Chemical Events in the Atmosphere and their Impact on Environment
Pontifical Academy of Sciences, *Scripta Varia* 56, Vatican City 1985
www.pas.va/content/dam/accademia/pdf/sv56/sv56-wiesenfeld.pdf

OXYGEN CYCLE IN THE ATMOSPHERE

JOHN R. WIESENFELD
Department of Chemistry, Cornell University, Baker Laboratory
Ithaca, New York 14853 U.S.A.

The introduction of oxygen into the Earth's atmosphere is, on a geological timescale, only a relatively recent phenomenon. It now seems clear that outgassing of the young Earth resulted in the formation of a mildly reducing atmosphere, consisting in the main of N_2 and CO_2 (Abelson, 1966). An earlier hypothesis (Urey, 1952) requiring the existence of a strongly oxidizing paleo-atmosphere containing significant quantities of CH_4 and NH_3 now appears untenable. The atmospheric lifetimes of such materials would be too short for their chemistry to play an important role in, for example, the eventual synthesis of amino acids either through photochemistry, in electric discharges, or on hot surfaces.

Biological sources account for the overwhelming fraction of O_2 found in the present atmosphere. Considerable controversy and no small degree of uncertainty surrounds the mechanism of oxygen formation in the *prebiological* atmosphere (Levine *et al.*, 1981; Levine, 1982). The attractive suggestion that the photodecomposition of H_2O by vacuum ultraviolet light in

$$H_2O + h\nu \rightarrow H_2 + 1/2\, O_2 \qquad (1)$$

fails to take account of the many chemical processes which lead to the reoxidation of H_2 with subsequent water formation. Indeed, the rate of O_2 formation following (1) actually depends on the rate of H_2 gravitational escape from the atmosphere and not the photolysis rate itself. An alternative chemical process involving the disproportionation of OH radicals

$$OH + OH \rightarrow H_2O + O \qquad (2)$$

must compete with other reactions of OH that yield H_2O, *viz,*

$$OH + H_2S \rightarrow H_2O + SH$$

$$OH + CH_4 \rightarrow H_2O + CH_3 .$$

The actual quantity of O_2 predicted on the basis of model calculations appears to vary wildly depending on the assumed gas phase chemistry, the role of O_2 reactions with Fe^{2+} in the early oceans, and the transport mechanism. Oxygen levels reported as the result of recent theoretical calculations (Levine, 1982) range between 10^{-14} and 10^{-1} of the present atmospheric level (PAL). Enhanced levels of solar activity would have significantly increased the prebiological O_2 levels. At the current level of uncertainty, relatively little can be deduced about the actual chemical mechanism responsible for fixing the O_2 density prior to the establishment of photosynthetic sources of oxygen.

The development of oxygen in the early atmosphere led to a concomitant buildup in the ozone density and hence a significant decrease in middle ultraviolet radiation impinging upon the Earth's surface. As will be discussed in detail below, ozone arises following the photodissociation of O_2 in the far ultraviolet below 242 nm,

$$O_2 (X^3\Sigma^-_g) + h\nu (\lambda < 242 \text{ nm}) \rightarrow O (^3P_J) + O (^3P_J) \qquad (3)$$

followed by the combination of atomic and molecular oxygen,

$$O (^3P_J) + O_2 (X^3\Sigma^-_g) + M (N_2, O_2) \rightarrow O_3 + M . \qquad (4)$$

The dependence of the ozone column density upon the oxygen level is a matter of considerable interest for it will fix the degree of UV-B penetration through the atmosphere and hence presumably would establish the surface conditions for the emergence of life onto land from the sea during the Silurian period (Berkner and Marshall, 1965). Recent calculations seem to suggest that the column density of O_3 exceeded 10% of its current value even at O_2 densities as low as 1% PAL (Levine *et al.*, 1981). This behavior (Figure 1) at relatively low O_2 densities is attributed to the increased penetration of actinic radiation capable of O_2 photolysis in (3) and the enhanced rate of N_2O photodissociation

$$N_2O + h\nu (\lambda < 341 \text{ nm}) \rightarrow N_2 (X^1\Sigma^+_g) + O(^1D_2)$$

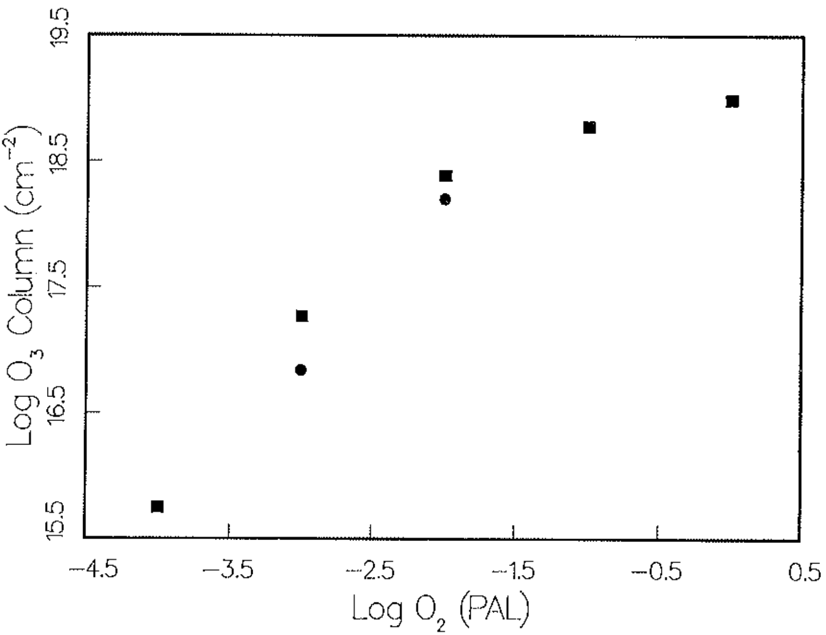
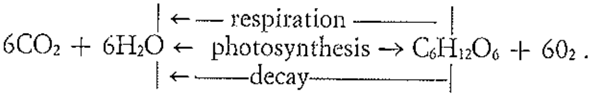


FIG. 1. Dependence of ozone column density upon level of O_2 in early atmosphere in the presence (●) and absence (■) of chlorine chemistry. [Source: Levine, 1982].

which would decrease the NO density (and hence rate of catalytic O_3 destruction) in the upper atmosphere. Clearly all such model calculations of the early atmosphere depend critically upon currently unknown parameters such as the prebiological rate of N_2O formation; they do however provide an interesting backdrop against which to examine the current role of oxygen chemistry in the atmospheric environment.

The O_2 level of the present atmosphere is fixed primarily by the biological photosynthesis/respiration cycle which converts CO_2 and O_2,



$$\begin{array}{l} \qquad\qquad\quad |\leftarrow \text{— respiration —} | \\ 6CO_2 + 6H_2O \leftarrow \text{photosynthesis} \rightarrow C_6H_{12}O_6 + 6O_2 . \\ \qquad\qquad\quad |\leftarrow \text{—decay—} | \end{array} \qquad (5)$$

A minute fraction of the O_2 produced in (5) is 'fixed' in association with deep ocean sedimentation of organic material. Consumption of O_2 by combustion of the Earth's entire inventory of recoverable hydrocarbons (*ca.* 10^{19} gm) would only result in a 2% decrease in the atmospheric O_2

level. Whether the concomitant production of CO_2 would lead to significant changes in climate and hence environment is quite another (and far more worrying) matter.

In contrast to the case of atmospheric O_2, the continued integrity of the stratospheric ozone layer remains a matter of intense concern to environmental chemists. Here, we must deal with the characterization of the photochemical system in which O_2 photolysis (3) followed by recombination (4) forming ozone is balanced by parallel, largely catalytic cycles involving trace constituents. Detailed discussions of these reactive cycles are presented in other contributions to these proceedings. This paper will primarily be concerned with a discussion of the photodissociation of O_2 and O_3 as well as the chemistry of the reactively labile electronically excited oxygen atoms which result from such photolysis processes. Particular emphasis will be placed on the details of energy flow and deposition both following photodissociation and in bimolecular collisions. Of special interest will be the characterization of elementary reactions that may profitably be included in the further development of refined models of atmospheric chemistry.

Photodissociation of Molecular Oxygen

The entire cycle of odd oxygen chemistry in the upper atmosphere is initiated by the photolysis of O_2 below 242 nm, the thermochemical threshold (Table 1) for dissociation into ground state atomic oxygen formation in

$$O_2\,(X^3\Sigma^-_g) + h\nu \rightarrow O\,(^3P_J) + O\,(^3P_J)\,. \tag{3}$$

Several laboratory measurements of the total absorption cross-section for the critical $O_2\,(A^3\Sigma^+_u \leftarrow X^3\Sigma^-_g)$ Herzberg continuum have been reported

TABLE 1 - Threshold wavelengths for photolytic production of oxygen atoms from O_2.

