

A New Laboratory Source of Ozone and Its Potential Atmospheric Implications

T. G. SLANGER, L. E. JUSINSKI, G. BLACK, G. E. GADD

Although 248-nanometer radiation falls 0.12 electron volt short of the energy needed to dissociate O₂, large densities of ozone (O₃) can be produced from unfocused 248-nanometer KrF excimer laser irradiation of pure O₂. The process is initiated in some undefined manner, possibly through weak two-photon O₂ dissociation, which results in a small amount of O₃ being generated. As soon as any O₃ is present, it strongly absorbs the 248-nanometer radiation and dissociates to vibrationally excited ground state O₂ (among other products), with a quantum yield of 0.1 to 0.15. During the laser pulse, a portion of these molecules absorb a photon and dissociate, which results in the production of three oxygen atoms for one O₃ molecule destroyed. Recombination then converts these atoms to O₃, and thus O₃ production in the system is autocatalytic. A deficiency exists in current models of O₃ photochemistry in the upper stratosphere and mesosphere, in that more O₃ is found than can be explained. A detailed analysis of the system as it applies to the upper atmosphere is not yet possible, but with reasonable assumptions about O₂ vibrational distributions resulting from O₃ photodissociation and about relaxation rates of vibrationally excited O₂, a case can be made for the importance of including this mechanism in the models.

THE FIRST DISSOCIATION LIMIT OF O₂ IS AT 41,260 cm⁻¹ (242.4 nm) (1). At the KrF laser wavelength of 248 to 249 nm, O₂ is expected to be transparent, except for the weak Herzberg band adsorption (A-X, A'-X, c-X) in this region (2). The original intent of this work was to establish whether excitation to the O₂ (A, A', c) states in the laser tuning range could produce O₃, either by two-photon processes or through O₂*-O₂ collisions. Generation of O₃ was observed, but was not correlated with the Herzberg transitions. We discuss the mechanism for the observed 248-nm photodissociation of O₂, and calculate the spectroscopic and kinetic requirements for this process to have atmospheric significance.

The need for an adjustment of the upper atmospheric ozone models is reflected by the discrepancy between model predictions and satellite observations for ozone densities in the region from 50 to 80 km [the models are low by a factor of 1.5 to 2 (3, 4)]. Various changes to the input data have been proposed to improve agreement (4), but consensus has not yet been achieved; mechanisms for

increased ozone production or decreased ozone losses are needed. Frederick *et al.* (5) have argued that underestimation of ozone production is the likely source of the discrepancy.

Increased ozone production can only occur through increased O₂ dissociation. If all of the processes involving O₂ in local thermodynamic equilibrium (LTE) have been taken into account, then mechanisms must be found that involve O₂ in non-LTE. One such attempt was made by Frederick and Cicerone (6), who considered the *a*¹Δ_g state of O₂ that is copiously produced by O₃ photodissociation at 200 to 300 nm. They proposed that the continuum of the *A*¹Δ_u ← *a*¹Δ_g transition might have a large enough cross section to fulfill this role. Experiment (7) and calculation (8) showed that the cross section was orders of magnitude too small for this process to be significant.

Another energetic O₂ entity is vibrationally excited oxygen (O₂[‡]). There is a 10 to 15 percent yield of O₂[‡] from O₃ photodissociation at 266 and 274 nm (9), and time-of-flight measurements have established that O₂[‡] is produced with excitation up to at least *v*^{''}=10, with much more energy actually available. We show that photodissociation of O₂[‡] is a process amenable to study and is responsible for O₃ production in our laboratory measurements. This mechanism has been overlooked as an atmospheric O₃ source, mainly because O₂[‡] is a species that is not generally observable, yet it may account for the present imbalance between modeled and atmospheric O₃ profiles. We discuss these experimental observations and their atmospheric implications to the extent allowed by current knowledge. Before a full evaluation is possible, a number of spectroscopic and kinetic studies are needed.

Experimental studies. The irradiation of O₂ with broadband 248- to 249-nm KrF laser light showed a characteristic S-shaped

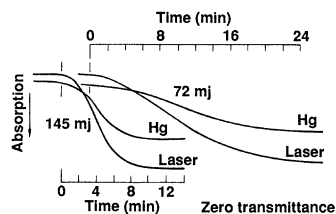
Table 1. Calculation of *J*_∞(O₂[‡]) for O₂(*v*^{''}=10).

Band	λ (nm)	<i>q</i> ^{<i>v</i>_{v'},<i>v</i>_{v''}} (cm ⁻¹)	Average cross section (cm ²)	Solar flux (cm ⁻² s ⁻¹)	<i>J</i> _∞ (O ₂ [‡]) (s ⁻¹)
0-10	287	1820	6.7(-18)*	2.1(14)	1.4(-3)
1-10	282	3250	1.2(-17)	1.5(14)	1.8(-3)
2-10	276	2110	7.8(-18)	1.1(14)	8.6(-4)
3-10	272	345	1.3(-18)	1.2(14)	1.6(-4)
4-10	267	110	4.0(-19)	1.3(14)	5.2(-5)
5-10	263	915	3.4(-18)	1.2(14)	4.1(-4)
6-10	259	1340	5.0(-18)	4.9(13)	2.5(-4)
7-10	256	970	3.6(-18)	5.8(13)	2.2(-4)
8-10	252	350	1.3(-18)	2.3(13)	3.0(-5)
9-10	249	18	6.7(-20)	2.4(13)	1.6(-6)
10-10	247	65	2.4(-19)	2.4(13)	5.8(-6)
11-10	244	275	1.0(-18)	2.4(13)	2.4(-5)
12-10	242	440	1.6(-18)	2.6(13)	4.2(-5)
13-10	240	480	1.8(-18)	1.8(13)	3.3(-5)

*To be read as 6.7 × 10⁻¹⁸.

