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METASTABLE OXYGEN MOLECULES IN THE TROPOSPHERE

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The sources and steady-state concentration of singlet oxygen in the atmosphere are assessed in view of potential effects on the biosphere. Collision-induced absorption of sunlight by molecular oxygen in 1 atm of air produces $O_2(a^1\Delta_g)$ at a rate $P = 1.6 \times 10^9 \mathrm{cm}^{-3}\mathrm{s}^{-1}$ in bright sunlight. Less than 10% are added to this purely natural source by the photolysis of ozone, and by anthropogenic sensitizers (SO_2, NO_2, volatile aromatics). Collisional quenching of $O_2(a^1\Delta_g)$ by ground state oxygen establishes a steady-state concentration of ca. $1.7 \times 10^8 \mathrm{cm}^{-3}$. Reactions of singlet oxygen with other atmospheric pollutants are entirely negligible when compared with the concurrent reactions of ambient OH and O_3. Potential effects of atmospheric singlet oxygen on the biosphere are limited by the deposition rate $F \leqslant 0.051\,P$, which depends on the production rate P of $O_2(a^1\Delta_g)$ in the air layer immediately above the flat surface.

KEY WORDS: metastable oxygen molecules, singlet oxygen reactions, OH reactions, O_3 reactions, gas-surface interaction.

INTRODUCTION

Molecular oxygen $O_2(X^3\Sigma_g^-)$ has two low-lying metastable states, $(a^1\Delta_g)$ and $(b^1\Sigma_g^+)$, with radiative lifetimes (excitation energies in brackets) of 3,900 s (0.98 eV) and 12 s (1.63 eV). The fairly high intensity of the $a^1\Delta_g, v' = 0 \rightarrow X^3\Sigma_g^-, v'' = 0$ transition at 1.27 μ in the dayglow of the sky, and of the (0, 1) band of the same transition at 1.58 μ, which is more readily observed at low altitudes owing to considerable self-absorption of the (0, 0) band,[1] revealed that considerable concentrations of metastable oxygen molecules must be present in the daytime atmosphere at high altitudes. This was confirmed by rocket-borne profile measurements of the (0, 0) band intensity, which revealed a maximum concentration of more than $10^{10} \mathrm{cm}^{-1}$ at 50 km altitude during the day.[2,3] Evidently the observed vertical intensity distribution could be rationalized by a simple reaction scheme, other excitation and de-excitation mechanisms being of very minor importance:

$$O_3 + h\nu \text{ (Hartley band)} \longrightarrow O_2(^1\Delta_g) + O(^1D) \quad (1)$$

$$O_2(^1\Delta_g) \longrightarrow O_2(^3\Sigma_g^-) + h\nu\ (1.27\,\mu) \quad (2)$$

$$O_2(^1\Delta_g) + M \longrightarrow O_2(^3\Sigma_g^-) + M\ (M = \text{air}) \quad (3)$$

Crutzen *et al.*[4] used a laboratory determination of k_3, $4.4 \times 10^{-19} \mathrm{cm}^3\mathrm{s}^{-1}$, in conjunction with observed ozone profiles, to calculate concentration profiles of $O_2(^1\Delta_g)$ from 70 km to the ground. They predicted a surface concentration in the order of 10^6 cm^{-3} $O_2(^1\Delta_g)$ during the day, but did not consider other excitation mechanisms of the metastable molecule. The result at low solar elevations depended on the assumed quantum yield of $O_2(^1\Delta_g)$ as function of wavelength in the photodissociation of ozone above 310 nm, which remains a matter of controversy.[5]

In the late sixties and early seventies measurements of $O_2(^1\Delta_g)$ reaction rate constants with a few gaseous olefins became feasible in discharge-flow systems. The results were taken as evidence that metastable oxygen is involved in photochemical smog formation.[6,7] However, later on many of the rate constants were found to be orders of magnitude too high, owing to incomplete scavenging of oxygen atoms and ozone in the discharge-flow apparatus used for the measurements. In order to corroborate the importance of metastable oxygen molecules in photochemical smog, several other sources of $O_2(^1\Delta_g)$ were suggested, some of them highly speculative at the time, which were supposed to yield substantially higher steady-state concentrations of the molecule than ozone photolysis alone.