Atomic products	Wavelength (nm)
$O\,(^3P_J) + O\,(^3P_J)$	242.4
$O\,(^3P_J) + O\,(^1D_2)$	175.0
$O\,(^3P_J) + O\,(^1S_0)$	133.2

(Ditchburn and Young, 1962; Shardanand, 1969; Hasson and Nicholls, 1971; Ogawa, 1971; Shardanand and Rao, 1977). Special attention has been focussed on the region 200-230 nm for it is in this range that the solar flux in the stratosphere is not so strongly attenuated by mesospheric O_2 or stratospheric O_3 (Nicolet, 1980). Severe experimental problems make the measurement of $\sigma_{O_2}(\lambda)$ (Figure 2) especially difficult. The exceptionally low cross-section for this transition, *ca.* 10^{-24} cm^2, can be overcome by the use of long pathlengths, but not high pressures, for the Herzberg continuum intensity displays a strong pressure dependence, presumably due to collisional perturbation and/or dimer formation. The end result is that the observed cross-section, $\sigma_{Total}(\lambda)$, represents the sum $\sigma_{O_2}(\lambda) + \sigma_{O_2-O_2}(\lambda)\, n_{O_2}$. As a consequence, experimental determination of $\sigma_{O_2}(\lambda)$ requires that measured values of $\sigma_{Total}(\lambda)$ must be extrapolated to zero oxygen pressure. This, in turn, appears to introduce significant random uncertainty and perhaps systematic error in the final result, for dimer absorption dominates at $P_{O_2} > 500$ torr, the pressure

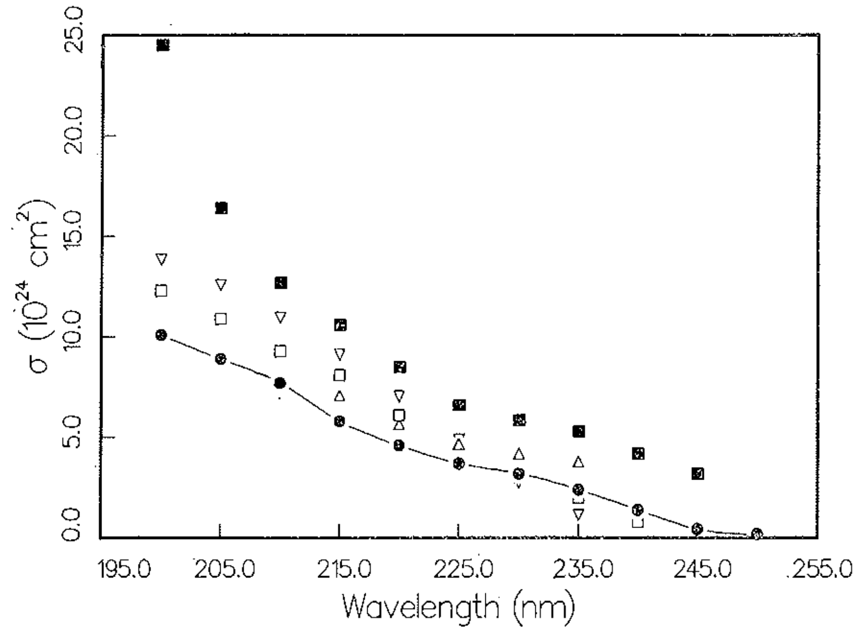


FIG. 2. Cross section for oxygen absorption in the Herzberg continuum region above 200 nm. [Sources: (☐) Ditchburn and Young, 1962, (■) Shardanand, 1969, (△) Ogawa, 1971, (▽) Hasson and Nicholls, 1971, (●) Shardanand and Rao, 1977].

at which absorption by O_2 over a one meter pathlength would be 1%! The trend in $\sigma_{O_2}(\lambda)$ with time appears to be downward, with the most recently reported laboratory values being smaller by at least 30% than earlier results.

Field studies of solar irradiance in the stratosphere suggest that even the latest values of $\sigma_{O_2}(\lambda)$ derived from the laboratory studies are still too large by a factor of at least 30%. The most recent estimates obtained for $\sigma_{O_2}(205)$ using balloon-borne spectrometers (Herman and Mentall, 1982; Frederick and Mentall, 1982; Anderson and Hall, 1983) are in the range $6.6\text{-}7.0 \times 10^{-24}$ cm^2 in contrast to the laboratory values for this wavelength which are between 8.9 and 16.4×10^{-24}. This discrepancy leads not only to difficulties in calculating the rate of odd oxygen formation but also to uncertainties in the rate of trace constituent photolysis in the narrow atmospheric window between the peak of the Hartley continuum absorption by O_3 near 250 nm and the intense Schumann-Runge bands of O_2 below 200 nm. A recent model calculation of stratospheric chemistry (Froidevaux and Yung, 1982) suggests a reduction in $\sigma_{O_2}(\lambda)$ by 0.6 would lead to a significant decrease in the computed concentrations of N_2O, CF_2Cl_2, and $CFCl_3$ in the upper stratosphere without a corresponding change in CH_4, H_2 or CO, none of which are photodissociated by actinic radiation in the region near 200 nm.

Recent measurements of the line strength of the Schumann-Runge $B^3\Sigma^-_u \leftarrow X^3\Sigma^-_g$ (Yoshino *et al.*, 1983) transitions have resolved outstanding uncertainties concerning the intensity of this structured absorption region. The determination of a quantitatively reliable cross-section in a region of continuous absorption is more challenging. In view of the importance of (3) to the generation of odd oxygen species in the upper stratosphere and, potentially, the partial restoration of ozone column density resulting from enhanced O_2 dissociation at lower altitudes in response to O_3 destruction above, it seems imperative that a reliable value of $\sigma_{O_2}(\lambda)$ be obtained. Laser-based techniques for maesurement of weak absorption signals should be considered in order to perform the required determination at low pressures where dimer absorption is not significant and over pathlengths that are of reasonable dimension, multipass cells being limited in utility by the mediocre performance of high reflectance coatings at 200 nm.

Turning to the second process of importance to ozone formation, the recombination of atomic oxygen with O_2 in

$$O(^3P_J) + O_2(X^3\Sigma^-_g) + M(N_2, O_2) \rightarrow O_3 + M \qquad (4)$$

has been studied by a variety of experimental techniques in order to obtain what now seem to be reliable kinetic parameters over the range of atmospherically important temperatures and pressures (Huie *et al.*, 1972; Klais *et al.*, 1980; Lin and Leu, 1982). Reaction (4) is well within the third-order regime at $P_{N_2} < 200$ torr; the most recent experimental studies have been carried out using highly direct detection of O (^3P_J) by resonance fluorescence or absorption at the 130 nm transition, $3^3S_1 \leftarrow 2^3P_J$, following vacuum ultraviolet photolysis of O_2. The results obtained in this manner (Table 2) seem to be in reasonable agreement, especially near 298 K. Greater discrepancies exist over the broad temperature range of stratospheric relevance and further examination of the low temperature kinetics may be warranted. Because third-order reactions such as (4) are relatively slow, significant corrections must be made for diffusion of O (^3P_J) out of the reaction zone as well as for reactions with trace contaminants such as O_3. The formation of the ozone product of (4) has been monitored using time-resolved absorption spectroscopy (Kleindienst, *et al.*, 1980). From these observations it was concluded that over half of the O_3 was formed in a low-lying metastable state, possibly $^3B_2$. This observation would be of atmospheric significance if these metastable O_3 molecules could undergo reaction prior to being quenched to the ground state.

Photodissociation of O_3

The wavelength thresholds for O_3 photodissociation into specific atomic and molecular fragments are presented in Table 3. There are two

TABLE 2 - Kinetic parameters, $k_4 = A \exp(C/T)$, describing three-body reaction of $O + O_2 + M \rightarrow O_3 + M$.

M	A (cm^6 molecule^{-2} sec^{-1})	C (K)	Reference
N_2	5.04×10^{-35}	724	Lin and Leu, 1982
	8.82×10^{-34}	575	Klais *et al.*, 1980
	1.82×10^{-35}	995	Arnold and Comes, 1979
O_2	6.40×10^{-35}	663	Lin and Leu, 1982
	2.15×10^{-34}	345	Klais *et al.*, 1980
	6.75×10^{-35}	635	Arnold and Comes, 1979

TABLE 3 - Threshold wavelengths (nm) for photolytic production of oxygen atoms and molecules from O_3.

O	O_2 $X^3\Sigma^-_g$	$a^1\Delta_g$	$b^1\Sigma^+_g$
^3P_J	1180	611	463
$^1D_2$	411	310	266
$^1S_0$	237	200	180

main regions of absorption by O_3 which are of interest to atmospheric photochemists. The first of these, the Chappuis bands, occurs in the visible region between 450 and 800 nm with a peak cross-section of only $\sigma_{O_3}(600) = 5.2 \times 10^{-21}$ cm^2. That the peak of this $1^1A_2 \leftarrow 1^1A_1$ transition coincides roughly with the threshold for formation of $O(^3P_J) + O_2(^1\Delta_g)$, might suggest that this channel plays a significant role in the photodissociation process, *viz.*

$$O_3 + h\nu \rightarrow O(^3P_J) + O_2(^1\Delta)\,. \tag{6}$$

However, the total quantum efficiency for O_3 destruction following photolysis is not observed to depend upon the wavelength of actinic radiation in this region (Castellano and Schumacher, 1962). Rather, the value of Φ_{-O_3} is measured as 2 both above and below the 611 nm threshold. In addition, lovely observations of the O_2 product of O_3 photolysis in the Chappuis bands using Coherent Anti-Stokes Raman Spectroscopy (CARS) have confirmed (Valentini, 1983) that it is only $O_2(X^3\Sigma^-_g)$ which is formed in

$$O_3 + h\nu \rightarrow O(^3P_J) + O_2(X^3\Sigma^-_g)\,, \tag{7}$$

process (6) playing no observable role. These same experimental studies revealed that the vibrational distribution of the $O_2(X^3\Sigma^-_g)$ fragment produced in (7) peaks in $v'' = 0$ with an apparent population inversion occurring between $v'' = 3$ and $v'' = 2$. The rotational state distributions peak in the region $30 < J'' < 38$, with a shift observed toward lower J'' in the higher vibrational levels. About 65% of the total available dissociation energy appears in relative translation of the fragments, the internal energy being roughly equally divided between vibration and rotation. Neither a simple impulsive nor a statistical model yields population distributions that are in satisfactory agreement with the observed results.

The ultraviolet Hartley band of O_3 spans the region 200-320 nm. This strong absorption feature, σ_{O_3} (255) = 1.1×10^{-17} cm^2, is associated with the $1^1B_2 \leftarrow 1^1A_1$ allowed transition arising from the charge transfer of the pπ orbital of the central oxygen to that of a terminal atom (Hay and Dunning, 1977). The identity of the absorption transition has been confirmed by determining the angular distribution of the photofragments of the dissociation at 266 nm (Fairchild *et al.*, 1978). The 1^1B_2 excited state correlates with electronically excited products,

$$O_3(1^1A_1) + h\nu \rightarrow O_3(1^1B_2) \rightarrow O(1^1D_2) + O_2(a^1\Delta_g)\,. \tag{8}$$

This is in good agreement with classical photochemical measurements which clearly demonstrated that the large quantum yield for ozone removal following excitation in the Hartley band was consistent with reactions of the electronically excited photofragments and subsequent chemical products (Wayne, 1969).

