

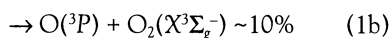
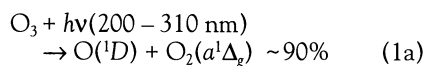
Energetic Molecular Oxygen in the Atmosphere

Tom G. Slinger

Industrialized nations now devote a substantial part of their atmospheric research to studies of ozone photochemistry. These studies have emphasized ways in which ozone loss has been accelerated by human activity. Relatively little attention, however, has been paid to the details of how atmospheric ozone is created. In the research article by Miller *et al.* on page 1831 of this issue (1), a mechanism is proposed for atmospheric ozone production—namely, reaction between highly vibrationally excited O_2 and ground-state O_2 —that may have relevance to the overall ozone balance.

The standard view is that solar radiation at wavelengths shorter than 242 nm photodissociates oxygen, and the resultant atoms form ozone by $\text{O} + \text{O}_2$ three-body recombination. However, the devil is in the details, and we know that the atmosphere is a stew (admittedly dilute) of high-energy particles. This is particularly true for oxygen and its allotropes (see figure). Note that the products of direct ozone photodissociation are not necessarily distinguishable from those originating with O_2 . Thus, ozone photodissociation, usually viewed as a do-nothing process in terms of changing the ozone balance, can have a significant effect in this regard, particularly because ozone photoabsorption rates are far larger than those for oxygen.

Life on Earth is protected from ultraviolet radiation in the range of 200 to 310 nm by stratospheric ozone photoabsorption and dissociation

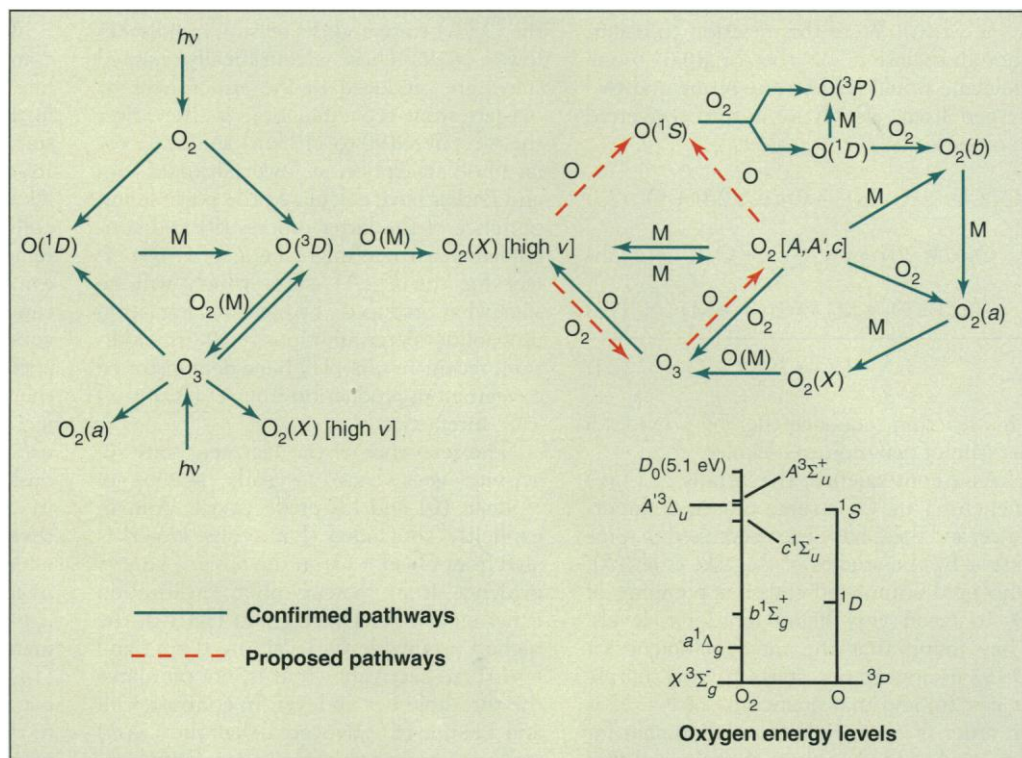


O(¹D) is quenched rapidly by all collision partners and is the single most important intermediate in the atmosphere because it is responsible for generating several molecules (OH, NO, and CH₃) whose sub-

sequent reactions in a sense define stratospheric chemistry. Early attempts at atmospheric ozone modeling—based only on O, O₂, and O₃ chemistry—did not consider these minor components, and only when

duction. In theory, these active O_2 molecules could have a substantial impact on atmospheric chemistry in that they are copiously produced and, unlike $\text{O}(^1\text{D})$, are not rapidly quenched by O_2 and N_2 .