The authors are at the Chemical Physics Laboratory, SRI International, Menlo Park, CA 94025.

Fig. 1. Time-dependent O_3 production, as measured by 248-nm transmitted light and 254-nm Hg line absorption. $[O_2]$, 1000 torr; laser repetition rate, 10 Hz.



curve of O_3 production (10). Such curves for laser light transmitted over 15 cm and 254-nm light transmitted over 5 cm are shown in Fig. 1. The high laser intensity was sufficient to partially bleach the O_3 , since the number of photons per pulse, $1 \times 10^{17} \text{ cm}^{-2}$, and the number of O_3 molecules in the 15-cm path length, $1.5 \times 10^{17} \text{ cm}^{-2}$ at 0.3 torr, were comparable, and the absorption cross section corresponded to an optical depth greater than unity.

The temporal behavior of these absorption plots depended on laser power. Time to equilibrium was lengthened when the intensity decreased, as was the induction time (Fig. 1); O_3 production seemed to be catalyzed by the presence of O_3 , indicating that there were at least two production sources.

To observe possible wavelength-dependent effects, we tuned the laser across the 248- to 249-nm region, starting at the broadband equilibrium density of O_3 (Fig. 2). The transmitted Hg(254 nm) radiation exhibited oscillations, which are variations in the O_3 density, but the time response was so slow that, although the spectrum was completely reproducible, it was insufficiently resolved for identification.

The second spectrum was taken by monitoring only the scattered laser light, of ~ 15 -ns duration, which had an undetermined pathway to the photomultiplier. Greatly improved data were obtained, and there was complete correlation between the features in the two traces.

This spectrum has been identified as the Schumann-Runge (SR) $O_2(B-X)$ 2-7 band, which has a head at 248.0 nm, and, being red-degraded, sweeps through the laser tuning region. The last line detected was $R(15)$ (a consequence of the abrupt end of the laser tuning range at ~ 248.7 nm). Also seen are a few lines of the 7-9 band, and one weak feature, marked with an asterisk, remains unidentified. Line positions are taken from the calculated tabulations of Creek and Nicholls (11).

Generation of O_3 through the SR transition does not fully explain these observations, as there is off-resonance O_3 production. The equilibrium O_3 densities were $1.5 \times 10^{16} \text{ cm}^{-3}$ on the 2-7 $P(5)$ line, $8.6 \times 10^{15} \text{ cm}^{-3}$ between the $P(5)$ and $R(9)$ lines, and $1.1 \times 10^{16} \text{ cm}^{-3}$ with the laser operating broadband. The photon flux was approximately the same in each case. If autocatalytic O_3 production occurred only when an SR line was being pumped, then there would be no O_3 generated by off-resonance radiation, and the yield from broadband excitation would be only ~ 5 percent of that produced on-resonance (based on the density of lines and their widths). That this is not the case is indicative of continuous absorption by some species that is a product of O_3 photodissociation.

The O_3 densities were obtained from the transverse Hg line absorption. Values only two-thirds as great were obtained from the reduction in transmitted laser radiation, a consequence of the system being partially bleached during the 15-ns period when the power meter received photons. During this period, the O_3 density in the beam path was reduced by one-third, although recovery by $O + O_2$ recombination occurred in 1.5 μs .

The O_3 equilibrium density in such a system is controlled by reactions that are equivalent to the consumption of odd oxygen by $O(^3P) + O_3 \rightarrow 2O_2$. Included in this category are that reaction itself,

which is quite slow, and the three catalytic cycles that involve HO_x , NO_x , and ClO_x . The effectiveness of the HO_x cycle was shown by mild heating of the cell walls, which drove off H_2O . The OH radical was produced in this manner through the interaction of H_2O with the $O(^1D)$ generated by O_3 photodissociation, and the equilibrium O_3 density immediately dropped by more than an order of magnitude. When the walls cooled, O_3 production returned. As the effect was only observed with the laser on, we conclude that it is a consequence of photochemistry, not thermally induced surface reactions.

Discussion. The shape of the O_3 generation curves in Fig. 1 implies at least two sources of O_3 ; an initiating mechanism that produces O_3 inefficiently, and a process that generates O_3 more effectively and that apparently requires the presence of O_3 . In unpublished work we performed a similar experiment in the same cell at 210 nm by using Raman shifting in H_2 of 193-nm ArF excimer radiation as the source (12). Moortgat (13) has recently performed the same type of study at 214 nm. At these wavelengths, O_2 is photodissociated in the Herzberg continuum [the dissociative portion of the $O_2(A-X)$ transition]. The buildup of O_3 was quite linear with time, with a decrease in rate only when the equilibrium density is approached, which was not the case at 248 nm.

With the high power of the KrF laser, there are a number of possibilities for the initiating step. Two-photon processes in $O_2(X)$ and $O_2(a)$ have recently been reported (14), which would lead to O_2 dissociation, although focused radiation is normally required. Anti-Stokes Raman shifting in O_2 would generate radiation at 238 nm, which could directly dissociate O_2 , albeit with a small cross section. Again, low efficiency would be expected with unfocused radiation. Finally, a small concentration of O_4 dimers might absorb 248-nm radiation directly, producing O_3 [see Moortgat (13)].