Several excellent reviews on gas phase kinetics and photochemistry of metastable oxygen molecules have appeared in recent years.[8-11] They come to the conclusion that $O_2(^1\Sigma_g^+)$ is quenched far too rapidly by water vapour and nitrogen to be chemically relevant in the troposphere. Likewise, the wealth of rate constants for reactions of $O_2(^1\Delta_g)$ in the gas phase which have accumulated over the years refute the initially claimed importance of $O_2(^1\Delta_g)$ in the photochemical smog formation. More recently there has been increasing concern in the phenomenon of forest decay, which does not seem to correlate convincingly with any of the suspect gaseous pollutants detected in the atmosphere. This has fostered the idea that unknown compound(s) could be responsible for the observed effects on vegetation. The concentration of metastable oxygen molecules in the troposphere has never been measured and is difficult to estimate, and one might speculate that anthropogenic sources have pushed it up to phytotoxic levels. It seems thus warranted to reassess its source strength and steady-state concentration in the troposphere, and to estimate the flux of metastable oxygen molecules from the ambient air to vegetation, particularly to leaf surfaces.

SOURCES OF METASTABLE OXYGEN MOLECULES IN THE TROPOSPHERE

A. Direct Excitation by Absorption of Sunlight

In spite of being rapidly quenched by water vapor ($\tau_{\text{quenching}} = 0.6\,\mu$s at 7.5 torr water vapour pressure), $O_2(^1\Sigma_g^+)$ is a potential source of $O_2(^1\Delta_g)$, since most of the quenching is believed to populate the nearby $(a^1\Delta_g)$ state for reasons of spin conservation.[12] The differential absorption rate in the (0, 0) band of $O_2(b \leftarrow X)$ can be calculated from the formula

$$\frac{dI}{dx} = \frac{N \cdot B \cdot h\nu_0}{\delta\nu} I \quad (\text{cm}^{-3}\,\text{s}^{-1}), \tag{4}$$

where N is the number density of oxygen, B the Einstein coefficient of the transition,[13] and I the light intensity (= the number of photons cm^{-2} s^{-1} in the specified frequency interval $\delta\nu$). The Franck Condon factor of the (0, 0) band is very close to unity, and need not be considered explicitly. Assuming a smooth solar spectrum, with intensity $I = 1.15 \times 10^{16}$ photons cm^{-2} s^{-1} (200 nm)$^{-1}$ for a solar zenith angle of 40° at ground level,[14,15] yields an excitation rate of 1.6×10^{11} cm^{-3} s^{-1} for the b-state, which corresponds to a steady-state concentration of 10^5 cm^{-3} in the presence of 7.5 torr water vapour. However, instead of being constant throughout the wavelength interval considered, the absorption is sharply peaked in rotational lines of only $0.06\,\mathrm{cm}^{-1}$ width at 1 atmosphere pressure. The atmosphere is practically opaque within the rotational lines, while remaining essentially transparent in the wide intervals between the lines. One therefore expects an excitation rate at ground level which is orders of magnitude lower than the above estimate, although at low resolution the solar spectrum appears to be only moderately attenuated by O_2 absorption.[16]

The situation for direct excitation of the $a^1\Delta_g$ state of oxygen by absorption of sunlight is similar in principle, but the atmosphere is considerably less opaque in this band, due to the 160 fold lower Einstein B coefficient of the ($a \leftarrow$ X) transition. In fact, emission of the (0, 0) band at $1.27\,\mu$, which originates mainly above 40 km altitude, has been measured with a ground-based spectrometer in the dayglow.[17] It was calculated that $\leqslant 5\%$ of the (0, 0) band is transmitted to the ground, depending on the solar zenith angle.[18] This leads us to an order of magnitude estimate of the $O_2(^1\Delta_g)$ excitation rate by sunlight of a few $10^7\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$. This excitation rate must be divided by the quenching rate of $10.3\,\mathrm{s}^{-1}$ in 1 atm air[19–21] to obtain the corresponding steady-state concentration.

It is well-known from absorption spectra of liquid oxygen and oxygen gas at very high pressures[10] that *collision-induced* absorption of the (0, 0) and (1, 0) bands of the ($a \leftarrow$ X) transition occurs with approximately equal intensities. The phenomenon has been discussed by Badger *et al.*,[13] who also measured the effective (pressure-dependent) Einstein B coefficients of both bands. They report that N_2 is less efficient in inducing the (0, 0) band, and does not induce the (1, 0) band. Contrary to the rotationally resolvable absorption spectra of isolated oxygen molecules, the collision pair bands are broad (FWHM ca. $200\,\mathrm{cm}^{-1}$) and structureless. Because of the pressure dependence, absorption of solar radiation by collision pairs is only significant in the lowest few km of the atmosphere, which is optically thin, to a good approximation, with respect to this absorption. 20–30% of the intensity in the (0, 0) band region are however absorbed by superimposed water vapour and monomer oxygen lines.

