that present photochemical models underestimate the observed ozone abundance in the upper stratosphere and lower mesosphere. The recent, thorough analysis of *Froidevaux et al.* [1985] clearly demonstrates that deficiencies still exist in our knowledge of the chemical mechanisms responsible for the observed high-altitude ozone abundance. In addition, the analysis of *Frederick et al.* [1984] concluded that the problem would best be removed by an increased source of odd oxygen as opposed to a reduced sink. Several potential mechanisms for increasing the atmospheric odd oxygen production rate exist. These involve reactions of excited states [*Mitchell and Zemansky*, 1971] and dissociation of molecular oxygen isotopes [*Cicerone and McCrumb*, 1980; *Blake et al.*, 1984]. However, quantitative analyses of these processes generally show that the enhanced odd oxygen production at stratospheric and mesospheric altitudes is negligible in comparison to the background source from the Herzberg continuum and Schumann-Runge bands of $O_2$.

This paper examines two potential sources of odd oxygen that have not received attention in previous atmospheric studies. These involve dissociation of the metastable $a^1\Delta_g$ and $b^1\Sigma_g^+$ states of molecular oxygen. The objectives of this work are (1) to assess the likelihood that these dissociations take place, given information from molecular physics, airglow observations, and atmospheric chemistry, and (2) to define the conditions under which these processes could be significant in comparison to dissociation of ground state $O_2$ in the Herzberg continuum and the Schumann-Runge bands. One must acknowledge the limitations of this analysis from the outset. In the absence of measurements that specify the dissociation cross sections of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$, any conclusions concerning the atmospheric importance of these processes must be considered speculative. However, by proposing and evaluating the potential of these new odd oxygen sources, this study seeks to provide the impetus for definitive theoretical and laboratory work.

## CONSIDERATIONS RELATED TO MOLECULAR PHYSICS AND THE AIRGLOW

The two processes examined here are

$$\text{(R1)} \qquad O_2(a^1\Delta_g) + h\nu \rightarrow O_2^* \rightarrow O(^3P) + O(^3P)$$

$$\text{(R2)} \qquad O_2(b^1\Sigma_g^+) + h\nu \rightarrow O_2^* \rightarrow O(^3P) + O(^3P)$$

where absorption produces the excited state $O_2^*$ at a position on its potential curve where dissociation results. Processes (R1) and (R2) are energetically possible for wavelengths less than 299.9 nm and 356.3 nm, respectively [*Herzberg*, 1950; *Krupenie*, 1972], and the identity of $O_2^*$ need not be the same in both (R1) and (R2). This section identifies the most probable states of $O_2^*$ with the requirement that they correlate with two ground state atoms. Although numerous excited molecules correlate with products such as $O(^3P) + O(^1D)$, the dissociations would require high photon energies where the available solar flux is small, thereby diminishing their atmospheric importance. A study of the potential energy diagrams of *Saxon and Liu* [1977] reveals three possibilities for $O_2^*$, being $O_2(c^1\Sigma_u^-)$, $O_2(C^3\Delta_u)$, and $O_2(A^3\Sigma_u^+)$. These excited states are closely spaced in energy, possess shallow potential wells, and have internuclear separations such that upward transitions from the lower-lying $a^1\Delta_g$ and $g^1\Sigma_g^+$ states could produce molecules with energies exceeding that required for dissociation. Figure 1 presents a highly simplified potential energy diagram for $O_2$, adapted from *Saxon and Liu* [1977], containing the states relevant to the present work.

The next consideration pertains to quantum mechanical selection rules. As pointed out by *Bates* [1982], all transitions between stable electronic states of $O_2$ that correlate with two $O(^3P)$ atoms are forbidden by one or more selection rules. However, it is critical to recognize that the term forbidden is far from absolute, and the violation of selection rules is a