For our purposes, the initiating mechanism is unimportant, because the apparent autocatalytic nature of subsequent O_3 production suggests that only a minute amount of O_3 is required to initiate the process. We believe that the spectra shown in Fig. 2 clarify the nature of the catalytic mechanism.

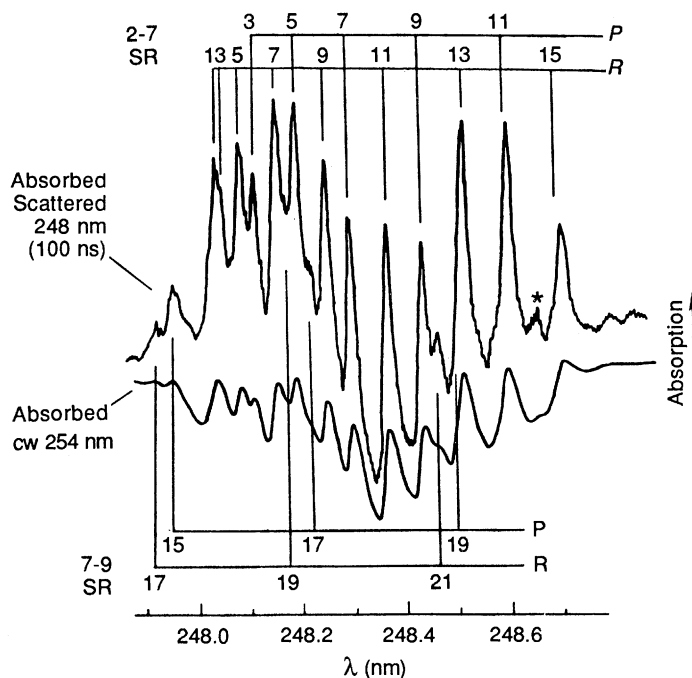
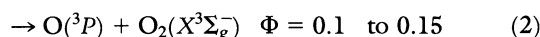
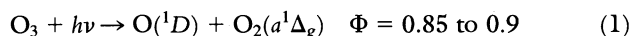


Fig. 2. Absorption spectra in O_2 photodissociation system. Comparison of transmitted 254-nm cw radiation and 248-nm scattered light with a 100-ns gate.

Table 2. Requisite single vibrational level quantum yields from O₃ photodissociation to equal 10 percent of the standard O₃ source term. Only O₂(B-X) absorption was used in the calculations.

ν''	Altitude (km)		
	50	60	70
14	2.6(-2)	4.4(-2)	8.2(-2)
16	4.0(-3)	9.2(-3)	1.8(-2)
18	6.6(-4)	2.6(-3)	7.6(-3)
20	2.8(-4)	9.2(-4)	4.2(-3)

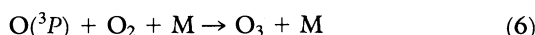
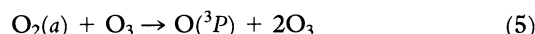
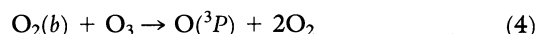
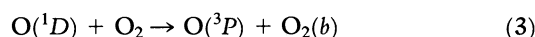
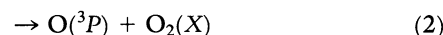
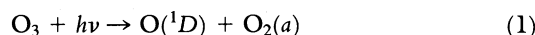
Photodissociation of O₃ occurs with a cross section of 1.1×10^{-17} cm² at 248 nm (15), near the peak of the 200- to 300-nm Hartley band. As noted by Wayne in a review article (16), there are two significant photodissociative channels for O₃ in the Hartley band (17):



Studies of the products of O₃ photodissociation (9) have established that O₂(a) is formed in $\nu=0-2$ at 274 nm and in $\nu=0-3$ at 266 nm, whereas O₂(X) is formed in all vibrational levels up to at least $\nu=10$. Since the O₂-O bond strength is only 1 eV, at 248 nm there is 4 eV of excess energy, and a wide vibrational distribution is possible in O₂(X).

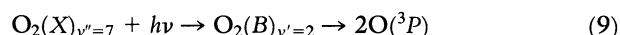
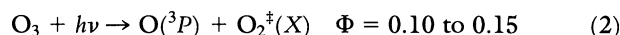
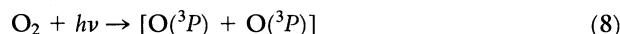
The O₃ production shown in Fig. 2 traces out the O₂(B-X) 2-7 and 7-9 bands, and the production of O₂(X) in $\nu=7,9$ is consistent with the above studies. All levels of the O₂(B) state are predissociated; the observed line broadening is substantial, maximizing for the $\nu'=4$ level at 3 to 4 cm⁻¹ (18). The $\nu'=2$ level shows linewidths of ~ 0.4 cm⁻¹, which correspond to a predissociation efficiency of >99 percent, and thus photoabsorption in the 2-7 band leads to dissociation, and production of two O₃ molecules (following three-body recombination with O₂).

The conventional view of the results of irradiating an O₂-O₃ mixture at 248 nm is that the O₃ will slowly disappear through the sequence



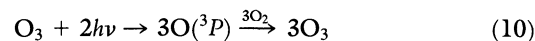
In none of these reactions is an O-O bond broken in O₂, and thus O₃ is recycled but there is never a net gain. Although reaction 7 is quite low, odd oxygen is irreversibly destroyed, and eventually the system is converted to O₂.