We have calculated the rate of $O_2(^1\Delta_g)$ formation by direct absorption of solar radiation in the (0, 0) and (1, 0) bands of the collision-induced transition at $1.27\,\mu$ and $1.065\,\mu$ at ground level, adopting the effective Einstein B coefficients published by Badger *et al.*[13] The opacity of the atmosphere due to collision pairs in the optical column was explicitly taken into account in the calculation. It amounts to an intensity reduction of about 5% at a solar zenith angle of 40°, and can thus be neglected for all practical purposes, in view of the much larger uncertainties involved in estimating the attenuation of the extraterrestrial solar flux by water vapor and other absorbers. The resulting excitation rate for singlet oxygen amounts to $10^9\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$. This rate varies by less than 50% for solar zenith angles between 0° and 60°.

Blickensderfer and Ewing[22] have carried out a laboratory study of collision-induced absorptions in pure oxygen as function of pressure and temperature, using a White cell system for the visible region. The broad structureless bands at 630 nm, 580 nm and 480 nm have been attributed to the following cooperative transitions:

$$2\,O_2(^3\Sigma_g^-) + h\nu \longrightarrow O_2(^1\Delta_g, v = 0) + O_2(^1\Delta_g, v = 0) \tag{5}$$

$$\longrightarrow O_2(^1\Delta_g, v = 1) + O_2(^1\Delta_g, v = 0) \tag{6}$$

$$\longrightarrow O_2(^1\Delta_g, v = 0) + O_2(^1\Sigma_g^+, v = 0). \tag{7}$$

The bands appear as weak absorptions in the solar spectrum at low solar elevations,[16] and must therefore also be taken into account as direct sources of singlet oxygen. We have adopted the binary absorption coefficients measured by Blinckensderfer and Ewing at 300 K to calculate the rate of singlet oxygen formation, taking into account that each absorbed photon produces two excited molecules in these cooperative bands. The overall result is $6.2 \times 10^8 \mathrm{cm}^{-3} \mathrm{s}^{-1}$ for a solar zenith angle of 40°, slightly less than the rate in the infrared transitions.

B. $O_2(^1\Delta_g)$ Formation by Ozone Photolysis

The photolysis of ozone in the Hartley band, reaction (1), is the dominant source of metastable oxygen molecules in the $^1\Delta_g$ state in the upper atmosphere. The stratosphere is essentially opaque for u.v. which can be absorbed by ozone, resulting in a very low photolysis rate of the molecule in the troposphere. However, in view of the extreme importance of the process as a source of $O(^1D)$ radicals which produce OH radicals by reaction with water vapor,[23] it has been extensively studied both in the laboratory and in the field. We used a combination of calculated and measured photolysis frequencies of reaction (1)[24] to calculate the rates of $O_2(^1\Delta_g)$ formation listed in Table I as function of the solar zenith angle. The data, which are very sensitive to the ozone column density of the atmosphere, are given for an ozone column of $8.6 \times 10^{18} \mathrm{cm}^{-1}$. The values at low solar elevations must be taken as lower limits, since the quantum yields of $O(^1D)$ and $O_2(^1\Delta_g)$ were assumed to be equal, which has been questioned for wavelengths in excess of 300 nm. Anyway, the rate of singlet oxygen formation by reaction (1) is considerably lower than the rates derived in section A.

C. Excitation of $O_2(^1\Delta_g)$ by Energy Transfer

A general mechanism for the excitation of $O_2(\Delta_g)$ is energy transfer from a sensitizer S, which has been excited into some nondissociative electronic state by absorption of sunlight:

TABLE I

Rates of $O_2(^1\Delta_g)$ formation in air by photolysis of 40 p.p.b. ozone, as function of solar zenith angle. The integrated ozone column was assumed to be $8.6 \times 10^{18} \mathrm{cm}^{-2}$. Rates at low solar elevations (= large zenith angles) could be exceeded if the quantum yield of $O_2(^1\Delta_g)$ in reaction (1) exceeds the quantum yield of $O(^1D)$ significantly above 310 nm.

Solar zenith angle	Effective ozone column	Formation rate of $O_2(^1\Delta_g)$ by ozone photolysis
0	$0.86 \times 10^{19} \mathrm{cm}^{-2}$	$2.7 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$
10	$0.87 \times 10^{19} \mathrm{cm}^{-2}$	$2.7 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$
20	$0.92 \times 10^{19} \mathrm{cm}^{-2}$	$2.5 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$
30	$0.99 \times 10^{19} \mathrm{cm}^{-2}$	$2.3 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$
40	$1.12 \times 10^{19} \mathrm{cm}^{-2}$	$2.0 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$
50	$1.34 \times 10^{19} \mathrm{cm}^{-2}$	$1.6 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$
60	$1.72 \times 10^{19} \mathrm{cm}^{-2}$	$1.1 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$
70	$2.51 \times 10^{19} \mathrm{cm}^{-2}$	$0.47 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$
80	$4.95 \times 10^{19} \mathrm{cm}^{-2}$	$0.12 \times 10^{-5} \mathrm{cm}^{-3} \mathrm{s}^{-1}$

$$S + h\nu \longrightarrow S^* \tag{8}$$

$$S^* + N_2 \longrightarrow S + N_2 \text{ (quenching)} \tag{9}$$

$$S^* + O_2 \longrightarrow S + O_2 \text{ (quenching)} \tag{10}$$

$$S^* + O_2 \longrightarrow S + O_2(^1\Delta_g) \text{ (energy transfer).} \tag{11}$$