We next examine the details of energy deposition in the fragments of O_3 photodissociation in the Hartley continuum. Recent time-of-flight studies (Sparks *et al.*, 1980) of the internal energy distribution in the $O_2(a^1\Delta_g)$ product of (8), have revealed that over 50% of the products are formed in $v'' = 0$, 24% in $v'' = 1$, 12% in $v'' = 2$ and 7% in $v'' = 3$. Rotational excitation accounts for another 17% of the available energy in $v'' = 0$. These results can be rationalized on the basis of an impulsive release of energy on the excited state potential surface with a weak minimum at an elongated bond length, but similar bond angle as the ground state.

CARS measurements have revealed an unexpected propensity for population of the even rotational levels in $v'' = 0$ and $v'' = 1$ (Moore *et al.*, 1983). No explanation based on symmetry or dynamical constraints for this interesting observation is immediately forthcoming. Further elucidation of the dynamics of (8) will probably require refinement of our understanding of the role of symmetry conservation in the dissociation of triatomic molecules.

Because of its importance to the chemistry of both the troposphere and stratosphere, it is the wavelength dependence of the $O(^1D_2)$ yield which is of greatest interest to the atmospheric chemist. From the relative yield, $\Phi_{O(^1D_2)}(\lambda) = O(^1D_2)/\{O(^1D_2) + O(^3P_J)\}$, the absorption cross-section, $\sigma_{O_3}(\lambda)$, and the solar flux, $F(\lambda)$, the rate coefficient for $O(^1D_2)$ production may be calculated directly,

$$J_{O(^1D_2)} = \int \sigma_O(\lambda)\ \Phi_{O(^1D_2)}(\lambda)\ F(\lambda)\ d\lambda\ .$$

Until quite recently, direct measurements of $\Phi_{O(^1D_2)}(\lambda)$ were limited by the very real experimental difficulties associated with the highly efficient deactivation of $O(^1D_2)$ by O_3, as well as the need to provide a sensitive probe for atomic oxygen atoms in the ground ^3P_J state as well as in the electronically excited $^1D_2$ state. The development of resonance spectroscopic techniques for time-resolved detection of $O(^3P_J)$ has permitted monitoring of this state at densities of *ca.* 10^{12} cm^{-3} with an instrumental bandwidth in excess of 10 MHz. When combined with the use of high intensity photolysis sources such as the excimer lasers and frequency quadrupled Nd/YAG, it has proved possible to measure directly the yield of $O(^1D_2)$ and $O(^3P_J)$ at several discrete wavelengths in the middle ultraviolet.

Two basic schemes have been utilized in the direct measurement of $\Phi_{O(^1D_2)}(\lambda)$ in the Hartley band region. The first (Brock and Watson, 1980a; Wine and Ravishankara, 1982) permits the use of slower detection methods because the yield of $O(^3P_J)$ following ozone photolysis in the presence of known quenchers of $O(^1D_2)$ (such as N_2) that convert all of the excited atoms to the ground state is compared to that observed when all of the $O(^1D_2)$ is collisionally deactivated by a molecule (e.g., CH_4) that is known to undergo chemical reaction with the excited state. Thus the total oxygen atom yield and that associated with processes (6) and (7) only may be obtained in separate experiments. Although this scheme is conceptually relatively simple, its successful execution requires that the apparatus remain stable over the long times required to achieve good signals for data analysis.

In our laboratory at Cornell, an alternative scheme has been developed (Amimoto *et al.*, 1980; Greenblatt and Wiesenfeld, 1983) in which the magnitude of the $O(^3P_J)$ signal *immediately* following laser photolysis is compared quantitatively to that seen following the deactivation of $O(^1D_2)$ by O_3, a process which is known (Davenport *et al.*, 1972; Amimoto *et al.*, 1978) to yield one ground state atom for each $O(^1D_2)$ deactivated, probably in (Arnold and Comes, 1980 a,b)

$$O\,(^1D_2) + O_3 \rightarrow O_2 + 2O\,(^3P_J) \qquad (9a)$$

$$\rightarrow 2O_2 \qquad (9b)$$

where $k_{9a} = k_{9b}$. The temporal profile of $O\,(^3P_J)$ obtained in these experiments provides an estimate of $\Phi_{O(^1D_2)}(\lambda)$ for each laser pulse. The nonlinear least squares procedures employed to yield the desired photochemical parameter require good signal quality (Figure 3), so tens of thousands of laser pulses are sometimes averaged in order to achieve satisfactory results.

A compendium of $\Phi_{O(^1D_2)}(\lambda)$ values reported to date is presented in Table 4. In the region near the peak of the Hartley continuum, namely at 248 and 266 nm, the yields of $O\,(^1D_2)$ are in the range 0.88-0.94, but certainly not unity as was earlier assumed. The value of $\Phi_{O(^1D_2)}(308)$ is especially important in that it places on an absolute scale the body of *relative* measurements of $\Phi_{O(^1D_2)}(\lambda)$ in the wavelength region above 300 nm which is so important in tropospheric photochemistry (Moortgart and Kudszus, 1978). These had been made using a variety of methods based either on chemical analysis or chemiluminescent detection of photolysis products; all were indirect when compared to the schemes described above. Results were normalized to a value of $\Phi_{O(^1D_2)}(300) = 1.0$. The most recent direct measurements of $\Phi_{O(^1D_2)}(308)$ suggest that a more appropriate value of $\Phi_{O(^1D_2)}(300)$ would be 0.96-0.97. Apparently the yield of $O\,(^1D_2)$ actually *increases* to the long wavelength side of the Hartley band peak.

Several recent studies have centered on the theoretical description of O_3 spectroscopy in the Hartley continuum. Potential energy surfaces for the four $^1A'$ states which play an important role in (8) have been calculated using the generalized valence bond multiconfiguration SCF technique (Hay *et al.*, 1982). Analytic surfaces were fitted to a set of 18 reference configurations for each of these states. The 1^1B_2 surface, upon which occurs the dissociative interaction leading to production of $O\,(^1D_2)$ and $O_2\,(a^1\Delta_g)$, is characterized by an asymmetric equilibrium geometry. The 2^1A_1 state which also correlates with electronically excited products but cannot be accessed by an electric dipole-allowed transition from the ground 1^1A_1 state lies very close in energy to the 1^1B_2. Both of these states are crossed by a repulsive state at an O_2-O bond distance of *ca.* 0.17 nm when the bond angle is 110°. The calculated absorption spectrum in the middle ultraviolet agrees well with that observed experimentally. Dynamics calculations designed to probe the

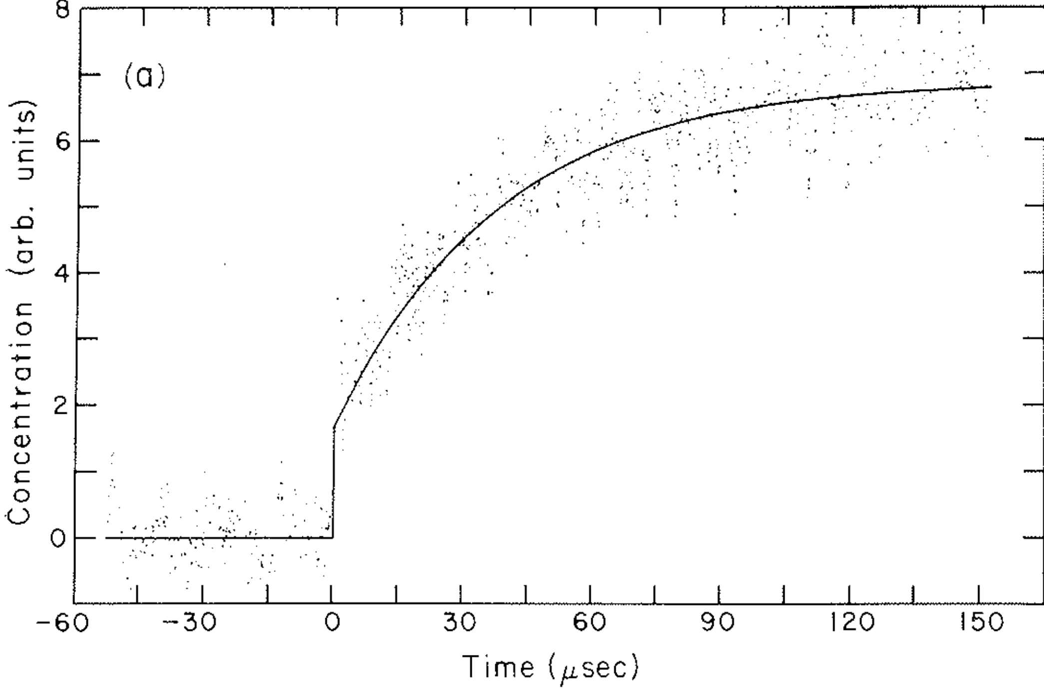


FIG. 3. Transient profile of O(^3P_J) density obtained by monitoring the vacuum ultraviolet atomic resonance fluorescence signal following laser photodissociation of O_3. (a) Photolysis at 308 nm, P_{O3} = 1 mTorr, P_{He} = 5.7 Torr, 40288 averaged. (b) Photolysis at 248 nm, P_{O3} = 1 mTorr, P_{He} = 9.7 Torr, 8192 shots averaged. The solid lines through the points representing non-linear least squares fit to the data. [Source: Greenblatt and Wiesenfeld, 1983].