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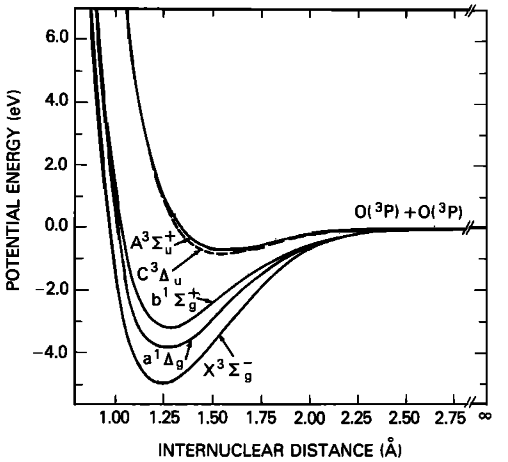

Fig. 1. Simplified potential energy diagram for the oxygen molecule showing only those states relevant to this work. Curves are from *Saxon and Liu* [1977].

common occurrence [*Garstang*, 1962]. Furthermore, a dissociation that involves a forbidden transition can still have tremendous atmospheric significance. A prime example is the Herzberg continuum dissociation of $O_2$, described by

(R3) $O_2(X^3\Sigma_g^-) + h\nu \rightarrow O_2(A^3\Sigma_u^+) \rightarrow O(^3P) + O(^3P)$

This process is strictly forbidden in Hund's coupling cases (*a*) and (*b*) by the change in parity from negative to positive [*Herzberg*, 1950]. The violation of this fairly rigorous selection rule leads to a small cross section whose peak value is slightly less than $1.0 \times 10^{-23}$ cm² [*Johnston et al.*, 1984]. On the other hand, a fully allowed transition such as the Schumann-Runge continuum absorption,

(R4) $O_2(X^3\Sigma_g^-) + h\nu \rightarrow O_2(B\ ^3\Sigma_u^-) \rightarrow O(^1D) + O(^3P)$

has a peak cross section near $1.5 \times 10^{-17}$ cm² [*Hudson*, 1971], exceeding that of the strictly forbidden process by 6 orders of magnitude.

Application of the selection rules presented by *Herzberg* [1950] shows that the most likely paths for dissociation of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ are

(R5) $O_2(a^1\Delta_g) + h\nu \rightarrow O_2(C^3\Delta_u) \rightarrow O(^3P) + O(^3P)$

(R6) $O_2(b^1\Sigma_g^+) + h\nu \rightarrow O_2(A^3\Sigma_u^+) \rightarrow O(^3P) + O(^3P)$

The change in spin multiplicity from singlet to triplet in both (R5) and (R6) violates a relatively weak selection rule. However, *Herzberg* [1950] and *Garstang* [1962] point out that conservation of electron spin is valid only to a first approximation and that this selection rule becomes less rigorous as nuclear charge increases. Hence it would be premature to dismiss (R5) and (R6) purely because of the change in spin multiplicity, although the peak cross sections for these processes would likely be substantially lower than that for a fully allowed transition (~$10^{-17}$ cm²), although still larger than is typical of a strictly forbidden process (~$10^{-23}$ cm²).

The arguments presented above demonstrate the plausibility of (R5) and (R6), but they in no way prove that these dissociations actually occur in the earth's atmosphere. Observations of the nightglow have here provided critical information. *Chamberlain* [1958] tentatively identified the transition

(R7) $O_2(C^3\Delta_u) \rightarrow O_2(a^1\Delta_g) + h\nu$

in photographic spectra of the night sky, where the observed emission covers the spectral region 370–438 nm [*Krupenie*, 1972]. The identity of this transition has since been confirmed in the laboratory by *Slanger* [1978]. These observations dem-

TABLE 1. Processes Used to Compute the Abundance of $O_2(a^1\Delta_g)$

| Process | Rate Coefficient |
|---|---|
| $O_3 + h\nu \rightarrow O(^1D) + O_2(a^1\Delta_g)$ | $J_a(O_3)$ $\lambda < 313.0$ nm* |
| $O_2(a^1\Delta_g) + N_2 \rightarrow O_2 + N_2$ | $q_a(N_2) = 3.0 \times 10^{-21}$† |
| $O_2(a^1\Delta_g) + O_2 \rightarrow O_2 + O_2$ | $q_a(O_2) = 2.0 \times 10^{-18}$† |
| $O_2(a^1\Delta_g) + CO_2 \rightarrow O_2 + CO_2$ | $q_a(CO_2) = 8.0 \times 10^{-20}$† |
| $O_2(a^1\Delta_g) \rightarrow O_2 + h\nu$ | $A(^1\Delta) = 2.58 \times 10^{-4}$† |
| $O_2(a^1\Delta_g) + h\nu \rightarrow O(^3P) + O(^3P)$ | $J(^1\Delta)$ $\lambda < 299.9$ nm* |

*Computed from cross section and solar irradiance values, units s⁻¹.