Fluorescence or phosphorescence of the sensitizer may be neglected in 1 atmosphere of air. The rate of singlet oxygen formation by the mechanism is

$$d(O_2{}^1\Delta_g)/dt = R_s\phi(^1\Delta_g) \tag{12}$$

R_s denotes the excitation rate of the sensitizer. The energy transfer efficiency $\phi(^1\Delta_g)$ is given by equation (13):

$$\phi(^1\Delta_g) = \frac{k_{10}(O_2)}{k_9(N_2) + (k_{10} + k_{11})(O_2)}, \tag{13}$$

Reaction (10) becomes more likely if the sensitizer flips spin in the process. Benzene and a few other aromatic compounds are known sensitizers of singlet oxygen when excited by u.v. radiation, but the energy transfer efficiencies are not well-known.[25,26] Benzene does not absorb solar radiation,[27] and the concentrations of other aromatic compounds with red-shifted absorption spectra are far too low to contribute significantly to the formation of singlet oxygen in the planetary boundary layer.

Another potential singlet oxygen sensitizer is SO_2. The rate of light absorption into both the singlet and triplet states has been reported to be $6 \times 10^{-5} s^{-1}$ at a solar zenith angle of 40°.[28] Davidson *et al.*[26] estimate the energy transfer efficiency to be much less than 0.02. This establishes an upper limit of $d(O_2{}^1\Delta_g)/dt = (SO_2) \times 1.2 \times 10^{-6}\, cm^{-3} s^{-1}$ for the rate of SO_2-sensitized singlet oxygen formation, equivalent to $4 \times 10^5\, cm^{-3}\, s^{-1}$ in rural air containing 12 p.p.b. SO_2. This is entirely negligible in comparison with the processes considered in sections A and B.

NO_2 is the most efficient absorber of sunlight throughout the u.v. and visible region. Transfer of energy from electronically excited NO_2^* to oxygen in reaction (10) is spin-allowed because NO_2 is a doublet. The energy transfer efficiency in pure oxygen has been investigated by two groups.[29,30] Jones and Bayes find that $\phi(^1\Delta_g)$ is in the order of a few %, and varies smoothly from 600 to 300 nm, with no discontinuity at the dissociation limit of 400 nm, which was a rather unexpected result.[30] We have adopted their transfer efficiencies, corrected for quenching of 80% NO_2^* by nitrogen, to calculate the rate of $O_2(^1\Delta_g)$ formation by the process for a solar zenith angle of 40°. The result is $d(O_2{}^1\Delta_g)/dt = (NO_2) \times 1.7 \times 10^{-4} cm^{-3} s^{-1}$, corresponding to a singlet oxygen formation rate of $2 \times 10^7 cm^{-3} s^{-1}$ in rural air containing 5 p.p.b. NO_2. A considerably lower rate has been estimated by Frankiewicz and Berry.[29]

D. Chemical Sources of $O_2(^1\Delta_g)$ in the Troposphere

It has been speculated[6] that the reaction of ozone with NO might be an abundant source of singlet oxygen in the polluted atmosphere:

$$NO + O_3 \longrightarrow NO_2 + O_2(^3\Sigma_g^- \text{ or } ^1\Delta_g). \tag{14}$$

TABLE II

Processes contributing to the formation of $O_2(^1\Delta_g)$. The rates are calculated for a solar zenith angle of 40°, trace gas mixing ratios as specified