The interest in new ozone sources arises because current models of altitude-dependent ozone concentration profiles underestimate the amount of ozone actually present in the higher atmosphere (above the region affected by chlorofluorocarbon chemistry). The discrepancy is 10 to 20% at altitudes of 40 to 70 km, being larger at the higher altitude (2), and has become known as the "ozone deficit problem."



Devilish details. A partial diagram of oxygen allotrope cycles in an O_2 -M system that has been subjected to solar radiation, including both confirmed and proposed reaction pathways ($\text{M} = \text{O}_2, \text{N}_2$). Electronic states of O and O_2 are shown at right.

the importance of the HO_x and NO_x catalytic cycles was recognized did modeled ozone profiles fall into reasonable agreement with observation. This evolving process continues with the addition of the ClO_x cycle and (ClO)₂ chemistry in the Antarctic, and as a more precise understanding of ozone photochemistry becomes necessary, attention shifts to more transient species.

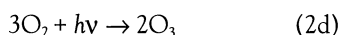
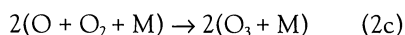
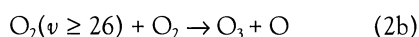
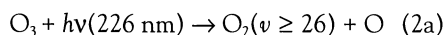
Until recently, the channel shown in reaction 1b, giving ground-state products, was ignored, on the assumption that vibrationally excited oxygen would innocuously convert its energy into heat. However, the extent of vibrational excitation was not fully appreciated, and it now appears that this entity may have interesting chemical properties in terms of ozone pro-

The article by Miller *et al.* (1) proposes a new way by which ozone may be generated and addresses the question of the ozone deficit. In this study, imaging techniques combined with resonant multiphoton ionization (REMPI) are used to measure the translational energy of ground-state oxygen atoms produced from the 226-nm photodissociation of ozone. From such a measurement, the internal energy of the accompanying ground-state O_2 fragment can be deduced, and the authors find that vibrationally excited $O_2—O_2(v)$, where v is the level of vibrational excitation—is produced up to the limit of available energy, $v = 27$, for 226-nm dissociation. This is consistent with our finding that $O_2(v)$ is produced up to $v = 22$ as a result of 248-nm photodissociation of ozone (3, 4).

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Of particular interest in the new results is that there is a bimodal distribution of vibrational population, with molecules in $v = 27$ having a comparable nascent concentration to those at the maximum of the "low- v " peak, at $v \sim 15$. Because 10 to 15% of ozone molecules photodissociated in the 200- to 310-nm Hartley band give $O_2(v)$ and because the ozone turnover rate is quite high (the typical photodissociative lifetime for an ozone molecule above 50 km is 2 min), the rate of production of $O_2(v)$ is large.

The possible relation between $O_2(v)$ production and ozone generation comes from the hypothesis that reaction of $O_2(v \geq 26)$ with molecular oxygen makes ozone (5, 6). Were this reaction to occur, photodissociation of the original ozone molecule would lead to one ozone and two oxygen atoms, which are in turn converted to ozone



This reaction sequence thereby provides a net gain of two ozone molecules.

As a consequence, the details of $O_2(v)$ quenching by O_2 assume practical importance, and these have been addressed to some extent by the studies of Rogaski *et al.* (5), who used stimulated-emission pumping of O_2 to reach very high vibrational levels. They found that the rate coefficient for $O_2(v)$ disappearance starts to rise sharply at $v = 26$, and that quenching of $v = 27$ is an order of magnitude faster than that for $v = 25$. At the same time, they showed that quenching of these levels by nitrogen is quite slow, so O_2 has the dominant atmospheric effect.

Miller *et al.* (1) and Rogaski *et al.* (5) assume that this increase in rate coefficient corresponds to the opening of the ozone production channel, reaction 2b. With appropriate averaging over the ozone absorption wavelengths and with assumptions about yields, the new study concludes that there is significant impact on the modeled atmospheric ozone profiles, with a maximum increase of 10% observed at ~ 50 km. This important result stresses the potential significance of atmospheric $O_2(v)$. The caveat, however, is that ozone production was not directly measured, and thus, the evidence is circumstantial.