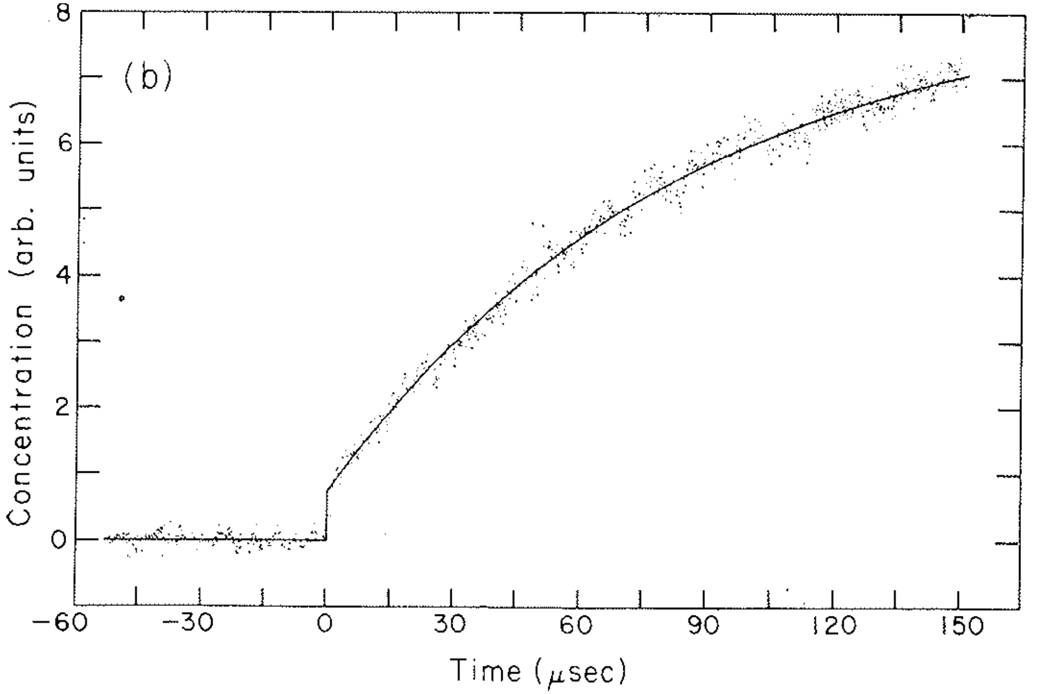


TABLE 4 - Direct determinations of $\Phi_{O(^1D_2)}$ following photodissociation of O_3 in the Hartley band.

Wavelength (nm)	$\Phi_{O(^1D_2)}$	
308	0.79 (0.02)	Greenblatt and Wiesenfeld, 1983
266	0.88 (0.02)	Brock and Watson, 1980
266	*ca.* 0.90	Sparks *et al.*, 1980
248	0.94 (0.01)	Greenblatt and Wiesenfeld, 1983
248	0.91 (0.03)	Wine and Ravishankara, 1982
248	0.85 (0.02)	Amimoto *et al.*, 1980

Numbers in parentheses represent reported errors.

distribution of internal energy in the fragments of photodissociation have not yet been reported. The observed lack of dependence of $\Phi_{O(^1D_2)}(\lambda)$ in the region 248-300 nm seems difficult to explain in view of the calculated curve crossing, for the velocity of system passage through the region of nonadiabaticity near 0.17 nm would vary widely depending upon the wavelength of actinic radiation. The J distribution of the O (^3P_J) produced in O_3 photolysis at 266 nm has been determined in our laboratory using resonance enhanced multiphoton ionization techniques (Figure 4). These results (Sivaram and Wiesenfeld, in progress) suggest that the spin-orbit levels are formed in a statistical distribution, the population ratios being roughly in proportion to the degeneracies of the $J = 0$, 1, and 2 levels. Such information may shed further light on the nature of the excited state potential surfaces governing O_3 photodissociation in the gas phase.

A relatively simple spectroscopic model of O_3 absorption in the middle ultraviolet has been proposed (Adler-Golden *et al.*, 1982). This model assumes that the internal energy of an O_3 molecule adds fully to that of the absorbed ultraviolet photon and that the quantum yield of O ($^1D_2$) varies smoothly from zero at some threshold energy (calculated as being 32900 cm^{-1}) to unity 600 cm^{-1} above this threshold. The model, which is quite successful in rationalizing the observed Hartley band spectrum for vibrationally excited O_3, accurately reflects the experimental temperature dependence of the O ($^1D_2$) yield at 313 nm and also predicts a dependence of $\Phi_{O(^1D_2)}(\lambda)$ upon wavelength in the region above 304 nm that is quite similar to that observed in a previous experimental study

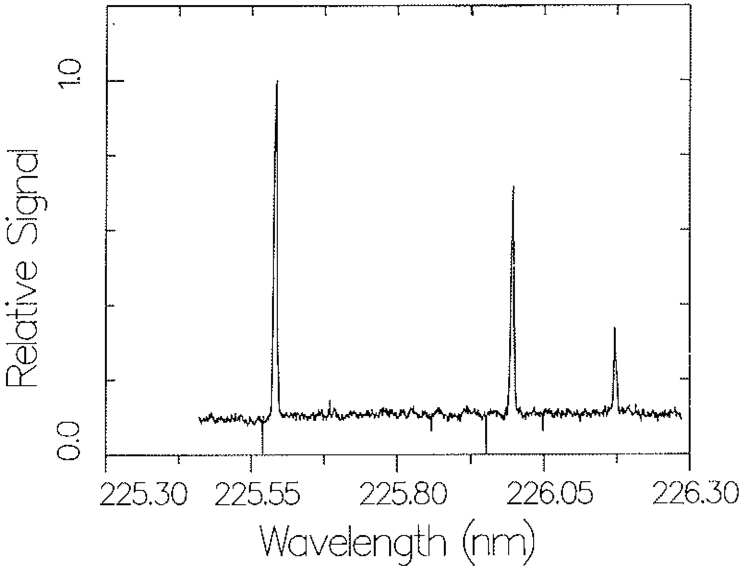


FIG. 4. Resonance enhanced, three-photon spectrum of atomic oxygen, $^3P_{2,1,0}$ observed following excitation of the $3^3P_J \leftarrow 2^3P_J + 2h\nu$ transition in a flow discharge apparatus. Atomic oxygen at a density of *ca.* 10^{13} cm^{-3} was generated in the $N+NO \longrightarrow N_2+O$ reaction.

(Brock and Watson, 1980b). This latter set of observations noted the presence of a pronounced 'tail' in the $O(^1D_2)$ yield which would play an important role in tropospheric chemistry at high solar zenith angles; earlier experiments did not reveal the existence of this absorption feature. The values of $\Phi_{O(^1D_2)}(\lambda)$ at these longer wavelengths seem quite worthy of further experimental and theoretical examination.

Oxygen chemistry

The profusion of reactive atomic and molecular oxygen species (including O_3) present in the atmosphere suggests an important role for these materials in fixing its physical structure and chemical composition. This is, in fact, the case. Other contributions to the present proceedings will describe many of the complex chemical cycles involving oxidizers such as OH, HO_2, O_3, and O that have been identified in both the troposphere and stratosphere. Hydrogen peroxide appears to be responsible for a significant fraction of SO_2 oxidation in the aqueous aerosol, hence contributing strongly to wet deposition of acidic materials. Atomic oxygen and $O_2(a^1\Delta_g)$ react with olefins in polluted air yielding free radicals. In the remainder of this contribution, attention will be focussed upon the pivotal role played by the primary photoproduct of the ultraviolet dissociation of O_3, namely $O(^1D_2)$. Because these highly reactive atoms can either be *physically quenched* to the electronic ground state

$$O(^1D_2) + Q \rightarrow O(^3P_J) + Q^*$$

where Q^* represents internal excitation, or undergo *chemical reaction* to yield distinct chemical products, as in

$$O(^1D_2) + RH \rightarrow OH + R\cdot\ ,$$

the following discussion will be organized along these logical lines (see also, Wiesenfeld, 1982).

The magnetic dipole allowed transition $O(^1D_2) \rightarrow O(^3P_{1,2}) + h\nu$ ($\lambda = 630$ nm) may be observed in the aurora. Below the mesosphere, collision times are short in comparison to the optical lifetime of $O(^1D_2)$ ($\tau = 143$ sec) so bimolecular encounters dominate the removal of excited oxygen atom at these altitudes. The development of sophisticated atmospheric models requires specification of the detailed rate constants for particular deactivation processes. Thus, it becomes necessary not only to know the total rate of $O(^1D_2)$ removal, but also to account for the relative efficiency with which the various possible product species are formed (NASA, 1981). For all deactivators, the relative contributions of quenching and chemical reaction must be assessed. The role of energy transfer should be understood for quenching processes, and the excitation efficiency of the available internal modes of the collision partner determined. In the case of chemical reaction, the high energy of $O(^1D_2)$, $\Delta H^\circ_f = 105$ kcal/mole, often makes necessary the characterization of a potential profusion of reactants. To some extent, such kinetic parameters were obtained from classical chemical experiments carried out in the 1960's (see Schiff, 1972, and Nicolet, 1972), but detailed information has primarily become available over the course of the last decade during which have been developed highly specific diagnostic techniques, often based on laser spectroscopy.

Measurement of absolute rate constants for $O(^1D_2)$ removal requires the application of techniques which permit time-resolved monitoring of either the excited atom or some product. In the earliest of these direct studies (Heidner *et al.*, 1972, 1973), the attenuation of the O ($^1P_1 \leftarrow {}^1D_2$) resonance line at 115 nm was monitored in the vacuum ultraviolet following the broad-band photolysis of ozone in the presence of various deactivators. The bimolecular rate constants for deactivation, k_d, were estimated from the variation in the observed removal rate with collision partner concentration, [D],

$$[O(^1D_2)]_t = [O(^1D_2)]_{t=0} \exp(-k_d[D]t) .$$

This technique required that the observed attenuation signal be corrected for non-linearity induced by the mismatch between the atomic absorption line and the resonance emission from the microwave-powered resonance lamp which was used as the source of the 115 nm radiation. This empirical correction appears to have resulted in a systematic discrepancy between the values obtained in these measurements and those reported in later work in which the temporal progress of the O ($^1D_2$) deactivation process was followed by monitoring either the profile of the weak 630 nm emission (Davidson *et al.*, 1976, 1977; Streit *et al.*, 1976) or the growth in the O (^3P_J) resonance absorption or fluorescence at 130 nm (Amimoto *et al.*, 1979, Wine and Ravishankara, 1981). The later technique also makes possible the estimation of relative quenching efficiencies for specific deactivating molecules because not only the temporal profile but also the magnitude of the O (^3P_J) signal is obtained. The rates of O ($^1D_2$) deactivation by a wide range of molecules have now been reliably measured at room temperature (Table 5), and the temperature effect over the range of stratospheric and tropospheric importance demonstrated to be insignificant.

As noted above, development of reliable atmospheric models requires the elucidation of detailed rate constants for specific deactivation pathways. Presented below is a discussion of the collisional dynamics of O ($^1D_2$) deactivation by molecules of atmospheric interest. Additional species which are not of primary importance to environmental chemistry will also be mentioned in order to illustrate the general behavior of O ($^1D_2$) in gas phase encounters with quenching and reactive substrates.