Process contributing of $O_2(^1\Delta_g)$ formation	Corresponding source strength
A1 direct excitation of $O_2(^1\Sigma_g^+)$ followed by $O_2(^1\Sigma_g^+) + M \rightarrow O_2(^1\Delta_g) + M$	negligible
A2 direct excitation of $O_2(^1\Delta_g)$ by sunlight	$10^7 - 10^8 \mathrm{cm}^{-3}\mathrm{s}^{-1}$
A3 collision-induced absorption of sunlight	$1.6 \times 10^9 \mathrm{cm}^{-3}\mathrm{s}^{-1}$
B ozone photolysis, 40 p.p.b. ozone, integrated ozone column 8.6×10^{18}	$1.9 \times 10^7 \mathrm{cm}^{-3}\mathrm{s}^{-1}$
C1 sensitization by volatile aromatics	negligible
C2 sensitization by 12 p.p.b. SO_2	$4 \times 10^5 \mathrm{cm}^{-3}\mathrm{s}^{-1}$
C3 sensitization by 5 p.p.b. NO_2	$2 \times 10^7 \mathrm{cm}^{-3}\mathrm{s}^{-1}$
D reaction $O_3 + NO$, 5 p.p.b. NO_2 in photostationary state	$\leqslant 2 \times 10^6 \mathrm{cm}^{-3}\mathrm{s}^{-1}$
total	ca. $1.7 \times 10^9 \mathrm{cm}^{-3}\mathrm{s}^{-1}$
steady state concentration of $O_2(^1\Delta_g)$ in 1 atm of air	ca. $1.7 \times 10^8 \mathrm{cm}^{-3}$

TABLE III

Reactivity of $O_2(^1\Delta_g)$, OH, and O_3 in the gas phase. Rate constants with selected organic and a few inorganic compounds. Data were taken from recent reviews,[9,11,34,35] unless otherwise noted

Compound reacting or quenching	Room temperature rate constants in molecular units ($\mathrm{cm}^3\mathrm{s}^{-1}$) with $O_2(^1\Delta_g)$	with OH	with O_3
O_2	1.5×10^{-18}	no reaction	no reaction
O_3	3.5×10^{-15}	6.8×10^{-14}	no reaction
ethene	2×10^{-18}	8.5×10^{-12}	1.45×10^{-18}[a]
propene	2.2×10^{-18}	2.5×10^{-11}	1.05×10^{-17}[a]
1-butene	2.3×10^{-18}	3.2×10^{-11}	1.03×10^{-17}[a]
cis-2-butene	3.8×10^{-18}	5×10^{-11}	1.2×10^{-16}[a]
trans-2-butene	1.5×10^{-18}	6×10^{-11}	1.95×10^{-16}[a]
2-methylbutene-2	5×10^{-17}	9×10^{-11}	3.2×10^{-16}[a]
2,3-dimethylbutene-2	1.3×10^{-15}	1.1×10^{-10}	$9 \pm 3 \times 10^{-16}$[a]
furan	3.5×10^{-17}	4×10^{-11}	2.4×10^{-18}
1,1-dimethylfuran	1.8×10^{-14}	n.d.	n.d.
α-pinene	$< 1.6 \times 10^{-18}$(36)	6×10^{-11}	8×10^{-17}
β-pinene	$< 1.6 \times 10^{-18}$(36)	7×10^{-11}	2.1×10^{-17}
myrcene	$< 1.6 \times 10^{-18}$(36)	n.d.	$4.4 - 12.5 \times 10^{-16}$
limonene	$< 1.6 \times 10^{-18}$(36)	1.5×10^{-11}	$4.4 - 6.4 \times 10^{-16}$
dimethylamine	9.3×10^{-17}	6.5×10^{-11}	2.6×10^{-18}
dipropylamine	1.4×10^{-15}(37)	n.d.	n.d.
H_2S	2.1×10^{-19}	5.2×10^{-12}[39]	$< 2 \times 10^{-20}$[40]
methylmercaptane	1×10^{-18}	3×10^{-11}	n.d.
dimethylsulphide	1.1×10^{-16}	9.7×10^{-11}	$< 8 \times 10^{-19}$
dimethylsulphide	$< 1.6 \times 10^{-18}$(38)	2.4×10^{-10}	n.d.
thiophene	5.8×10^{-18}(38)	9×10^{-12}	$< 6 \times 10^{-20}$
H_2CO	2.3×10^{-18}	1.5×10^{-11}	$< 2 \times 10^{-24}$

[a] unpublished results from our laboratory; measurements in 1 atm air, in an environmental chamber.

The overall rate of this reaction in approximately equal to the NO_2 photolysis rate under conditions of photostationary state. Formation of singlet O_2 is spin allowed and energetically feasible. However, Gauthier and Snelling[31] were able to set upper limits of 0.003 and 0.005, respectively, for the yields of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ in reaction (14). A theoretical interpretation of the result has been proposed by Redpath *et al.*[32] A conservative upper limit for the rate of $O_2(^1\Delta_g)$ formation via reaction (14) is $d(O_2{}^1\Delta_g)/dt = (NO_2) \times 4 \times 10^{-5}\,cm^{-3}s^{-1}$ under photostationary state conditions in bright sunlight, which yields $5 \times 10^6\,cm^{-3}s^{-1}$ in rural air containing 5 p.p.b. NO_2.