Furthermore, the modeled addition to ozone concentrations, although of the right magnitude, does not have the correct altitude dependence to ameliorate the "ozone deficit" problem: Its effect is maximum at

the lower part of the deficit region, whereas the problem is greatest at higher altitudes (2). It may well be that there is not a single solution and that this new mechanism has relevance to only a portion of the discrepancy.

Related to these studies are recent investigations of electronically excited O_2 (7), for which it was long ago suggested that reaction with O_2 produces ozone (8). For the so-called Herzberg states, $O_2(A, A', c)$, lying 4 to 5 eV above the ground state (see figure), we find that oxygen atoms (and by inference, ozone) are generated, the yield being close to unity for the highest vibrational level ($v = 11$) of the $O_2(A)$ state and decreasing rapidly below $v = 9$. These electronically excited states are produced in the atmosphere by oxygen atom recombination in the lower thermosphere (90 to 110 km) and by O_2 solar photoabsorption at lower altitudes. Shi and Barker have calculated the possible importance of the latter process (9) and concluded that there might be a 5 to 10% effect for the $O_2(A)$ state, which will be somewhat reduced by recent transition probability determinations (10). In addition, recent results (11) have demonstrated oxygen atom production from $O_2(A, v = 8) + O_2$ interaction.

The relevance of the Herzberg state reactivity goes back to early studies of Volman (6) and his predecessors. Volman explicitly concluded that ozone is generated from $O_2(v) + O_2$ on the basis of kinetic evidence from mercury-photosensitization experiments. For $Hg(^3P_1)$ and $Hg(^3P_0)$, the highest attainable O_2 levels are $v = 34$ and $v = 31$, respectively—that is, not far above the threshold $v = 26$ level. In contrast, Gill and Laidler (8) advocated that the $O_2(A)$ state was responsible for ozone formation, but in this case, the maximum vibrational level is $v = 7$, for which we deduce a rather small ozone quantum yield (7). To put these matters in perspective, it is illuminating to recognize that 80 years ago, Warburg (12) discussed ozone production, with relatively high yields, from irradiation of high-pressure oxygen at 254 nm, far from the 242-nm O_2 dissociation limit. These issues are not new.

The possible significance of vibrationally excited oxygen in the atmosphere was recognized as a consequence of our laboratory studies, which indicated the breadth of the $O_2(v)$ distribution from ozone photodissociation (3, 4). At that time, we proposed that secondary photodissociation of the high- v levels could result in atom production and subsequent ozone formation. The essential point was that, whereas atmospheric photodissociation of cold O_2 takes place at wavelengths below 242 nm with large cross sections only below 190 nm, a

vibrationally excited molecule can be dissociated with less energetic photons. For instance, a $v = 27$ molecule is dissociated by visible solar radiation, which is much more plentiful than vacuum ultraviolet radiation.

The critical issue is the rate at which $O_2(v)$ is quenched because such a process is competitive with solar photoabsorption. It was ultimately shown that collisional removal by both O_2 and N_2 , although not rapid, is fast enough to prevent this mechanism from making a substantial contribution to existing ozone (3, 13). Of course, for the mechanism proposed by Miller *et al.* (1), collisional removal is itself the ozone source.

The presence of high- v O_2 molecules, combined with their substantial production rate from O_3 photodissociation, should spur further studies. In the present case, for instance, it would be important to demonstrate actual ozone production and yields. As the diagram shows, the complexities of collisional processes in excited O_2 are quite remarkable, and not all of them have been evaluated for their atmospheric significance. Although the importance of energetic transient O_2 molecules has been long appreciated in nightglow investigations, the involvement of ozone makes the subject of more general concern. The study of excited oxygen entities has been notoriously difficult, but the recent developments in state-to-state techniques are making their investigation more accessible. Stimulated-emission pumping and time-of-flight imaging (1, 5) are important tools for these applications, as is the double-resonance metastable REMPI technique of Copeland (14). With our models of the atmosphere becoming more sophisticated, it is essential to develop a complete view of the system, which includes an understanding of the role played by the transient O_2 species.

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