Nitrogen. The overwhelming fraction of electronically excited oxygen atoms formed in the photolysis of O_3 in the atmosphere are deactivated by collisions with N_2 and O_2, with $k_{N_2}[N_2]/k_{O_2}[O_2] = 2.4$. This de-

TABLE 5 - Overall rate constants and quenching efficiencies for deactivation of $O(^1D_2)$ as determined at Cornell by laser photolysis-resonance absorption spectroscopy.

Deactivator	$10^{10} \times k_d$ (cm^3 molecule^{-1} sec^{-1})		k_q/k_d
O_3	2.4	(0.11)	0.0
N_2	0.24	(0.01)	1.0
O_2	0.42	(0.02)	1.0
N_2O	1.2	(0.1)	0.0
CO_2	1.3	(0.1)	1.0
H_2O	1.9	(0.3)	0.0
CH_4	1.6	(0.1)	0.0
CH_3F	1.4	(0.1)	0.25
CHF_3	0.084	(0.008)	0.75
CF_4	0.0018	(0.0001)	1.0
CH_3Cl	2.1	(0.2)	<0.1
CH_2Cl_2	2.7	(0.2)	<0.1
$CHCl_3$	3.0	(0.2)	0.1
CCl_4	3.5	(0.3)	0.15
$CFCl_3$	2.4	(0.2)	0.15
CF_2Cl_2	1.4	(0.2)	0.15
CF_3Cl	1.12	(0.02)	0.50

Numbers in parentheses represent errors.
References: Amimoto *et al.*, 1978, 1979; Force and Wiesenfeld, 1981.

activation accounts for a significant degree of heating in the stratosphere when the energy released in

$$O(^1D_2) + N_2 \rightarrow O(^3P_J) + N_2(v'', J'') \qquad (10)$$

is eventually degraded into translation probably via the efficient self-relaxation of N_2

$$N_2(v'' = n) + N_2(v'' = 0) \rightarrow N_2(v'' = n-1) + (v'' = 1)$$

and the far slower

$$N_2(v'' = 1) + M \rightarrow N_2(v'' = 0) + M\,.$$

The efficiency of electronic-to-vibrational energy transfer in (10) is in some doubt, the only measurement reported to date suggesting that *ca.* 40% of the available 45 kcal/mole is converted into vibration (Slanger and Black, 1974). However, in the related deactivation process,

$$O(^1D_2) + CO \rightarrow O(^3P_J) + CO(v'', J'') \tag{11}$$

small signal absorption measurements using a tunable laser probe beam (Lin and Shortridge, 1974; Shortridge and Lin, 1976) revealed that only 21% of the electronic quantum in the excited atom was transferred to CO.

Processes such as (10) and (11) have been treated theoretically using models in which long-lived intermediates (N_2O and CO_2, respectively) are formed as the result of collisional encounters between $O(^1D_2)$ and the quencher (Tully, 1974; Zahr *et al.*, 1975). These intermediate species are strongly bound, the ground electronic state of the molecules correlating with the diatomic and $O(^1D_2)$, not the lower-lying ^3P_J ground state. Multiple traversals of the region of non-adiabatic interaction between the singlet and triplet state, the latter correlating with $O(^3P_J)$, can occur during the long lifetime (in excess of 10^4 vibrational periods) of the collision intermediate. Thus, even relatively weak coupling between the two surfaces can, given enough opportunity, result in a quenching efficiency which is quite high (roughly corresponding to one quenching event for every 5-10 gas kinetic collisions). That the lifetime of the collision complex is relatively long is confirmed by the observation of a distribution of vibrational energy in the CO product of (11) which would be expected by a statistical partitioning of energy in the CO_2 intermediate complex.

The collisional deactivation of $O(^1D_2)$ by N_2 (and O_2 as well) will result in the formation of *translationally* excited $O(^3P_J)$ atoms. These will, through further collisions with the major constituents, become thermalized to the ambient temperature. However, it has been recognized (Logan and McElroy, 1977), that, at any given instant, there must exist a distribution of oxygen atom velocities which is certainly not thermal. Indeed, the density of energetic oxygen atoms arising from (10) is quite comparable to that of $O(^1D_2)$ especially in the lower atmosphere where direct photolysis of O_3 in the Chappuis band in (3) gains in relative importance. The chemistry of thermally excited atoms is only beginning to be explored and we can expect to develop a significantly better understanding of such interesting processes in the near future.

Oxygen. The deactivation of $O(^1D_2)$ by O_2 is interesting for it offers several exoergic spin-conserving pathways leading to electronic excitation of the collision partner,

$$O(^1D_2) + O_2(X^3\Sigma^-_g) \rightarrow O(^3P_J) + O_2(b^1\Sigma^+_g) \qquad (12)$$

$$\rightarrow O(^3P_J) + O_2(a^1\Delta_g) \qquad (13)$$

in parallel with the quenching pathway analogous to (10) and (11)

$$O(^1D_2) + O_2(X^3\Sigma^-_g) \rightarrow O(^3P_J) + O_2(X^3\Sigma^-_g, v'', J'')\,. \qquad (14)$$

Process (12) is probably of atmospheric interest because the subsequent deactivation of $O_2(b^1\Sigma^+_g)$ by O_3

$$O_2(b^1\Sigma^+_g) + O_3 \rightarrow 2O_2(X^3\Sigma^-_g) + O(^3P_J) \qquad (15)$$

is both relatively fast, $k_{15} = 2 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}, and efficient in destroying O_3, roughly 25-50% of the deactivating collisions resulting in decomposition (Slanger and Black, 1979). This may be contrasted with a similar dissociative deactivation of the lower-lying $a^1\Delta_g$ state of O_2 which proceeds with a rate constant 10^4 X smaller than k_{15}.

A variety of experimental techniques has been applied to the study of $O(^1D_2)$ deactivation by O_2. The total yield of atomic oxygen following (12) followed by (14) has been determined to be in the range 0.5-0.6 (Slanger and Black, 1979; Amimoto and Wiesenfeld, 1980), which suggests that $0.6 < k_{12}/k_{O_2} < 1.0$. On the basis of these measurements, it has been concluded that these processes may play a role in O_3 destruction at high altitudes, reducing its density by as much as 12%.

Carbon Dioxide. Collisional deactivation of $O(^1D_2)$ by CO_2 is intriguing from a number of different viewpoints. Chemical reaction to yield CO and $O_2(a^1\Delta_g)$

$$O(^1D_2) + CO_2(X^1\Sigma^+_g) \rightarrow CO\,X(^1\Sigma^+) + O_2(a^1\Delta_g) \qquad (16)$$

is both highly exothermic and conservative of electronic spin and orbital angular momentum. Yet experiments clearly demonstrate (Shortridge and Lin, 1975; Amimoto *et al.*, 1979) that $k_{16}/k_{CO_2} \ll 0.01$, i.e., the deactivation proceeds entirely by physical quenching and not chemical reaction, albeit at a rate essentially identical to the rapid reaction of $O(^1D_2)$ with N_2O. This behavior, which is all the more striking because N_2O and CO_2 are isoelectronic, has been rationalized (Wiesenfeld, 1977) in terms of *diabatic* correlations of reactants with high-lying product states, in particular those arising from the interaction of *two* $O(^1D_2)$. Avoided crossings between the states correlating with reactants and those correlating with low-lying molecular excited states of N_2O (such as $^3\Sigma^+$ and $^3\Delta$) occur at thermally accessible energies. Because no such low-lying states exist in CO_2, there is a substantial barrier to formation of products.

That the rates of $O(^1D_2)$ deactivation by N_2O and CO_2 are similar is fortuitous, the high efficiency of quenching by CO_2 arising from the intermediacy of a long-lived CO_3 complex, the existence of which can be inferred from isotope scrambling studies (Baulch and Breckenridge, 1966). Excitation of the internal modes of CO_2 following

$$O(^1D_2) + CO_2(000) \rightarrow O(^3P_J) + CO_2(mnp) \qquad (17)$$

can be monitored by observation of the infrared emission at 4300 nm following laser photolysis of O_3/CO_2 mixtures (Robertshaw and Smith, 1980). This emission arises from the CO_2 (mnp → mnp-1) transition. Insertion of a CO_2 sample between the photolysis cell and infrared detector selectively removes the fundamental emission, 001 → 000, even at low pressures, while use of higher CO_2 pressures removes the 011→010 contribution as well. Preliminary measurements carried out in our laboratory (Greenblatt, 1983) suggest strongly that formation of either the 001 or 011 states is quite inefficient; electronic-to-vibrational energy transfer appears to strongly favor deposition of energy in higher-lying states. This is somewhat surprising, for models based on a statistical distribution of energies in the CO_3 intermediate would predict substantial population of the lowest-lying states. Interestingly the vibrational population distribution of the CO_2 resulting from (17) seems to be quite similar to that observed (Moore *et al.*, 1983) following the deexcitation by CO_2 of translationally excited hydrogen atoms with energies quite similar to that of the electronic quantum in $O(^1D_2)$. Whether the mechanisms of these two seemingly different interactions are similar remains to be determined.

Nitrous Oxide. With N_2, attention is turned to those molecules which undergo chemical reaction with $O(^1D_2)$. Specifically, it is the formation of NO in

$$O\,(^1D_2) + N_2O \rightarrow 2NO\,(X^2\pi_i) \qquad (18)$$

which has profound consequences for stratospheric chemistry, the resultant nitric oxide being the catalytic agent primarily responsible for O_3 destruction in the unperturbed atmosphere. Reaction (18) proceeds in competition with

$$O\,(^1D_2) + N_2O \rightarrow N_2\,(X^1\Sigma^+_g) + O_2\,(a^1\Delta g)\,, \qquad (19)$$

the critical ratio k_{18}/k_{N_2O} apparently remaining constant at 0.60 over the atmospheric temperature range (Marx *et al.*, 1979; Voltrauer *et al.*, 1979; Lam *et al.*, 1981). It is not yet completely clear whether there exists any dependence of this ratio upon the kinetic energy of the $O\,(^1D_2)$. The very latest studies discern no such dependence.