About 20% of the NO_2 formed in reaction (14) is electronically excited.[33] Therefore the possibility of $O_2(^1\Delta_g)$ formation by energy transfer from NO_2^* to O_2 has to be considered as well. However, the onset of the chemiluminescence due to reaction (14) is at 600 nm, where the transfer efficiency has already dropped to zero.[30]

We have summarized the rates of $O_2(^1\Delta_g)$ formation by various mechanisms in Table II. Clearly the natural processes A2 and A3 are by far the most efficient sources of singlet oxygen in the troposphere, unpolluted or polluted. The sources which are under anthropogenic influence are of marginal importance, with the exception of process C3 (sensitization by NO_2), which may become significant in *extremely* polluted air.

CHEMISTRY OF $O_2(^1\Delta_g)$ IN THE GAS PHASE

The reactions of $O_2(^1\Delta_g)$ in the troposphere must be compared with competitive reactions of other reactive species, particularly OH radicals and ozone, which are simultaneously present. The following daytime concentrations of reactive species in the planetary boundary layer, sunny summer conditions, which have been measured and/or estimated, provide a basis for comparison:

ozone:	$10^{12}\,cm^{-3}$ typical; $2.5 \times 10^{12}\,cm^{-3}$ during photosmog episodes[41]
OH:	$5 \times 10^5 - 5 \times 10^6\,cm^{-3}$ [42]
$O_2(^1\Delta_g)$:	$1.7 \times 10^8\,cm^{-3}$ (this work).

Table III lists rate constants of $O_2(^1\Delta_g)$, OH and ozone with selected organic and inorganic trace constituents of the atmosphere. Rate constants for alkanes, simple aromatic compounds and inorganic trace gases have been omitted, since these compounds do not react chemically with $O_2(^1\Delta_g)$, and the rate constants reported in the literature pertain to physical quenching of the molecule only. The rate constant for O_2, although purely physical, has been included in the table for comparison, and so have a few other slow rate constants of compounds which are unlikely to react chemically with $O_2(^1\Delta_g)$.

Table III shows that the rate constant ratio $k(^1\Delta_g): k_{OH}$ is always less, usually much less, than 10^{-5}[†]. Since the concentration of $O_2(^1\Delta_g)$ in the planetary boundary layer is at most three orders of magnitude higher than the OH concentration, reactions with $O_2(^1\Delta_g)$ can be ignored, in comparison with OH reactions, as a loss mechanism for atmospheric trace species. The same conclusion can be drawn from the concentrations and rate constant ratios of $O_2(^1\Delta_g)$ and ozone.

[†] With the possible exception of 1.1-dimethylfuran, which reacts fastest with $O_2(^1\Delta_g)$ of all the neutral gas phase species studied to date.

Little is known about the reaction products of $O_2(^1\Delta_g)$ under atmospheric conditions. Products detected in low pressure flow systems are peroxides, as well as carbonyl compounds resulting from the fragmentation of dioxetane intermediates.[9,11] Radical formation does not seem to be important, particularly at higher pressures. It should be noted that reactions of $O_2(^1\Delta_g)$ with unsaturated hydrocarbons are generally about two orders of magnitude slower in the gas phase than in the liquid phase.[9]

SURFACE INTERACTION OF ATMOSPHERIC $O_2(^1\Delta_g)$

Direct interaction of atmospheric $O_2(^1\Delta_g)$ with vegetation surfaces is limited by its flux F from the gas phase to the surface. This process is better known as dry deposition in the atmospheric sciences. It has been extensively studied for SO_2 and other stable trace gases.[43,44] Transfer from the free atmosphere to the ground is accomplished by turbulent diffusion, while in the last few mm above the surface viscous drag impedes turbulent mixing, and transport is determined by molecular diffusion. Under steady state conditions the flux of a stable trace gas very close to the surface must equal the turbulent flux farther away from the surface. It is the interplay of turbulent and molecular diffusion which is difficult to describe.

The mean lifetime of $O_2(^1\Delta_g)$ at ambient pressure is only $\tau = 0.097\,\mathrm{s}$, corresponding to a root mean square displacement d,

$$d = \sqrt{2\mathrm{D}\tau}, \tag{15}$$

$$\mathrm{D}_{O_2/\mathrm{air}} = 0.208\,\mathrm{cm}^2\,\mathrm{s}^{-1},$$ [45]

of only 0.20 cm during its lifetime. This facilitates the problem, because turbulent transport of $O_2(^1\Delta_g)$ farther away from the surface need not be considered in calculating its flux F to the surface. It suffices to solve the differential equation for molecular diffusion perpendicular to a flat surface which acts as a sink of $O_2(^1\Delta_g)$:

$$\left(\frac{\partial c}{\partial t}\right)_x = 0 = \mathrm{D}\left(\frac{\partial^2 c}{\partial x^2}\right)_t - c/\tau + P \tag{16}$$

c = concentration of $O_2(^1\Delta_g)$
P = rate of $O_2(^1\Delta_g)$ formation in the gas phase, cf. Table II