Only if there is a mechanism for breaking the O-O bond can we account for the O₃ buildup. The spectra of Fig. 2 indicate that the steps are



The last step breaks the O-O bond in O₂, and thus the O₃

photodestruction quantum yield can in a sense be viewed as negative—destruction of one molecule of O₃ can lead to production of three. In effect,



The overall efficiency of the process need not be great to observe a rapid O₃ buildup, because of the large photon flux. At the maximum of the 254-nm absorption change in Fig. 1, O₃ in the cell is increasing at 5×10^{15} molecules s⁻¹, averaged over the cell volume. However, at the average [O₃] of 5×10^{15} molecules cm⁻³, the O₃ photodissociation rate is 1.1×10^{18} molecules s⁻¹. Thus only 0.5 percent of the photodecomposed O₃ molecules have the product O₂⁺ photodissociated, which is a consequence of the overlap between the broadband laser output and the SR lines, the quantum yield of O₂(ν'') production, the fraction of molecules in $\nu''=7$, and possibly other factors, such as the rotational distribution in $\nu''=7$.

The difference between the two spectra in Fig. 2 is mainly due to the difference between the average gas composition, measured by continuous wave (cw) 254-nm absorption, and the transient gas composition existing during a 100-ns period after the laser pulse. The cw absorption measures only the slowly varying O₃ density, which reflects O₂⁺ production indirectly, whereas in the transient absorption measurement, O₂⁺ is detected directly. Although its concentration is much less than that of O₃, its absorption cross section is more than two orders of magnitude greater, based on measured cross sections for the SR 2-0 band (19), a comparison of Franck-Condon factors for the SR 2-0 and 2-7 bands (20), and the rotational partition function. We note that O₂($\nu''=7$) rotational levels created above $N = 15$ would relax into the tuning range of the laser with a time scale considerably shorter than that of the laser pulse. Thus rotational relaxation may lead to replenishment of bleachable O₂($\nu''=7$) levels, whereas the O₃ replenishment time constant in the irradiated volume, 1.5 μ s at 1000 torr O₂, is long compared with the pulse length.

There can be no dispute about the identification of the two SR bands in Fig. 2, but off-resonance ozone production also generated with an S-shaped production curve characteristic of autocatalysis needs explanation. The O₂ potentials calculated by Saxon and Liu (21), emphasizing those that involve allowed transitions from the ground state and the $a^1\Delta_g$ state (Fig. 3), are helpful in this respect.

In our first analysis of the data we paid attention only to the SR transition as a source of O atoms and thus of O₃. However, it was subsequently pointed out to us that excitation of O₂⁺ to the $1^3\Pi_u$ state is fully allowed, and thus some continuous (that is, off-resonance) absorption might be expected (22). Our data bear this out. The $1^1\Pi_u \leftarrow a^1\Delta_g$ transition is also optically allowed and could contribute to the continuous absorption. This idea is attractive, because the O₂(a) quantum yield from O₃ photodissociation is near unity (16). However, it is hampered in that vibrational excitation in O₂(a) is limited by the energy necessary to simultaneously excite the partner atom, O(¹D). Valentini *et al.* (23) have shown that the Huggins band of O₃, at 310 to 350 nm, appears to involve a forbidden dissociative process, giving O₂($a^1\Delta_g$) and O(³P). The internal energy restriction on O₂(a) would then be lifted, and thus $1^1\Pi_u \leftarrow a^1\Delta_g$ absorption may have some atmospheric importance.

Calculations of the transition moments for the B-X and $1^3\Pi_u$ -X systems have been made by Buenker *et al.* (24) and indicate that the oscillator strength for the former is much greater, a conclusion with which we have concurred for the SR continuum region (25). However, at 248 nm, the comparison is between a bound-bound SR transition and a bound-free $1^3\Pi_u$ -X transition, and in that case the relative absorption strengths are more difficult to obtain by calculation. In the 248-nm region, the SR peak cross section is

Fig. 3. Potential energy curves for selected O_2 states (21).

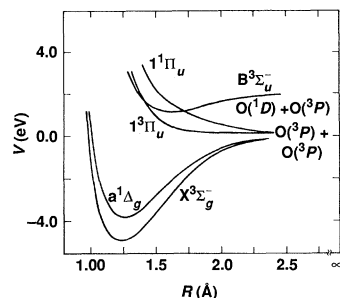
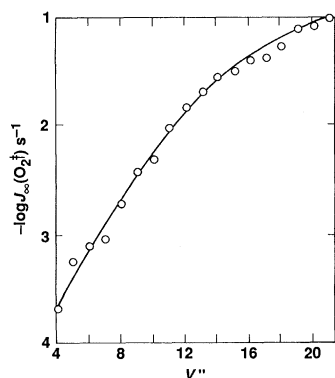


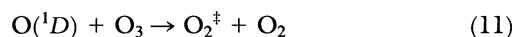
Fig. 4. Atmospheric photodissociation rates through $O_2(B)$ predissociation for vibrationally excited O_2 (zero optical depth).



somewhat less than the continuum cross section, so that for an extended spectral source such as the sun, continuum absorption is much more important than line absorption. Using the equilibrium O_3 densities along with the density of lines and the 0.4-cm^{-1} linewidth of the $v'=2$ SR lines, the continuum contribution for the broadband production of O_3 , appears to be more than an order of magnitude greater than that from the SR lines.

Both the $v''=7$ and $v''=9$ levels of $O_2(X)$ are populated (Fig. 2). The levels are not directly comparable because of the different rotational levels involved, but consideration of the Franck-Condon factors and the predissociated linewidths for the two bands shows that the population in $v''=9$ is probably substantially greater than that in $v''=7$.