†Values from *Bates* [1982], $q_a$ in cm³ s⁻¹, $A(^1\Delta)$ in s⁻¹.

TABLE 2. Processes Used to Compute the Abundance of $O_2(b^1\Sigma_g^+)$

| Process | Rate Coefficient |
|---|---|
| $O(^1D) + O_2 \rightarrow O(^3P) + O_2(b^1\Sigma_g^+)$ | $k_b = 3.2 \times 10^{-11} e^{67/T}$* |
| $O_2 + h\nu \rightarrow O_2(b^1\Sigma_g^+)$ | $\varepsilon_b = 8.5 \times 10^{-9} e^{-\tau \sec\theta}$† |
| $O_2(b^1\Sigma_g^+) + N_2 \rightarrow O_2 + N_2$ | $q_b(N_2) = 2.1 \times 10^{-15}$‡ |
| $O_2(b^1\Sigma_g^+) + O_2 \rightarrow O_2 + O_2$ | $q_b(O_2) = 4.0 \times 10^{-17}$‡ |
| $O_2(b^1\Sigma_g^+) + CO_2 \rightarrow O_2 + CO_2$ | $q_b(CO_2) = 3.0 \times 10^{-13}$‡ |
| $O_2(b^1\Sigma_g^+) + O_3 \rightarrow O_2 + O_3$ | $q_b(O_3) = 2.2 \times 10^{-11}$‡ |
| $O_2(b^1\Sigma_g^+) \rightarrow O_2 + h\nu$ | $A(^1\Sigma) = 8.5 \times 10^{-2}$‡ |
| $O_2(b^1\Sigma_g^+) + h\nu \rightarrow O(^3P) + O(^3P)$ | $J(^1\Sigma)$ $\lambda < 356.3$ nm§ |

*Value in cm³ s⁻¹ from *Hudson* [1982].

†Computed result in s⁻¹ based on unattenuated value of *Bates* [1982]. Optical depth is $\tau = (3.1 \times 10^{-23}) \times$ (column ozone in cm⁻²); $\theta$ is the solar angle.

‡Values from *Bates* [1982], $q_b$ in cm³ s⁻¹, $A(^1\Sigma)$ in s⁻¹.

§Computed from cross section and solar irradiance values, units s⁻¹.

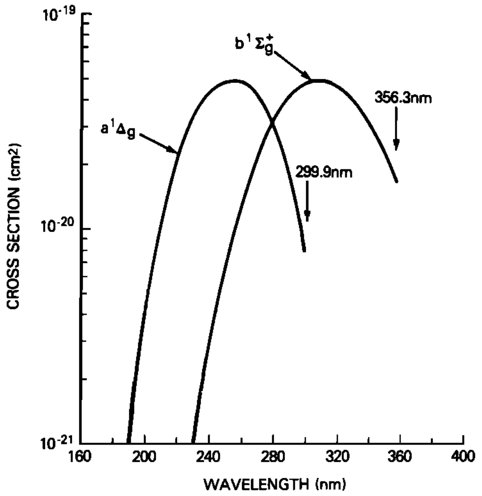

Fig. 2. Models adopted for dissociation cross sections of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$. The peak cross section assumed in the curves shown here is $5 \times 10^{-20}$ cm². Dissociation of $O_2(a^1\Delta_g)$ is energetically possible for a wavelength of 299.9 nm. The corresponding wavelength for $O_2(b^1\Sigma_g^+)$ is 356.3 nm.