The flux F immediately above the surface is equal to the surface loss of $O_2(^1\Delta_g)$:

$$F = -\mathrm{D}\left(\frac{\partial c}{\partial x}\right)_{x=0} = -\gamma\frac{\bar{v}}{4}c_0 \tag{17}$$

c_0 = concentration of $O_2(^1\Delta_g)$ immediately adjacent to the surface
$\bar{v}$ = mean molecular speed of oxygen, $4.4 \times 10^4\,\mathrm{cm\,s^{-1}}$
γ = "sticking coefficient" = number of $O_2(^1\Delta_g)$ lost in a surface collision, divided by the total number of $O_2(^1\Delta_g)$ colliding with the surface.

The steady-state solution of the problem is

$$c_x = c_0 + (c_\infty - c_0)\left(1 - \exp\left(-\frac{x\sqrt{2}}{d}\right)\right) \tag{18}$$

$$c_0 = c_\infty\Big/\left(1 + \gamma\frac{\bar{v}\tau}{d}\right) \tag{19}$$

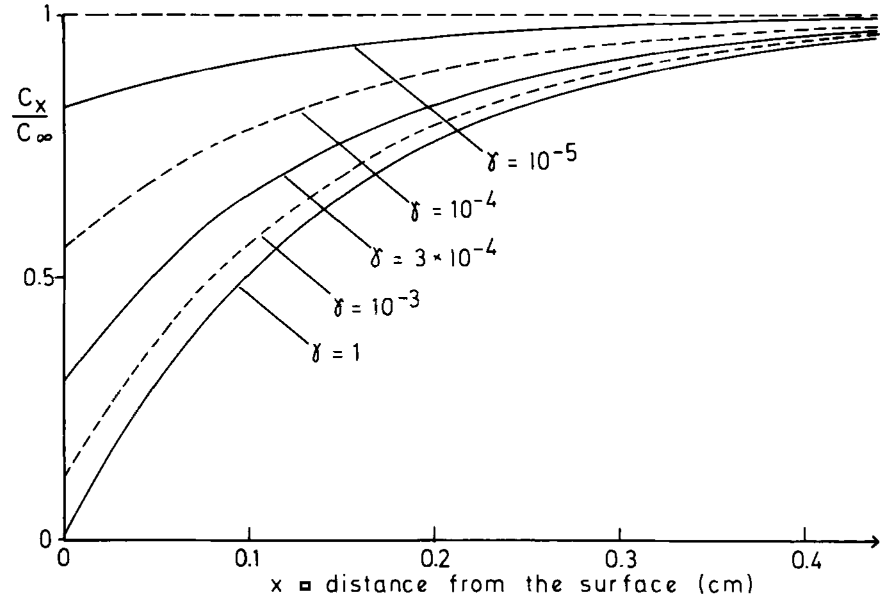

FIGURE 1 Concentration profiles of $O_2(^1\Delta_g)$ normal to a flat surface, as function of the sticking coefficient γ (equations (18) and (19)).

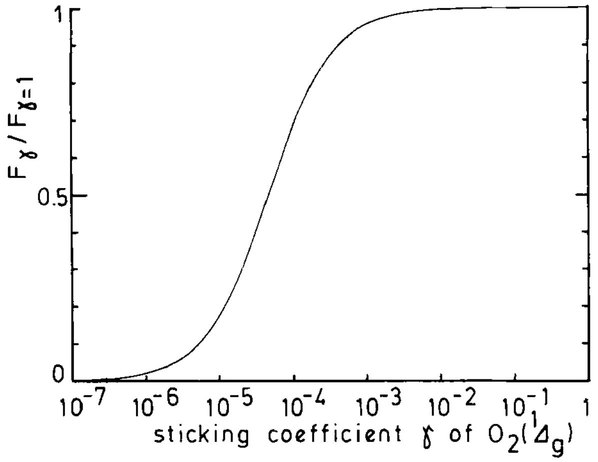

FIGURE 2 Normalized net flux of $O_2(^1\Delta_g)$ to a flat surface as function of the sticking coefficient γ (equation (20)).

$c_x = \tau \cdot P = 0.097\, P$ at ambient pressure.