The dynamics of (18) have been the subject of considerable recent interest in our laboratory. An earlier study of the NO product energetics following (18) using kinetic absorption spectroscopy (Chamberlain and Simons, 1975) revealed the presence of vibrational levels as high as $v'' = 6$. Approximately one quarter of the overall exothermicity of (18) appeared in product vibration. A long-lived ONNO intermediate complex was inferred. Because of the importance of (18) to stratospheric chemistry, we have been engaged in a detailed examination of the NO product energetics. Photolysis with a KrF laser of an O_3/N_2O mixture leads to production of the $O\,(^1D_2)$ reactant. State-resolved detection of NO is accomplished at some fixed time delay following photolysis (typically in the range 50-2000 nsec) through the use of one-photon enhanced, two-photon laser ionization spectroscopy. This technique involves the generation of tunable far ultraviolet radiation in the region 220-300 nm. Excitation of the $NO\,(A^2\Sigma^+ \leftarrow X^2\pi_i)$ transition and subsequent ionization, $NO^+\,(X^1\Sigma^+) + e^- \leftarrow NO\,(A^2\Sigma^+)$ is detected using a pair of biased electrodes and a charge sensitive amplifier (Figure 5). To date, vibrational levels as high as $v'' = 12$ have been observed (Greenblatt *et al.*, 1983) and significant rotational excitation of product NO detected. Currently, these experimental results are being analyzed in order to provide quantitative information concerning product distributions. We hope to extend these measurements using isotopic labelling to provide detailed, hitherto unavailable information concerning energy flow during the course of (18).

Water. The reaction of $O\,(^1D_2)$ with H_2O proceeds exclusively via

$$O\,(^1D_2) + H_2O \rightarrow 2OH\,(X^2\pi_i)\,, \qquad (20)$$

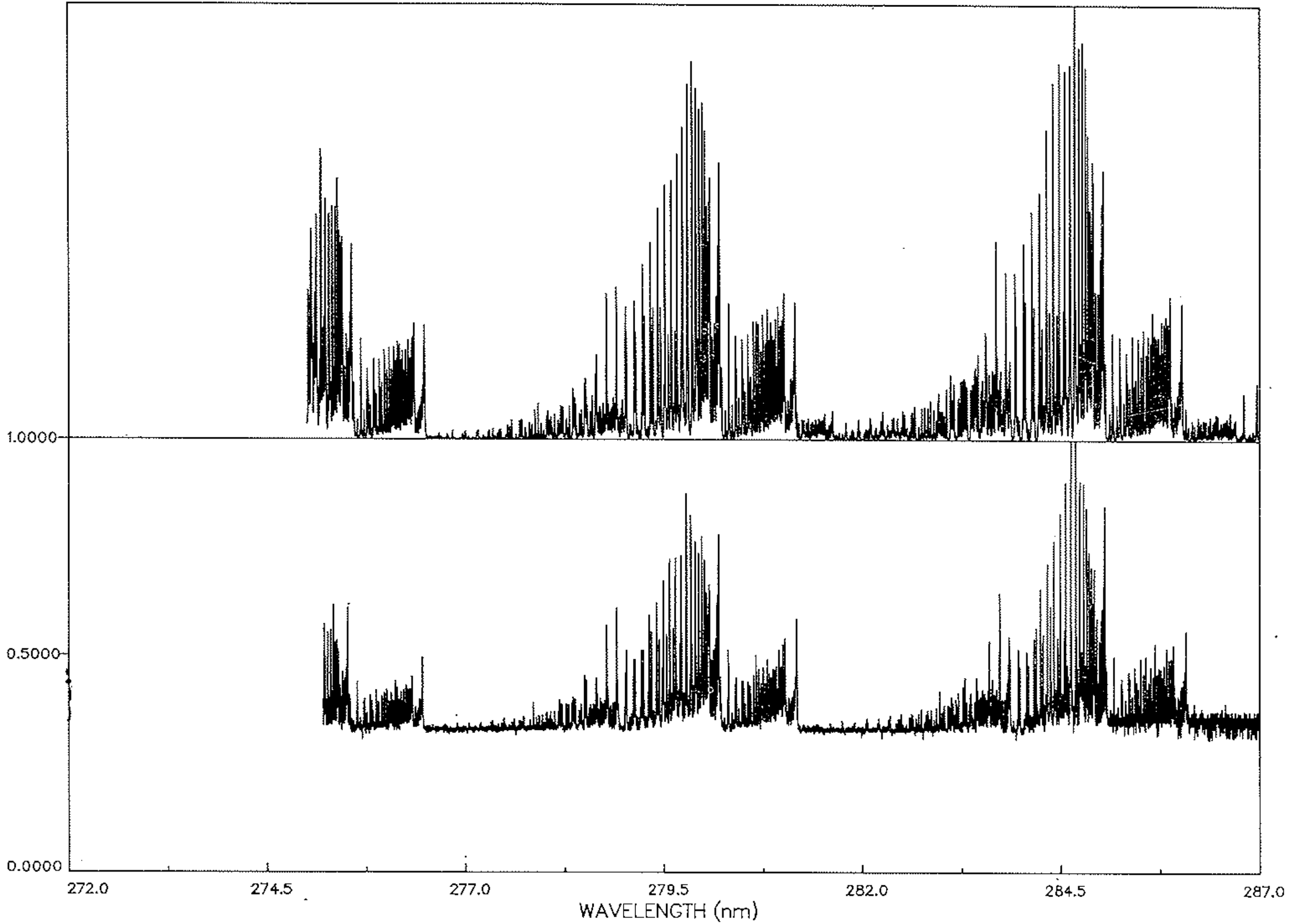


FIG. 5. Resonance enhanced, two-photon spectrum of rotationally relaxed NO produced in reaction (18) initiated by the KrF laser photolysis of an $O_3/N_2O/He$ mixture, the helium having been added to achieve rotational relaxation of the product molecule. This small

both physical quenching and reaction to form $H_2 + O_2$ (Zellner *et al.*, 1980) appearing to play no significant role. Reaction (20) is of special importance in the troposphere where the resultant OH is involved in the oxidation of CO to CO_2 and the formation of free radicals as in

$$OH + RH \rightarrow R\cdot + H_2O \, .$$

The dynamics of (20) have now been subjected to exhaustive examination primarily using laser induced fluorescence (Butler *et al.*, 1981) and laser absorption (Gericke *et al.*, 1981) detection of the $A^2\Sigma^+ \leftarrow X^2\pi_i$ transition in the wavelength region near 300 nm. The absorption technique, although experimentally much more difficult because it requires exceptionally narrow laser linewidths, offers the significant advantage of being capable of detecting ground state vibrational levels that are inaccessible to the fluorescence technique because of predissociation of the excited state. As in the case of the $O(^1D_2) + N_2O$ experiments, the nascent population distribution of the OH product can be detected by careful selection of the time delay between the laser pulse that causes O_3 photodissociation and that which probes the OH spectrum.

Perhaps the most elegant of the experiments carried out on (20) involved the detection of products arising from the reaction of $^{16}O(^1D_2)$ with $H_2{}^{18}O$ (Gericke *et al.*, 1981). Spectroscopic discrimination of the ^{18}OH and ^{16}OH fragments revealed that the 'old' ^{18}OH fragment is primarily formed in the ground vibrational state, while about half of the 'new' ^{16}OH fragments are formed in vibrational states above $v'' = 1$. Rotational state distributions for both fragments are quite similar and over half of the total reaction exoergicity is released in translation. Analysis of the spectroscopic data suggests that (20) proceeds via a direct abstraction of an H atom by $O(^1D_2)$ and does not involve the intermediacy of a long-lived complex as do so many other reactions of electronically excited oxygen atoms.

Organics. The current interest in the reactions of $O(^1D_2)$ with organic molecules stems only in part from the importance of

$$O(^1D_2) + CH_4 \rightarrow OH(X^2\pi_i) + CH_3 \qquad (21)$$

in the stratosphere. In addition, these reactions serve as useful models for a variety of chemical processes involving the isoelectronic carbene, $CH_2(^1A_1)$. By studying the dynamics of reactions involving excited oxygen, it is possible to gain considerable insight into a variety of reaction schemes which are of significance in synthetic organic chemistry.

Turning first to (21) and analogous oxidation reactions involving heavier saturated hydrocarbons, an insertion/elimination mechanism involving the formation of internally excited alcohols, e.g., CH_3OH, seems to play a major role. Direct abstraction of hydrogen is manifest by the observation of bimodal rotational population distributions following (21) (Luntz, 1980). In larger hydrocarbons, alternative routes involving C-C bond scission become important and abstraction appears to become of increasing significance. Because the product of direct abstraction is characterized by a rotational distribution similar to that seen in the reaction of O (^3P_J) with hydrocarbons (Andresen and Luntz, 1980; Luntz and Andresen, 1980), it has been hypothesized that abstractions involving O $(^1D_2)$ actually proceed *via* a triplet surface.

A study of the analogous reaction of O $(^1D_2)$ with alcohols (Goldstein and Wiesenfeld, 1983), while of no direct atmospheric importance, reveals interesting details concerning the reactive characteristics of electronically excited oxygen atoms and provides information about the unimolecular dissociation dynamics of chemically activated molecules. In the generic case of O $(^1D_2)$ reaction with methanol, a variety of reactive pathways are available:

$$O\,(^1D_2) + CH_3OH' \rightarrow HOCH_2OH' \rightarrow OH + CH_2OH' \qquad (22a)$$

$$\rightarrow CH_3O + OH' \qquad (22b)$$

$$\rightarrow CH_2O + H_2O\,. \qquad (22c)$$

Note that (22a-c) represent the interesting case of a spatially symmetric molecule being formed with an initially asymmetric energy distribution. In addition to direct abstraction processes which appear to play no significant role, there is the attack of O $(^1D_2)$ upon the hydroxylic moiety

$$O\,(^1D_2) + CH_3OH' \rightarrow CH_3OOH' \rightarrow CH_3O + OH'\,. \qquad (23)$$

Laser induced fluorescence studies of the O $(^1D_2)$ reaction with alcohols as heavy as butanol revealed that attack upon the O-H site in (23) is favored as would be expected of an electrophillic reagent such as O $(^1D_2)$. From an analysis of the fragmentation pattern following reaction (22), it was concluded that energy redistribution is not complete prior to bond scission. Interestingly the elimination of H_2O from the *gem*-diol in (22c) appears to play no significant role whatsoever. This is in agreement with the observation (Casavecchia *et al.*, 1980) that H_2 is not formed in the reaction of $O\,(^1D_2)$ with CH_4 although hydrogen atoms *are* produced in low yield.