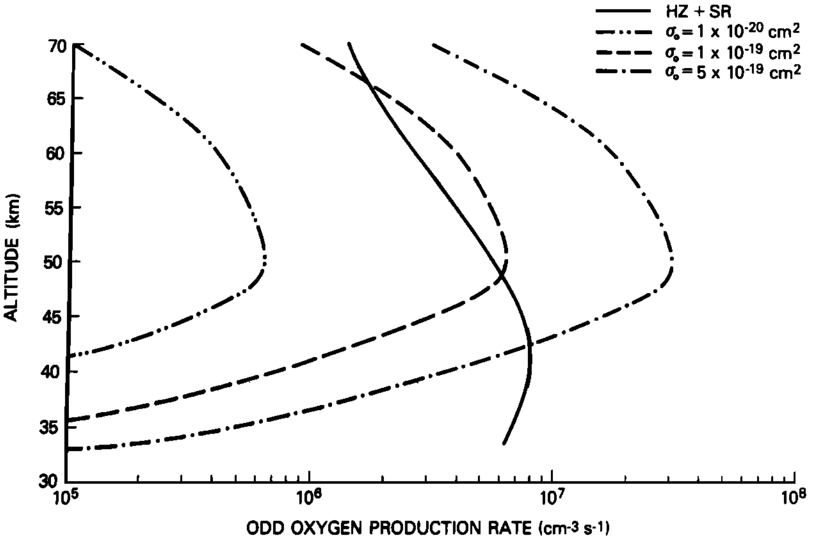

Fig. 3. Comparison of the odd oxygen production rate arising from the Herzberg continuum and Schumann-Runge bands (HZ + SR) with that predicted from $O_2(a^1\Delta_g)$ dissociation for several values of the peak cross section $\sigma_0$. The solar zenith angle is 60°.

onstrate conclusively that process (R7) takes place in the atmosphere, and therefore the reverse transition (R5) must occur as well. The only remaining issue concerns the magnitude of the dissociation cross section. One should note that *Slanger* [1978] estimated a long radiative lifetime for the discrete vibrational levels of $O_2(C^3\Delta_u)$ prior to decay to $O_2(a^1\Delta_g)$, being of the order of tens of seconds. This would imply very small oscillator strengths for any absorptions that excite these levels, but the relevant concern for process (R5) is a transition leading to a point on the $C^3\Delta_u$ potential curve above the dissociation threshold. Given the internuclear distances for the $a^1\Delta_g$ and $C^3\Delta_u$ states as shown in Figure 1, the oscillator strengths for bound-free transitions might be much larger than for the bound-bound process involved in the nightglow. However, a quantitative evaluation of the cross section for dissociation would require a detailed molecular physics treatment including accurate wave functions for the states involved [e.g., *Garstang*, 1962]. Such a calculation is not feasible here. Finally, airglow emissions corresponding to the reverse of (R6) have apparently not been observed [*Bates*, 1982].

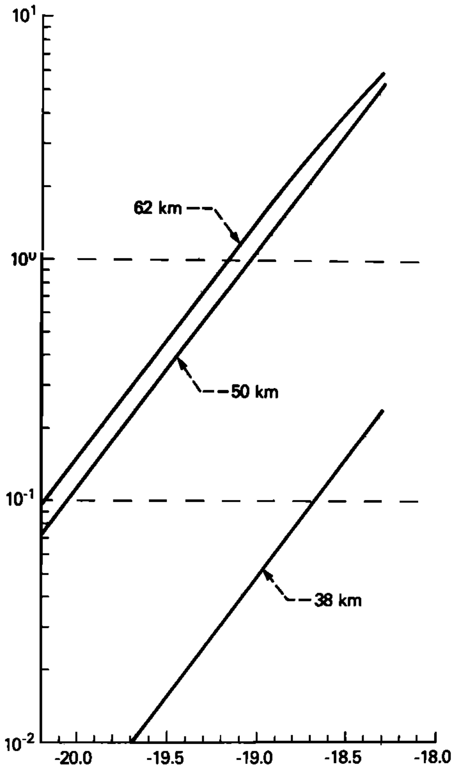

Fig. 4. Ratio of the odd oxygen production rate from $O_2(a^1\Delta_g)$ dissociation, $P(^1\Delta)$, to the Herzberg and Schumann-Runge contributions, $P$(HZ + SR), as a function of the peak $O_2(a^1\Delta_g)$ cross section. Values appear for altitudes of 38, 50, and 62 km all for a solar zenith angle of 60°.