Higher O_2 vibrational levels produced from 248-nm photolysis of O_3 have been studied by Cleveland and Wiesenfeld (26). They have observed levels over the range $v''=14\text{--}23$, the production of which is largely dominated by the secondary reaction



More detailed studies will be required to isolate small yields of primary $O_2^{\ddagger}$ in these levels.

The earlier flash photolysis experiments of Baiamonte *et al.* (27) showed the delayed generation of $O_2^{\ddagger}$ in the range of $v''=14\text{--}30$, attributed to the reaction of both $O(^3P)$ and $O(^1D)$ with O_3 . Their data (for $v''=16$) are not inconsistent with a small amount of nascent $O_2(v''=16)$ generation.

Apart from the atmospheric ramifications, these observations are significant because the KrF laser is an important laboratory tool, and it has generally been assumed that O_2 is not photodissociated at 248 nm. As this assumption is not warranted, experimentalists should be aware in planning future experiments and in evaluating past studies that $O(^3P)$ and O_3 [and thus $O(^1D)$ and $O_2(a^1\Delta_g)$] can be present in such systems. Furthermore, the same phenomenon can occur at longer wavelengths in the Hartley band, and must be considered when more powerful lasers operating at 250 to 300 nm are designed. Excimer laser systems producing 800-mJ pulses at 248 nm are commercially available, and these can be expected to generate O_3

from O_2 quite efficiently.

Atmospheric applications. It is not evident a priori that these concepts can be transferred to solving the atmospheric problem of finding an additional O_3 source at 50 to 80 km. One reason is that the instantaneous photon flux of the laser is some ten orders of magnitude greater than the total solar flux in the 200- to 300-nm region. Since photoabsorption by the $O_2^{\ddagger}$ molecules in the laboratory experiment occurs before there have been any deactivating collisions, it is not clear without calculations whether the analogous process will occur in the atmosphere.

Two types of information are needed to pursue this question. The vibrational distribution of O_2 produced from O_3 in the Hartley band determines the wavelengths at which dissociation can occur. The higher the $O_2^{\ddagger}$ level, the less photon energy is needed for dissociation, and the greater the available flux of solar photons. The collisional loss rate of $O_2^{\ddagger}$ is also needed, since if the autocatalytic process is enhanced by high vibrational excitation in the $O_2^{\ddagger}$, as we show below, then rapid vibrational relaxation can nullify the process.

We concentrate on O_3 generation by the SR part of the overall process. We do not at present have enough information to deal with the continuous absorption, yet as described above, it appears to be even more important than the SR process at 248 nm. If a case can be made that the SR mechanism alone provides a significant new O_3 source, then the importance of the total process can only increase with a full treatment.

We have discussed the evidence for an extensive $O_2^{\ddagger}$ distribution from O_3 photodissociation in the Hartley band—our own measurements, the time-of-flight studies (9), and possibly the recent results of Cleveland and Wiesenfeld (26). The excess energy available from O_3 photodissociation at 248 nm for the ground-state product channel is 4.1 eV, enough to excite $v''=25$ in the O_2 fragment.

Valentini *et al.* (23) investigated by continuous Anti-Stokes Raman spectroscopy (CARS) the production of vibrationally excited O_2 molecules generated from O_3 photodissociation at 230 to 311 nm. They reported seeing only $O_2(a^1\Delta_g)[v=0\text{--}6]$, concluding that the lack of observation of ground-state molecules was due to the very broad vibrational distribution with which they must be formed. In related work, Levene *et al.* (28) showed that the relatively narrow distribution of vibrationally excited ground-state molecules, $v=0\text{--}4$, generated from 530- to 638-nm photodissociation of O_3 , is easily measurable.

To compare O_2 photodissociation rates from standard models with that from the $O_2^{\ddagger}$ process, we must calculate the term $J_{\infty}(O_2^{\ddagger})[O_2^{\ddagger}]$, where $J_{\infty}(O_2^{\ddagger})$ represents the photodissociation rate of $O_2^{\ddagger}$, and $[O_2^{\ddagger}]$ is its concentration. Neither of these terms is well defined, since $O_2^{\ddagger}$ may be dispersed among up to 25 vibrational levels, and thus photolytic and collisional processes depend on the vibrational distribution.

The calculation of $J_{\infty}(O_2^{\ddagger})$ (the photodissociation rate for solar radiation unattenuated by O_3 absorption) involves two terms, solar flux and absorption cross sections. For SR continuum absorption, this is a simple calculation, but for the structured absorption of the SR bands, a rigorous treatment involves line-by-line calculations. Various authors have used approximate methods (29, 30) in which a mean cross section across a band is used over some frequency interval. We scaled up the results of Kockarts (29) for the $v''=0$ progression to other progressions using a 500-cm^{-1} interval for each band, over which range the solar flux can be taken as constant. Absorption cross sections were taken as proportional to the product of frequency and Franck-Condon factors.

In Table 1 we list for the $v''=10$ progression the product of Franck-Condon factor (q) and transition frequency ($\nu_{v',v''}$) (20). For the 8-0 SR band, Kockarts (29) gives a mean cross section of

Fig. 5. Wavelength ranges over which 70 to 80 percent of vibrationally excited O_2 in a given level is photodissociated in the atmosphere, in the B-X transition (altitude ≥ 50 km).