The deactivation of $O\,(^1D_2)$ by halocarbons has been studied in a number of laboratories and both the overall kinetics and reaction mechanisms quite thoroughly examined (Fletcher and Husain, 1976; Davidson *et al.*, 1978; Force and Wiesenfeld, 1981). Both quenching and reaction play significant roles here, although reaction dominates except in the cases of CF_4 and CHF_3. Electrophillic attack upon the chlorine atom may well dominate deactivation of $O\,(^1D_2)$ by the chlorocarbons (Addison *et al.*, 1979). Molecular elimination of hydrogen halides as in

$$O\,(^1D_2) + CH_3F \rightarrow CH_2O + HF \tag{24}$$

must represent a significant pathway because laser emission can be obtained from the diatomic product of this and similar reactions (Burks and Lin, 1978). The extent to which (24) contributes to the overall deactivation of $O\,(^1D_2)$ by the partially halogenated hydrocarbons is not known, nor is it clear how the availability of alternate pathways leading from the chemically activated intermediate complexes, e.g., CH_2FOH in the case of the example, would affect the observed deposition of energy into the OH fragment produced in parallel with the hydrogen halide.

Hydrogen. The reaction of $O\,(^1D_2)$ with H_2 takes place on the ground state potential surface of water, $H_2O\,(^1A_1)$. On the basis of trajectory calculations, (Whitlock *et al.*, 1982) it has been suggested that, as is true for the hydrocarbons, parallel mechanisms involving insertion/elimination and direct abstraction govern the course of this reaction. The observation using laser induced fluorescence spectroscopy (Luntz *et al.*, 1979; Smith and Butler, 1980) of a highly excited, non-Boltzmann rotational distribution and a nearly statistical vibrational distribution for $v'' = 1$ and $v'' = 0$ is consistent with the insertion/elimination

$$O\,(^1D_2) + H_2 \rightarrow HOH \rightarrow OH\,(X^2\pi) + H\,(^2S_{1/2})\,. \tag{25}$$

Laser induced fluorescence cannot detect $OH\,(X^2\pi)$ in vibrational levels above $v'' = 1$ because of the previously mentioned predissociation in the

$A^2\Sigma^+$ state. Calculations predict that the direct abstraction of hydrogen atoms by $O(^1D_2)$ would result in the production of an OH vibrational distribution peaked at $v'' = 2$. Quite recently, highly vibrationally excited products of (25) have, in fact, been detected by observation of infrared chemiluminescence (Butler *et al.*, 1983). Because of the relative facility with which reliable potential surfaces for this simple reaction may be calculated and trajectory studies performed, complete characterization of the products seems most worthwhile.

Summary

The importance of odd oxygen chemistry in fixing the chemical composition and physical structure of the atmosphere has encouraged the application of the most sophisticated methods of modern physical chemistry to its study. Overall rate constants and, to a large extent, chemical branching ratios have now been quite well established for the deactivation of $O(^1D_2)$ and precise yields for its formation following O_3 photolysis in the Hartley continuum are now known. Currently, attention is being focussed on the detailed energetics of these important processes and information concerning the distribution of available energy in photodissociative and reactive fragments is increasingly becoming available. Such data will permit the identification of the mechanisms by which such processes occur and lead to their theoretical description at a microscopic level. To what extent this information will be included in future atmospheric models remains a matter of speculation, but it seems certain that, at the very least, energy transfer mechanisms must be identified in order to understand the various airglow phenomena, radiative energy loss, etc. Much depends on the degree to which chemical reactivity is enhanced by internal excitation, a question which is still being addressed. An especially attractive area for future research is the field characterization of internal energy distributions of small molecules in the atmosphere using laser-based, state-selective analytical methods.

REFERENCES

ABELSON P.H., « Proc. Natl. Acad. Sci. (USA) », *55*, 1365 (1966).

ADDISON M.C., DONOVAN R.J. and GARRAWAY J., « Discuss. Faraday Soc. », *67*, 286 (1979).

ADLER-GOLDEN S.M., SCHWEITZER E.L. and STEINFELD J.I., « J. Chem. Phys. », *76*, 2201 (1982).

AMIMOTO S.T., FORCE A.P. and WIESENFELD J.R., « Chem. Phys. Lett. », *60*, 40 (1978).

AMIMOTO S.T., FORCE A.P., GULOTTY Jr. R.J. and WIESENFELD J.R., « J. Chem. Phys. », *71*, 3640 (1979).

AMIMOTO S.T., FORCE A.P., WIESENFELD J.R. and YOUNG R.H., « J. Chem. Phys. », *73*, 1244 (1980).

AMIMOTO S.T. and WIESENFELD J.R., « J. Chem. Phys. », *72*, 3899 (1980).

ANDERSON G.P. and HALL L.A., « J. Geophys. Res. », *88*, 6801 (1983).

ANDRESEN P. and LUNTZ A.C., « J. Chem. Phys. », *72*, 5842 (1980).

ARNOLD I. and COMES F.J., « Chem. Phys. », *42*, 231 (1979).

ARNOLD I. and COMES F.J., « J. Mol. Struct. », *61*, 223 (1980a).

ARNOLD I. and COMES F.J., « Chem. Phys. », *47*, 125 (1980b).

BAULCH D.L. and BRECKENRIDGE W.H., « Trans. Faraday Soc. », *62*, 2768 (1966).

BERKNER L.V. and MARSHALL L.C., « J. Atmos. Sci. », *22*, 225 (1965).

BROCK J.C. and WATSON R.T., « Chem. Phys. Lett. », *71*, 371 (1980a).

BROCK J.C. and WATSON R.T., « Chem. Phys. », *46*, 477 (1980b).

BUTLER J.E., TALLEY L.D., SMITH G.K. and LIN M.C., « J. Chem. Phys. », *74*, 4501 (1981).

BUTLER J.E., MACDONALD R.G., DONALDSON D.J. and SLOAN J.J., « Chem. Phys. Lett. », *95*, 183 (1983.

BURKS T.L. and LIN M.C., « Chem. Phys. », *33*, 329 (1978).

CASAVECCHIA P., BUSS R.J., SIBENER S.J. and LEE Y.T., « J. Chem. Phys. », *73*, 6351 (1980).

CASTELLANO E. and SCHUMACHER H.J., « Z. Phys. Chem. », *NF34*, 198 (1962).

CHU J.O., FLYNN G.W. and WESTON Jr. R., « J. Chem. Phys. », *78*, 2990 (1983).

CHAMBERLAIN G.A. and SIMONS J.P., « J. Chem. Soc. Faraday Trans 2 », *71*, 402 (1975).

DAVENPORT J.E., RIDLEY B., SCHIFF H.I. and WELGE K.H., « Discuss. Faraday Soc. », *53*, 230 (1972).

DAVIDSON J.A., SADOWSKI C.M., SCHIFF H.I., STREIT G.E., HOWARD C.J., JENNINGS D.A. and SCHMELTEKOPF A.L., « J. Chem. Phys. », *64*, 57 (1976).

DAVIDSON J.A. SCHIFF H.I., STREIT G.E., MCAFEE J.R., SCHMELTEKOPF A.L. and HOWARD C.J., « J. Chem. Phys. », *67*, 5021 (1977).

DAVIDSON J.A., SCHIFF H.I., BROWN T.J. and HOWARD C.J., « J. Chem. Phys. », *69*, 4277 (1978).

DITCHBURN R.W. and YOUNG P.A., « J. Atmos. Terrest. Phys. », *24*, 124 (1962).

FAIRCHILD C.E., STONE E.J. and LAWRENCE G.M., « J. Chem. Phys. », *69*, 3632 (1978).

FLETCHER I.S. and HUSAIN D., « J. Phys. Chem. », *80*, 1837 (1976).

FORCE A.P. and WIESENFELD J.R., « J. Phys. Chem. », *85*, 782 (1981).

Frederick J.E. and Mentall J.E., « Geophys. Res. Lett. », *9*, 461 (1982).

Froidevaux L. and Yung Y.L., « Geophys. Res. Lett. », *9*, 854 (1982).

Gericke K.H., Comes F.J. and Levine R.D., « J. Chem. Phys. », *74*, 6106 (1981).

Goldstein N. and Wiesenfeld J.R., « J. Chem. Phys. », *78*, 6725 (1983).

Greenblatt G.D., Ph.D. Thesis, Cornell University (1983).

Goldstein N., Greenblatt G.D. and Wiesenfeld J.R., « Chem. Phys. Lett. », *96*, 410 (1983).

Greenblatt G.D. and Wiesenfeld J.R., « J. Chem. Phys. », *78*, 4924 (1983).

Hasson V. and Nicholls R.W., « J. Phys. B. », *4*, 1789 (1971).

Hay P.J. and Dunning Jr. T.H., « J. Chem. Phys. », *67*, 2290 (1977).

Hay P.J., Pack R.T., Walker R.B. and Heller E.J., « J. Phys. Chem. », *86*, 862 (1982).

Heidner III R.F., Husain D. and Wiesenfeld J.R., « Chem. Phys. Lett. », *16*, 530 (1972).

Heidner III R.F., Husain D. and Wiesenfeld J.R., « J. Chem. Soc. Faraday Trans. 2 », *69*, 927 (1973).

Herman J.R. and Mentall J.E., « J. Geophys. Res. », *87*, 8967 (1982).

Huie R.E., Herron J.T. and Davis D.D., « J. Phys. Chem. », *76*, 2653 (1972).

Klais O., Anderson P.C. and Kurylo M.J., « Int. J. Chem. Kinet. », *12*, 469 (1980).

Kleindienst T., Locker J.R. and Bair E.J., « J. Photochem. », *12*, 67 (1980).

Lam L., Hastie D.R., Ridley B.A. and Schiff H.I., « J. Photochem. », *15*, 119 (1981).

Lee L.C. and Slanger T.G., « J. Chem. Phys. », *69*, 4053 (1978).

Levine J.S., « J. Mol. Evol. », *18*, 161 (1982).