## CONSIDERATIONS RELATED TO ATMOSPHERIC CHEMISTRY

Tables 1 and 2 summarize the production and loss mechanisms of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g{}^+)$, respectively. Processes (R5) and (R6) constitute new loss mechanisms that are not included in present photochemical models of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g{}^+)$. Yet, at least for $O_2(a^1\Delta_g)$, a theory that neglects photodissociation is sufficiently accurate for us to infer mesospheric ozone abundances from the 1.27-μm emission [*Thomas et al.*, 1984]. The photochemical theory of $O_2(b^1\Sigma_g{}^+)$ appears less well developed, although observations of the atmospheric bands $b^1\Sigma_g{}^+ - X^3\Sigma_g{}^-$ exist [*Wallace and Hunten*, 1968]. An additional constraint on (R5) and (R6) should be that the loss by dissociation remain small in relation to the other loss processes so as to have a minor impact on the number densities of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g{}^+)$. This is necessary for $O_2(a^1\Delta_g)$ only if ozone is known independently of the 1.27-μm airglow emission. However, the acceptable agreement between lower mesospheric ozone abundances derived from the same platform using different techniques [*Thomas et al.*, 1984; *Rusch et al.*, 1984] leads us to adopt the smallness condition on the dissociation rate of $O_2(a^1\Delta_g)$ at least up to 70 km. The equilibrium number densities of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g{}^+)$ are

$$[O_2(a^1\Delta_g)] = J_a(O_3)[O_3]/\{J(^1\Delta) + A(^1\Delta) + q_a(N_2)[N_2] + q_a(O_2)[O_2] + q_a(CO_2)[CO_2]\} \quad (1)$$

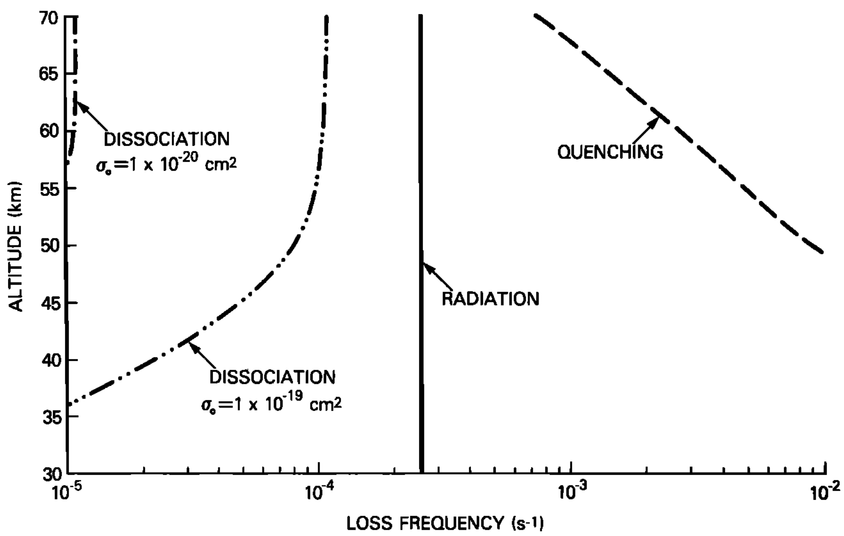

Fig. 5. Loss frequencies of $O_2(a^1\Delta_g)$ associated with quenching, infrared radiation, and dissociation. Values for the dissociation frequency appear for two values of the peak cross sections, $\sigma_0 = 1 \times 10^{-20}$ cm$^2$ and $1 \times 10^{-19}$ cm$^2$.

$$[O_2(b^1\Sigma_g{}^+)] = \{k_6[O(^1D)][O_2] + \varepsilon_b[O_2]\}/\{J(^1\Sigma) + A(^1\Sigma) + q_b(N_2)[N_2] + q_b(O_2)[O_2] + q_b(CO_2)[CO_2] + q_b(O_3)[O_3]\} \qquad (2)$$