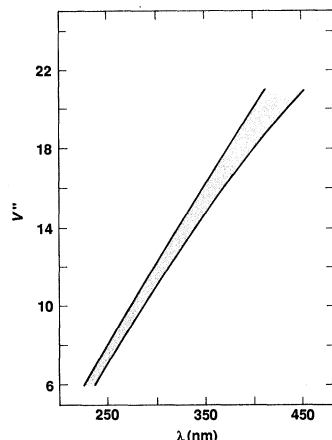
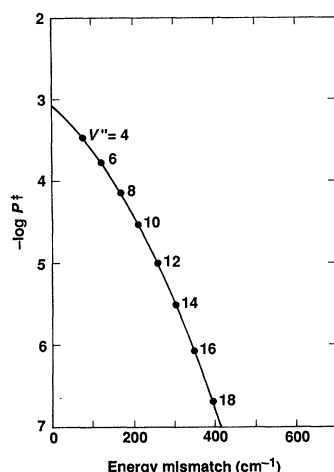


Fig. 6. Probabilities for V-V energy transfer for $O_2(\nu=n)-O_2(\nu=0)$ collisions, from the theory of Rapp and Englander-Golden. (32).



$1.2 \times 10^{-20} \text{ cm}^2$, and the $q\nu_{\nu',\nu''}$ product is 3.28 cm^{-1} . The $q\nu_{\nu',\nu''}$ product is converted to cross sections by means of this scaling factor, $3.66 \times 10^{-21} \text{ cm}^3$. Solar fluxes over 500-cm^{-1} intervals are from Nicolet (31). The sum of J_∞ values for all $\nu''=10$ bands, $5.3 \times 10^{-3} \text{ s}^{-1}$, represents the rate at which $O_2(\nu''=10)$ is photodissociated from this vibrational level above 50 km, where there has been little attenuation of solar radiation at the wavelengths of interest. This calculation is repeated for all ν'' over the range $\nu''=4\text{--}21$, and the results are shown in Fig. 4. The rate at which these molecules dissociate varies sharply with ν'' , in that a molecule in $\nu''=4$ has a lifetime against dissociation of 5000 s, whereas a molecule in $\nu''=21$ dissociates in 10 s. Thus a molecule in a high vibrational level is a much more potent source of O_3 (from $O + O_2$ recombination) than is one at lower levels, particularly if quenching of the high levels is a relatively slow process compared with low-level quenching.

In Fig. 5 are shown the wavelengths over which individual $O_2^\dagger$ levels are effectively dissociated, that is, the ranges shown account for 70 to 80 percent of the dissociation in the optically thin region above 50 km. Thus at $\nu''=21$ dissociation takes place at 410 to 450 nm. For the entire range $\nu''=8\text{--}21$, the upper state range is $\nu'=0\text{--}4$.

In order to estimate how quenching varies with vibrational level, we used the semiclassical theory for vibrational-to-vibrational state (V-V) transfer of Rapp and Englander-Golden (32). Although only strictly applicable to $(1 \rightarrow 0/0 \rightarrow 1)$ transfer (between the excited and ground-state molecules, respectively), it gives reasonable agreement for $[(\nu=n) \rightarrow (\nu=n-1)]/(0 \rightarrow 1)$ transfer with the extensive studies on V-V transfer in CO, to $\nu=14$ (33).

At the altitudes of interest, we assume that the only quencher is

O_2 , because potentially faster quenchers, the triatomic molecules O_3 , CO_2 , and H_2O , are present in very low concentrations. However, the CO_2 mixing ratio is 3×10^{-4} , and its effect will require evaluation. The fastest atmospheric quencher of $O_2^\dagger$ is $O(^3P)$, but the ratio $[O(^3P)]/[O_2]$ is only 10^{-5} at 70 km and 10^{-6} at 50 km (34). Quack and Troe (35) estimate rate coefficients for $O_2^\dagger + O(^3P)$ that are ~ 0.01 of collision frequency for low ν , and for vibrational levels in the range of interest, the data of Webster and Bair (36) indicate rate coefficients that are of a similar magnitude. Thus quenching of $O_2^\dagger$ by $O(^3P)$ should become significant only when the V-V transfer probability for $O_2^\dagger + O_2$ falls into the 10^{-7} to 10^{-8} range.

Figure 6 shows the calculated probability per collision, $P^\dagger$, for V-V transfer for a diatomic molecule of the mass of O_2 at 200 K as a function of the energy difference between $\Delta E(\nu=n \rightarrow \nu=n-1)$ and the O_2 fundamental, 1556 cm^{-1} . The probability is a strong function of this difference; for the highest vibrational levels, vibrational-to-translational (V-T) quenching may become important.

The O_3 production rate by the SR excitation process is given by

$$P_{O_3} = 2J_\infty(O_2^\dagger)[O_2^\dagger] = J_\infty(O_2^\dagger) \frac{2 \times 0.13 \times J_\infty(O_3)[O_3]}{k[O_2] + J_\infty(O_2^\dagger)} \quad (12)$$

where the factor of 2 occurs because two O_3 molecules are generated for each $O_2^\dagger$ destroyed, the factor of 0.13 is taken as the $O_2^\dagger$ yield from O_3 photodissociation, and k is the rate coefficient for $O_2^\dagger$ quenching by O_2 . Equation 12 reduces to

$$P_{O_3} = 0.26 J_\infty(O_2^\dagger) \frac{J_\infty(O_3)}{k} \frac{[O_3]}{[O_2]} \quad (13)$$

when $k[O_2] \gg J_\infty(O_2^\dagger)$. Since $J_\infty(O_2^\dagger)$ and k depend strongly on vibrational level, a vibrational distribution is needed to obtain a realistic evaluation of the O_3 production rate. Lacking this, we may still determine what fraction of the distribution needs to be in a particular level in order to perturb existing models.