The net flux of $O_2(^1\Delta_g)$ to the surface is

$$F = \gamma \frac{\bar{v}}{4} \frac{\tau \cdot P}{1 + \gamma \frac{\bar{v}\tau}{d}} = \frac{\gamma 1.1 \times 10^3 P}{1 + 2.1 \times 10^4 \gamma} \quad (\mathrm{cm}^{-2}\mathrm{s}^{-1}). \qquad (20)$$

Figure 1 shows calculated concentration profiles of $O_2(^1\Delta_g)$ perpendicular to a surface, for a range of sticking coefficients $\gamma = 1 - 1 \times 10^{-5}$. The latter value is typical for clean pyrex surfaces in low pressure flow tubes used in kinetic studies. Biological surfaces should exhibit considerably larger sticking coefficients for $O_2(^1\Delta_g)$, probably in the range of 10^{-3} or larger.

It is more instructive to examine the effect of γ on the net flux of $O_2(^1\Delta_g)$ to a surface. Setting $\gamma = 1$ yields the largest possible (diffusion-limited) flux of $O_2(^1\Delta_g)$ to a surface:

$$F_{\max} = P \cdot d/4 = 0.051\,\mathrm{P}. \tag{21}$$

Figure 2 illustrates the dependence of F on the sticking coefficient γ. There is little dependence on γ for sticking coefficients in excess of 10^{-4}, which is the range of interest for the interaction of atmospheric $O_2(^1\Delta_g)$ with a leaf surface.

A conservative estimate of the deposition rate of leaf surface is obtained by equating P in equation (21) with $1.7 \times 10^9\,\mathrm{cm^{-3}\,s^{-1}}$, the rate of $O_2(^1\Delta_g)$ formation listed in Table II. This yields $F_{\max} = 8.5 \times 10^7\,\mathrm{cm^{-2}\,s^{-1}}$. It must be stressed that this rate is only valid for leaf surfaces which are *directly* exposed to sunlight, because $O_2(^1\Delta_g)$ which are formed more than a few nm away from a shaded surface cannot be deposited. The integrated $O_2(^1\Delta_g)$ deposition to a leaf surface which has been permanently exposed to the sun during a fair summer day amounts to $4 \times 10^{12}\,\mathrm{cm^{-2}}$, or $6.7 \times 10^{-12}\,\mathrm{mol\,cm^{-2}}$. This is negligible compared with the integrated ozone deposition, which we estimate to be at least in the order of $10^{-8}\,\mathrm{mol\,cm^{-2}}$ for the same time period, and which is *not* restricted to sunlit surfaces. Chemical reactions of metastable oxygen are strictly confined to the outermost leaf surface, because the penetration depth of $O_2(^1\Delta_g)$ is limited by its lifetime of only a few μs in aqueous solutions.[46] The deposition rate to the surface of a small airborne particle (e.g. a pollen), to which equations (17)–(20) do not apply, exhibits a stronger dependence on γ, and may be significantly larger than the deposition rate to a flat surface.

SUMMARY AND CONCLUSIONS

Processes leading to the formation of $O_2(^1\Delta_g)$ in the troposphere have been quantified in view of the potential impact of metastable oxygen on plants. The most important source is direct absorption of sunlight by oxygen in collision-induced continuous bands at 480, 580, 630, 1065, and 1270 nm, which provide a source strength of $1.6 \times 10^9\,\mathrm{cm^{-3}\,s^{-1}}$ at a solar zenith angle of 40°. Minor sources are the photolysis of ozone and energy transfer from NO_2 which is electronically excited by sunlight. The ambient $O_2(^1\Delta_g)$ concentration in the sunlit tropospheric boundary layer amounts to approximately $1.7 \times 10^8\,\mathrm{cm^{-3}}$. The reaction rates of $O_2(^1\Delta_g)$ with atmospheric trace gases are orders of magnitude inferior to the reaction rates of OH radicals and ozone. Formulas have been presented for calculating the net flux of $O_2(^1\Delta_g)$ to vegetation surfaces. For sticking coefficients γ in excess of 10^{-4}, the flux is essentially diffusion controlled and independent of γ. $O_2(^1\Delta_g)$ molecules which have been created more than a few mm away from a surface cannot interact with the surface. The deposition of $O_2(^1\Delta_g)$ to leaf surfaces which are directly exposed to sunlight has been calculated. It is negligible compared with the deposition of ozone, which is far more reactive than $O_2(^1\Delta_g)$, and can also be deposited on shaded surfaces above which the concentration of $O_2(^1\Delta_g)$ is negligibly low.

Note added in proof: On the basis of a recent calculation (Bucholz, A., Skinner, W.R., Abreu, V.J. and Hays, P.B. *Planet. Space Sci.*, 34, 1031–1035, (1986)) the excitation rate of $O_2(^1\Sigma_g^+)$ by absorption of sunlight amounts to $1.5 \times 10^9 \text{cm}^{-3} \text{s}^{-1}$ at ground level (z = 45°), which is comparable with process A2 in Table II.

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