Equation (1) omits reactions with atomic hydrogen and nitrogen since the rate coefficients of *Schmidt and Schiff* [1973] require the loss rate of $O_2(a^1\Delta_g)$ in these processes to be negligibly small. In addition, the reaction of $O_2(a^1\Delta_g)$ with $O_3$ proceeds at a rate of approximately $2 \times 10^{-18}$ cm$^3$ s$^{-1}$ at a temperature of 270 K [*Clark et al.*, 1970]. This process is therefore of no consequence relative to quenching by $N_2$ and $O_2$ with the rate coefficients of Table 1 [*Bates*, 1982], and its neglect in (1) is justified. Equation (2) assumes that quenching of $O(^1D)$ by ground state $O_2$ produces $O_2(b^1\Sigma_g{}^+)$ with unit efficiency, where $O(^1D)$ is determined by a balance between dissociation of ozone, $J_a(O_3)$, at wavelengths less than 313 nm and quenching by $O_2$ and $N_2$. This gives an upper limit to the $O_2(b^1\Sigma_g{}^+)$ abundance. The rate of excitation by resonance absorption of sunlight, $\varepsilon_b$, is based on the emission rate factor $8.5 \times 10^{-9}$ s$^{-1}$ tabulated by *Bates* [1982] and the assumption that absorption occurs at the discrete wavelength 757.85 nm where the ozone Chappuis bands provide a small optical depth as given in Table 2.

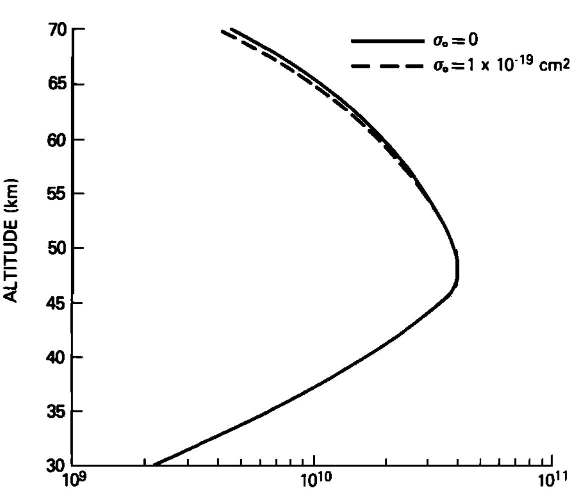

Fig. 6. Computed number density profiles of $O_2(a^1\Delta_g)$ for peak dissociation cross sections of $\sigma_0 = 0$ and $1 \times 10^{-19}$ cm$^2$. Dissociation has a negligible effect on the profile for $\sigma_0$ values up to $1 \times 10^{-19}$ cm$^2$.

The odd oxygen production rates corresponding to (R5) and (R6) are

$$P(^1\Delta) = 2J(^1\Delta)[O_2(a^1\Delta_g)] \qquad (3)$$

$$P(^1\Sigma) = 2J(^1\Sigma)[O_2(b^1\Sigma_g{}^+)] \qquad (4)$$

where the dissociation rates in s$^{-1}$ are

$$J(^1\Delta) = \int d\lambda\ \sigma(^1\Delta, \lambda)F(\lambda)e^{-\tau(\lambda)\sec\theta} \qquad (5)$$

$$J(^1\Sigma) = \int d\lambda\ \sigma(^1\Sigma, \lambda)F(\lambda)e^{-\tau(\lambda)\sec\theta} \qquad (6)$$

Here $\sigma(^1\Delta, \lambda)$ and $\sigma(^1\Sigma, \lambda)$ are the dissociation cross sections corresponding to (R5) and (R6), respectively, $F(\lambda)$ is the unattenuated solar irradiance at wavelength $\lambda$, $\tau(\lambda)$ is the vertical optical depth including absorption by $O_3$ and ground state $O_2$, and $\theta$ is the solar zenith angle. Values of the solar irradiance and cross sections used in the optical depth calculation are those prepared for the 1985 NASA Ozone Assessment Report [*Frederick*, 1985]. With the exception of Herzberg continuum $O_2$ cross sections coming from *Johnston et al.* [1984], the values are very similar to those of *Hudson* [1982]. The calculations use the ozone profile and bulk density model of the U.S. Standard Atmosphere (1976).