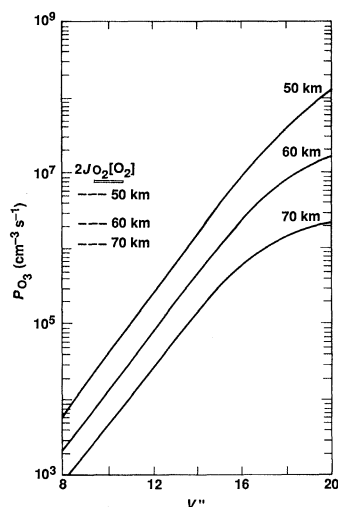
By using the data in Figs. 4 and 6, Eq. 12 is plotted as a function of vibrational level in Fig. 7, for three different altitudes. Implicit in such a plot is the artificial concept that photodissociation produces only a single vibrational level in $O_2(X)$. Values of $[O_2]$ and $[O_3]$ as a function of altitude are taken from Brasseur and Solomon (34), and $J_\infty(O_3)$ is $9 \times 10^{-3} \text{ s}^{-1}$ (31). The curvature at high altitudes occurs because as $[O_2]$ decreases, photodissociation of $O_2^\dagger$ becomes the dominant loss process for molecules in high ν'' . For more accurate calculations, the 50-km line in Fig. 7 requires some adjustment, because the O_3 photodissociation rate coefficient is affected by optical depth at that altitude, and is less than $J_\infty(O_3)$.

Also shown in Fig. 7 is the conventional O_3 source term, $2J(O_2)[O_2]$, with J values taken from the work of Omidvar and Frederick (37), which reflects a recent reduction of the cross sections in the Herzberg continuum (38). At 50, 60, and 70 km, this term is matched by the new process if all of the $O_2^\dagger$ is in $\nu'' = 15, 16$, and 17, respectively.

We must also consider vibrational cascading, since V-V transfer will only remove one vibrational quantum from $O_2(\nu''=n)$, leaving the molecule in $\nu''=n-1$. However, the steepness of the curve in Fig. 7 indicates that $O_2(\nu''=n)$ is quickly deactivated by cascading. A molecule in $\nu''=n-1$ is only 40 percent as effective as one in $\nu''=n$, so we correct for this effect with a factor of ~ 1.6 . Where the lines in Fig. 7 exhibit curvature, this factor is still valid, because the shallower slope is offset by the fact that the loss from the highest level is by photodissociation, not cascading.

If we define an "interesting" new O_3 source as one whose effect is at least 10 percent of the conventional O_2 photodissociative source,

Fig. 7. Production of O_3 versus O_2 vibrational level assuming a single-level distribution, for 50, 60, and 70 km ($O_2(B-X)$ transition only).



we then look for contributions of $5.2 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ at 50 km, $2.2 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ at 60 km, and $1.2 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ at 70 km. The necessary yields of O_2^+ molecules, based on total O_3 photodissociation, to provide 10 percent of the conventional O_3 source term are shown in Table 2. For example, this condition is met at 50 km if the yield in $v''=20$ is 2.8×10^{-4} , at 60 km if the yield is 9.2×10^{-4} , and at 70 km if the yield is 4.2×10^{-3} . Replacing the single-level assumption by a vibrational distribution causes these values to become correspondingly smaller for any single level.

If we now invoke the contribution of the continuum absorption, the necessary yields in Table 2 become more than an order of magnitude smaller if the data taken at 248 nm are representative of the 250- to 500-nm spectral region. Alternatively, a higher V-V transfer rate can be tolerated, or the vibrational distribution can be cooler than when only SR absorption is considered. It is evidently important to evaluate the $1^1\Pi_u$ and $1^3\Pi_u$ absorption strengths from high vibrational levels of the $a^1\Delta_g$ and ground states.

Although the reactions between O_3 and $O(^1D)$ or $O(^3P)$ may generate O_2^+ , this is irrelevant to the issue of atmospheric or laboratory O_3 sources, because O_3 produced at the expense of two odd oxygen particles cannot lead to a net gain of O_3 , even if all the O_2^+ were photodissociated. Reactions between $O(^3P)$ and the other species involved in the O_3 catalytic cycles, HO_2 , NO_2 , and ClO , may generate O_2^+ , but the low production rates and the relatively small exothermicities of these reactions make them of little interest in the present context.

If we have made reasonable estimates of the enumerated unknowns, there seems to be a reasonable chance that solar pumping of O_2^+ makes a contribution to O_3 production in the atmosphere. The process is most effective where the $[O_3]/[O_2]$ ratio is largest, although the situation is more complicated in that, below 50 km, solar radiation above 200 nm becomes attenuated by O_3 ; $[O_3]/[O_2]$ maximizes near 40 km and minimizes near 80 km (34). Further progress will require information on O_2^+ vibrational distributions from O_3 photodissociation, V-V transfer rate coefficients, and cross sections for the relevant photodissociation continua. Using theoretical V-V transfer rates, we have shown that if O_2^+ is formed with populations above $v'' \sim 15$, then the process could well aid in

rectifying the present imbalance between calculated and experimental atmospheric O_3 profiles.