Levine J.S., Augustsson T.R., Boughner R.E., Natarajan M. and Sacks L.J., in: *Comets and the Origin of Life*, Ed. Ponnameruma C., D. Reidel, Dordrecht, p. 161 (1981).

Lin C.L. and Leu M.T., « Int. J. Chem. Kinet. », *14*, 417 (1982).

Logan J.A. and McElroy M.B., « Planet. Space Sci. », *25*, 117 (1977).

Luntz A.C., « J. Chem. Phys. », *73*, 1143 (1980).

Luntz A.C. and Andresen P., « J. Chem. Phys. », *72*, 5851 (1980).

Luntz A.C., Schinke R., Lester Jr. W.A. and Gunthard H.H., « J. Chem. Phys. », *70*, 5908 (1979).

Marx W., Bahe F. and Schurath U., « Ber. Bunsenges. Phys. Chem. », *83*, 225 (1979).

Moore D.S., Bomse D.S. and Valentini J.J., « J. Chem. Phys. », *79*, 1745 (1983).

Moortgat G.K. and Kudszus E., « Geophys. Res. Lett. », *5*, 191 (1978).

NASA panel for data evaluation, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, J.P.L. Publication *81-3* (1981).

Nicolet M., « Planet. Space Sci. », *20*, 1671 (1972).

Nicolet M., « Pure. Appl. Geophys. », *118*, 3 (1980).

Ogawa M., « J. Chem. Phys. », *54*, 2550 (1971).

Robertshaw J.S. and Smith I.W.M., « J. Chem. Soc. Faraday II », *76*, 1354 (1980).

Schiff H.I., « Ann. Geophys. », *28*, 67 (1972).

Shardanand, « Phys. Rev. », *186*, 5 (1969).

Shardanand and Rao A.D.P., « J. Quant. Spectrosc. Radiat. Transfer », *17*, 433 (1977).

SHORTRIDGE R.G. and LIN M.C., « Chem. Phys. Lett. », *35*, 146 (1975).

SLANGER T.G. and BLACK G., « J. Chem. Phys. », *60*, 468 (1974).

SLANGER T.G. and BLACK G., « J. Chem. Phys. », *70*, 3434 (1979).

SMITH G.K. and BUTLER J.E., « J. Chem. Phys. », *73*, 2243 (1980).

SPARKS R.K., CARLSON L.R., SHOTATKE K., KOWALCZYK M.M. and LEE Y.T., *72*, 1401 (1980).

TULLY J.C., « J. Chem. Phys. », *61*, 61 (1974).

UREY H.C., « Proc. Natl. Acad. Sci. (USA) », *38*, 351 (1952).

VALENTINI J.J., « Chem. Phys. Lett. », *96*, 395 (1983).

VOLTRAUER H.N., FELDER W., PIRKLE R.J. and FONTIJN A., « J. Photochem. », *11*, 173 (1979).

WAYNE R.P., « Adv. Photochem. », *7*, 311 (1969).

WHITLOCK P.A., MUCKERMAN J.T. and FISHER E.R., « J. Chem. Phys. », *76*, 4468 (1982).

WIESENFELD J.R., « Chem. Phys. Lett. », *35*, 146 (1977).

WIESENFELD J.R., « Acc. Chem. Res. », *15*, 110 (1982).

WINE P.H. and RAVISHANKARA A.R., « Chem. Phys. Lett. », *77*, 103 (1981).

WINE P.H. and RAVISHANKARA A.R., « Chem. Phys. », *69*, 365 (1982).

YOSHINO K., FREEMAN D.E., ESMOND J.R. and PARKINSON W.H., « Planet. Space Sci. », *31*, 339 (1983).

ZAHR G.E., PRESTON R.K. and MILLER W.H., « J. Chem. Phys. », *62*, 1127 (1975).

ZELLNER R., WAGNER G. and HIMME B., « J. Phys. Chem. », *84*, 3196 (1980).

DISCUSSION

KNABE

I had expected a report on oxygen cycles which would be more concerned with the more general atmospheric problems of its formation and changes that might occur under certain regimes.

ROWLAND

I wonder if the speaker might like to state briefly, for people whose science might be geology, forestry, or agriculture, the important problems of current interest involving the atmospheric chemistry of oxygen.

WIESENFELD

In a sense, the chemistry of O_2 itself represents something of a "non-problem"; the photosynthetic cycle keeps in balance the production and removal (through respiration) of molecular oxygen. Net removal of O_2 accompanies the combustion of fossil fuel but even were the Earth's entire reserve of carbon burned to yield CO_2, the concomitant decrease in partial pressure of O_2 would be small and probably of little environmental consequence when compared to the enormous increase in atmospheric carbon dioxide. Our research efforts are primarily concerned with the establishment of a reliable base of kinetic and photochemical data that may be applied to the development of advanced models of atmospheric chemistry. Field measurements alone provide only part of the answer in that one cannot measure everything simultaneously and there are certain minor constituents (such as HO_2) which even now cannot be adequately monitored at ambient concentrations. All models are in a sense underdefined in that were one to vary freely the available parameters, perfectly good fits to the limited field data would be possible. The goal of laboratory studies is to constrain the number of free parameters that are available; to a large extent I think that we have been successful.

LAG

Have you investigated the possible influences of artificial nitrogen fertilizers?

WIESENFELD

No not personally, but this has been a matter of some concern. It requires knowledge of nitrogen balances between the hydrosphere and atmosphere; to the best of my knowledge, it is not a serious problem, but I would certainly welcome hearing more about this problem.

ROWLAND

In some respects, the oxygen cycle in the atmosphere is most concerned with ozone chemistry which will be discussed later today. The effect of nitrogen fertilizers on the atmosphere would be most strongly felt through perturbation of stratospheric ozone. The general consensus now seems to be that the effect of nitrogen fertilizers upon the atmosphere will be small compared to the magnitude of other sources.

FIOCCO

When you were discussing the photodissociation of ozone. I noticed that you left out the Huggins bands; the dissociation efficiency and O(^{1}D) branching ratio for this absorption feature would be interesting. Upon going from the Hartley to the Huggins region, I believe that one witnesses the onset of structured absorption. This is of interest not only from the standpoint of photochemistry, but also for diagnostics. So far, devices being used to measure atmospheric ozone are crude and we are not yet able to definitively state whether the total ozone column is being depleted. Improvement of these techniques requires a better knowledge of the absorption spectrum.

WIESENFELD

Where does the Hartley region end and the Huggins region begin? To what extent can they be considered separate features? Structured absorption features can be observed even for bound-free transitions. The only information concerning the photochemistry of ozone in the Huggins band is derived from classical photochemical studies which suggest that the dissociation of O_3 in this region leads to the formation of ground state atomic oxygen and either O_2 ($^1\Delta$) or O_2 ($^1\Sigma$). Thus from the standpoint of the major photochemical cycles which were described by other speakers, the role of Huggins band absorption seems relatively minor. Because of the importance of excited oxygen atoms to tropospheric chemistry, direct field measurements of ozone photodissociation rates in the middle ultraviolet are currently being actively pursued and our laboratory hopes to apply new techniques to the determination of the wavelength dependence of the yield of excited atoms.

CRUTZEN

Is anything other than O (^{1}D) and O_2 ($^1\Delta$) produced at the high energy end of the Hartley continuum?

WIESENFELD

The thermochemical threshold for production of O_2 ($^1\Sigma$) in a spin-allowed process is 266 nm so one cannot *a priori* exclude the possibility of its formation in ozone photolysis. However I know of no evidence which would confirm the production of these higher excited states at high energies in the Hartley continuum. Looking at the characteristic red emission at 763 nm would make detection of O_2 ($^1\Sigma$) possible; a very real experimental problem arises because deactivation of O (^{1}D) by the trace of O_2 invariably present in any O_3 sample yields O_2 ($^1\Sigma$). This issue certainly deserves closer scrutiny.

ROWLAND

For the nonphotochemists, it should be pointed out that the interest in such excited states as O_2 ($^1\Sigma$) derives from the observation that their chemistry differs significantly from that of the electronic ground state. Because these excited states can be produced photochemically from ozone especially at short wavelengths the question is whether these molecules may be important to trace species chemistry.

LIBERTI

You mentioned the reaction between oxygen and nitrous oxide. Most environmental chemists pay attention to NO and NO_2 as well as their interconversion, but little attention is paid to N_2O. Does N_2O have a part in the nitrogen cycle? We are very curious about the fact that it is present uniformly in the troposphere at about 0.25 ppm. Is the reaction of oxygen and N_2O of direct relevance to the atmosphere?

WIESENFELD

Definitely yes. In the troposphere, to which I think you may be referring, N_2O is relatively inert. It is in the stratosphere where reaction (18) plays such an important role releasing the nitrogen oxides which dominate the catalytic destruction of ozone.

LIBERTI

As far as the troposphere is concerned, do you think it is absolutely inert?

ROWLAND

Because the estimated lifetime is 100 years or more, it must be completely inert.

LIBERTI

Why is the N_2O constant? What are its sources and sinks? Is it increasing or decreasing and does its concentration vary? If it is important to the chemistry of the stratosphere, then its concentration in the troposphere should certainly be relevant.

ROWLAND

The concentration in the stratosphere is directly dependent upon that in the troposphere and as the N_2O in the troposphere increases there will be more nitrogen oxides in the stratosphere. One sees no difference in N_2O concentrations at remote locations around the world because its lifetime is very long. Those gases with lifetimes in excess of 10 years display similar concentrations throughout the atmosphere.

ANDERSON

In searching for mechanisms involving excited oxygen atoms have you discovered any processes involving the vibrationally excited states of either the ground electronic state or low-lying excited states of O_2 which would drive these chemical cycles backward? Have you considered candidate reactions other than those already identified for the production of odd oxygen in the stratosphere?

WIESENFELD

No, we have not although I should emphasize that, using the newly developed laser spectroscopic tools described in my paper, studies of the chemistry of vibrationally excited states now become feasible. Destruction of ozone following collisions with vibrationally excited molecules is known, but the importance of vibrationally excited species in the atmosphere is a matter of some debate. Collisional quenching of these molecules must always compete with chemistry and so the question becomes one of understanding the relative efficiencies of such processes.