The final task involves development of analytic models for the unknown cross sections $\sigma(^1\Delta, \lambda)$ and $\sigma(^1\Sigma, \lambda)$. The expression of *Saxon and Liu* [1977], modified by *Johnston et al.* [1984] to use the wavelength as the independent variable, provides a physically realistic model for the dissociation cross section of $O_2$. This is

$$\sigma(\lambda) = \sigma_0 \frac{\lambda_0}{\lambda} \exp\left[-\alpha\left(\ln \frac{\lambda_0}{\lambda}\right)^2\right] \qquad (7)$$

where $\alpha$, $\lambda_0$, and $\sigma_0$ are parameters peculiar to the transition being studied. A rigorous derivation of the constants $\alpha$ and $\lambda_0$ from molecular physics considerations is not attempted here. Instead, the value $\alpha = 46.6$, appropriate to the Herzberg continuum, is adopted. Study of the Schumann-Runge and Herzberg continuum cross sections shows that the peak values occur 40 ± 10 nm shortward of the maximum wavelength at which dissociation is possible. Given this, the selections $\lambda_0 = 255$ nm for $O_2(a^1\Delta_g)$ and $\lambda_0 = 311$ nm for $O_2(b^1\Sigma_g{}^+)$ are reasonable. Figure 2 presents the final models for $\sigma(^1\Delta, \lambda)$ and $\sigma(^1\Sigma, \lambda)$ in the case $\sigma_0 = 5 \times 10^{-20}$ cm$^2$ for each. Note from (7) that $\sigma_0$ and $\lambda_0$ are not mathematically identical to the magnitude and wavelength of the cross-section maximum. However, these differences are insignificant, and the following discussion therefore refers to $\sigma_0$ as the peak cross section.

The dissociation rates $J(^1\Delta)$ and $J(^1\Sigma)$ and number densities $[O_2(a^1\Delta_g)]$ and $[O_2(b^1\Sigma_g{}^+)]$ were then evaluated for a range of $\sigma_0$ values to determine if and where the production rates of (3) and (4) can be significant in comparison to the odd oxygen production by dissociation of ground state $O_2$. Clearly, one can always select $\sigma_0$ values that make processes (R5) and (R6) appear significant. However, important constraints must be met. These are as follows: (1) an acceptable $\sigma_0$ value must be much smaller than that expected for a quantum mechanically allowed transition, and (2) an acceptable $\sigma_0$ value should not be so great as to make dissociation a major loss process for $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g{}^+)$. If $\sigma_0$ values can be found that simultaneously satisfy these constraints and still yield a significant production of odd oxygen, then the proposed source merits a detailed theoretical and laboratory analysis.

## RESULTS

Figure 3 compares the production rate of odd oxygen arising from dissociation of $O_2$ in the Herzberg continuum and the Schumann-Runge bands, $P$(HZ + SR), with that from $O_2(a^1\Delta_g)$ for three values of $\sigma_0$, $1 \times 10^{-20}$, $1 \times 10^{-19}$, and $5 \times 10^{-19}$ cm$^2$. The background source $P$(HZ + SR) is based on the Schumann-Runge band calculations of *Frederick and Hudson* [1980], with updated values for the solar irradiance and the Herzberg continuum cross sections. The solar zenith angle in this and subsequent calculations is 60°. With a peak cross section of $1 \times 10^{-19}$ cm$^2$, dissociation of $O_2(a^1\Delta_g)$ would be the largest source of atmospheric odd oxygen over the altitude range 49 to 66 km. If $\sigma_0$ were as great as $5 \times 10^{-19}$ cm$^2$, the Schumann-Runge bands and Herzberg continuum would become minor sources of odd oxygen throughout the region 45 to 70 km. Figure 4 presents these results in a different manner by plotting the ratio $P(^1\Delta)/P(\mathrm{HZ + SR})$ against log $\sigma_0$ for the altitudes 38, 50, and 62 km. At the stratopause, $P(^1\Delta)$ constitutes from 10 to 100% of $P$(HZ + SR) for $\sigma_0$ values in the range $8 \times 10^{-21}$ cm$^2$ to $9 \times 10^{-20}$ cm$^2$. Such peak cross sections are reasonable given the molecular physics arguments of the previous section. The proposed odd oxygen source becomes slightly more important on a percentage basis as one moves into the mesosphere. Quenching of $O_2(a^1\Delta_g)$ and attenuation of solar radiation makes the production rate $P(^1\Delta)$ decrease rapidly below the stratopause.