REFERENCES AND NOTES

1. C. Pernot *et al.*, *J. Chem. Phys.* **71**, 2387 (1979).
2. D. A. Ramsay, *Can. J. Phys.* **64**, 717 (1986); P. M. Borrell, P. Borrell, D. A. Ramsay, *ibid.*, p. 721; B. A. Coquart and D. A. Ramsay, *ibid.*, p. 726.
3. L. Froidevaux, M. Allen, Y. L. Yung, *J. Geophys. Res.* **90**, 12999 (1985).
4. R. T. Clancy, D. W. Rusch, R. J. Thomas, M. Allen, R. S. Eckman, *ibid.* **92**, 3067 (1987).
5. J. E. Frederick, G. N. Serafino, A. R. Douglass, *ibid.* **89**, 9547 (1984).
6. J. E. Frederick and R. J. Cicerone, *ibid.* **90**, 10733 (1985).
7. R. Simonaitis and M. T. Leu, *Geophys. Res. Lett.* **12**, 829 (1985).
8. R. P. Saxon and T. G. Slanger, *J. Geophys. Res.* **91**, 9877 (1986).
9. C. E. Fairchild, E. J. Stone, G. M. Lawrence, *J. Chem. Phys.* **69**, 3632 (1978); R. K. Sparks, L. R. Carlson, K. Shobatake, M. L. Kowalczyk, Y. T. Lee, *ibid.* **72**, 1401 (1980).
10. A Lambda Physik EMG 150 MSC excimer laser was operated on KrF. This laser is tunable over the 248- to 249-nm range and can be operated with almost the full broadband intensity of 200 mJ compressed to a linewidth of $\sim 0.3 \text{ cm}^{-1}$. The reaction cell was a 15-cm-long, 4-cm-diameter Pyrex cylinder with quartz windows. It was filled with 1000 torr of 99.99 percent O_2 , and closed off. The laser radiation was unfocused, filling an area of 2 cm^2 . Thus a pulse gave a photon density of $1 \times 10^{17} \text{ h}\nu \text{ cm}^{-2}$. The longitudinally transmitted radiation was measured beyond the cell by a volume-absorbing power meter with a response time of 3 s. In addition, a filtered photomultiplier monitored 254-nm light from an Hg pen lamp transversely, through quartz windows. The filter has a full-width at half-maximum (FWHM) of 10 nm, and thus had some sensitivity to 248-nm radiation. Thus the photomultiplier summed the directly viewed Hg radiation and the KrF scattered-light contribution, but when making intensity measurements with a 100-ns gate triggered by the laser pulse, only the KrF radiation was detected. However, the contribution from KrF scattered light could be neglected when 254-nm radiation was monitored in a continuous-wave (cw) mode.
11. D. M. Creek and R. W. Nicholls, *Proc. R. Soc. London Ser. A* **341**, 517 (1974); *ibid.*, (suppl. 1), p. 10016.
12. R. L. Sharpless and T. G. Slanger, unpublished results.
13. G. Moortgat, unpublished results.
14. R. D. Johnson III, G. R. Long, J. W. Hudgens, *J. Chem. Phys.* **87**, 1977 (1987).
15. L. T. Molina and M. J. Molina, *J. Geophys. Res.* **91**, 14,501 (1986).
16. R. P. Wayne, *Atmos. Environ.* **21**, 1683 (1987).
17. J. C. Brock and R. T. Watson, *Chem. Phys. Lett.* **71**, 371 (1980); S. T. Amimoto, A. F. Force, J. R. Wiesenfeld, R. H. Young, *J. Chem. Phys.* **73**, 1244 (1980).
18. B. R. Lewis, L. Berzins, J. H. Carver, S. T. Gibson, *J. Quant. Spectrosc. Radiat. Transfer* **36**, 187 (1986).
19. M. Nicolet, S. Cieslik, R. Kennes, *Aeron. Acta A No.* **318** (1987).
20. P. H. Krupenie, *J. Phys. Chem. Ref. Data* **1**, 423 (1972).
21. R. P. Saxon and B. Liu, *J. Chem. Phys.* **67**, 5432 (1977).
22. J. J. Valentini, personal communication.
23. ———, D. P. Gerrity, D. L. Phillips, J.-C. Nieh, K. D. Tabor, *J. Chem. Phys.* **86**, 6745 (1987).
24. R. Buenker, S. D. Peyerimhoff, M. Peric, *Chem. Phys. Lett.* **42**, 383 (1976).
25. L. C. Lee, T. G. Slanger, G. Black, R. L. Sharpless, *J. Chem. Phys.* **67**, 5602 (1977).
26. C. Cleveland and J. R. Wiesenfeld, personal communication.
27. V. D. Baiaomonte, L. G. Hartshorn, E. J. Bair, *J. Chem. Phys.* **55**, 3617 (1971).
28. H. B. Levene, J.-C. Nieh, J. J. Valentini, *ibid.* **87**, 2583 (1987).
29. G. Kockarts, *Planet. Space Sci.* **24**, 589 (1976).
30. M. Allen and J. E. Frederick, *J. Atmos. Sci.* **39**, 2066 (1982).
31. M. Nicolet, *Etude des reactions chimiques de l'ozone dans la stratosphere* (Institut Royal Meteorologique de Belgique, Brussels, 1978).
32. D. Rapp and P. Englander-Golden, *J. Chem. Phys.* **40**, 573 (1964); D. Rapp, *ibid.* **43**, 316 (1965).
33. R. L. DeLeon and J. W. Rich, *Chem. Phys.* **107**, 283 (1986).
34. G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere* (Reidel, Boston, 1984).
35. M. Quack and J. Troc, *Ber. Bunsenges. Phys. Chem.* **81**, 160, (1977).
36. H. Webster III and E. J. Bair, *J. Chem. Phys.* **56**, 6104 (1972).
37. K. Omidvar and J. E. Frederick, *Planet. Space Sci.* **35**, 769 (1987).
38. A. S.-C. Cheung, K. Yoshino, W. H. Parkinson, S. L. Guberman, D. E. Freeman, *ibid.* **34**, 1007 (1986).
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