Figure 5 demonstrates that $O_2(a^1\Delta_g)$ dissociation rates great enough to provide a significant source of odd oxygen still make minor contributions to the total loss rate. For $\sigma_0 = 1 \times 10^{-19}$ cm$^2$, dissociation constitutes only 10.1% of the total loss rate at 70 km and decreases rapidly at lower altitudes. Indeed, Figure 6 shows that the $O_2(a^1\Delta_g)$ profiles computed for $\sigma_0 = 0$ and $1 \times 10^{-19}$ cm$^2$ differ insignificantly. However, a value of $\sigma_0$ as great as $5 \times 10^{-19}$ cm$^2$ would reduce the computed $O_2(a^1\Delta_g)$ number density at 70 km to 60–65% of that predicted in the absence of dissociation. We note that atmospheric $O_2(a^1\Delta_g)$ abundances deduced from measurements of the 1.27-$\mu$m airglow are in reasonable agreement with those shown in Figure 6. For example, the number densities reported by *Evans et al.* [1968] are approximately $1.3 \times 10^{10}$, $2.6 \times 10^{10}$, and $2.3 \times 10^{10}$ cm$^{-3}$ at 65, 55, and 45 km, respectively. On the basis of this analysis the conclusion is as follows. If the peak cross section for $O_2(a^1\Delta_g)$ dissociation lies in the range $10^{-20}$ to $10^{-19}$ cm$^2$, then this process provides a significant source of odd oxygen in the uppermost stratosphere and mesosphere. However, a peak cross section as large as $5 \times 10^{-19}$ cm$^2$ can probably be ruled out because of the consequent reduction in $[O_2(a^1\Delta_g)]$.

Calculations based on (2) showed that a peak cross section of $1 \times 10^{-16}$ cm$^2$ would make the odd oxygen production rate in (R6) equal to that from the Herzberg continuum and Schumann-Runge bands at and above 60 km, with a rapid decrease in importance at altitudes below 50 km. Clearly, a cross section of this magnitude is unacceptable given the spin forbidden nature of the transition. Yet, smaller values of $\sigma_0$ would make process (R6) a negligible source of atmospheric odd oxygen. This negative result regarding the importance of $O_2(b^1\Sigma_g{}^+)$ dissociation might have been anticipated given the absence of observed airglow emissions corresponding to the reverse of (R6).

## DISCUSSION

This analysis has shown that dissociation of $O_2(a^1\Delta_g)$ has the potential to provide a very substantial source of odd oxygen at and above the stratopause, provided the cross section exceeds $1 \times 10^{-20}$ cm$^2$ at its peak and has a wavelength dependence similar to that adopted here. Any contribution to odd oxygen production from dissociation of $O_2(b^1\Sigma_g{}^+)$ appears to be negligible.

The speculative nature of this work must again receive emphasis. Although nightglow observations clearly demonstrate that the $O_2(C^3\Delta_u)$–$O_2(a^1\Delta_g)$ transition occurs in the atmosphere, the major uncertainty in the present work is the assumed model for the $O_2(a^1\Delta_g)$ dissociation cross section. If the shape shown in Figure 2 or the inferred peak magnitudes are grossly in error, then dissociation of $O_2(a^1\Delta_g)$ could in fact be an insignificant source of odd oxygen. However, in view of the discrepancies that exist between observed ozone profiles and those computed with current photochemical models, a more detailed theoretical and experimental examination of excited state chemistry would clearly be of value.

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R. J. Cicerone, National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307.

J. E. Frederick, NASA Goddard Space Flight Center, Code 616, Greenbelt, MD 20771.

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