

A quantum yield determination of O(1D) production from ozone via laser flash photolysis

D. L. Philen, R. T. Watson, and D. D. Davis

Citation: *J. Chem. Phys.* **67**, 3316 (1977); doi: 10.1063/1.435251

View online: <http://dx.doi.org/10.1063/1.435251>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v67/i7>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

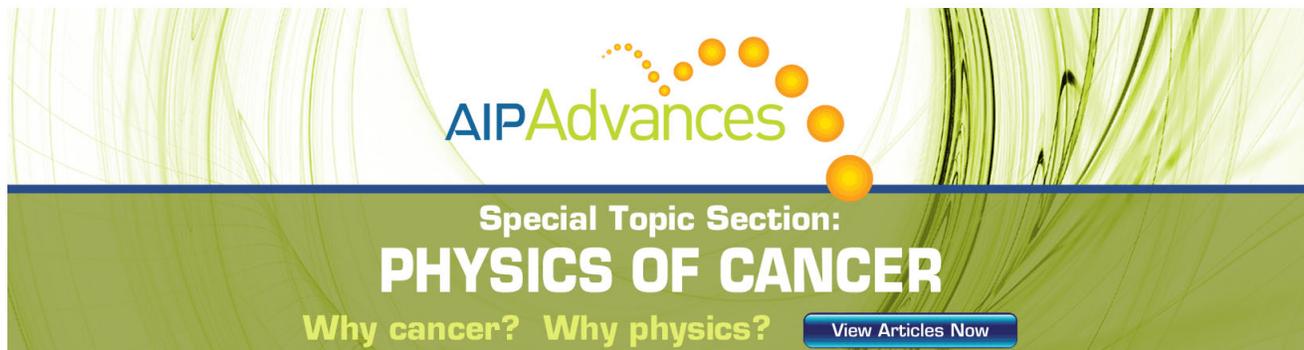
Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



AIP Advances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

A quantum yield determination of O(¹D) production from ozone via laser flash photolysis

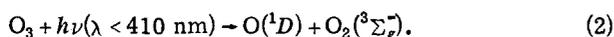
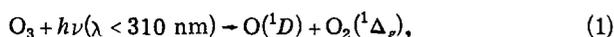
D. L. Philen, R. T. Watson,* and D. D. Davis†

Atmospheric Sciences Division, Applied Sciences Laboratory, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received 7 October 1976)

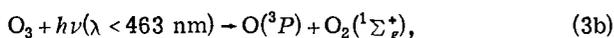
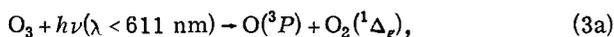
The quantum yield for O(¹D) production from ozone photolysis has been measured at 298 K from 293.0 to 316.5 nm. The O(¹D) was monitored by its reaction with N₂O to form excited NO₂*. The photolysis source was a frequency doubled flashlamp pumped dye laser which provided tunable uv in the desired spectral region with 0.1 nm linewidth. The results show ϕ to be constant below 300 nm, taken to be unity, with a sharp decrease centered at 308 nm and a value of less than 0.1 above 313.5 nm.

INTRODUCTION

It is generally accepted that the OH(²Π) free radical is one of the most important oxidizing agents in the troposphere and stratosphere since it controls the chemistry of numerous trace gases. The principal source of the hydroxyl radical is the reaction of electronically excited atomic oxygen, O(¹D), with atmospheric water vapor, O(¹D) + H₂O → OH + OH (a much smaller contribution is made via the reaction of O(¹D) with methane and molecular hydrogen). The source of O(¹D) is that of photolysis of ozone in the Hartley continuum, and possibly in the Huggins band, i. e.,



On thermochemical grounds, Processes (1) and (2) are allowed to occur at wavelengths shorter than 310 and 410 nm, respectively. However, it has now been established¹ that Process (1) is the dominant photolytic process below 300 nm and all evidence suggests that it occurs with unit quantum efficiency. Processes 3a or 3b



have been shown^{2,3} to be the only processes occurring at 340 nm, thus indicating that Process (2) is of no importance. In the 300–320 nm range, conflicting results have been reported for the O(¹D) quantum yield. This wavelength region has now been designated as the fall-off region for O(¹D) production.^{2–9} Even though the absorption cross section for ozone is rapidly decreasing above 300 nm, the exact nature of the fall off in O(¹D) production between 300 and 320 nm is of particular importance in the troposphere and lower stratosphere owing to the lack of radiation at wavelengths shorter than 300 nm. (Absorption cross-section data for ozone have been determined for both the visible and uv spectral regions,^{7,10–15} and have been recently reviewed¹⁶ and tabulated.⁷)

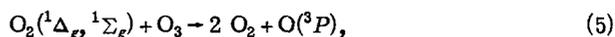
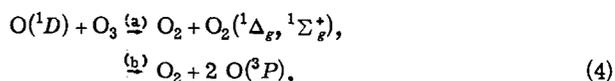
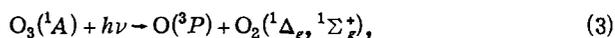
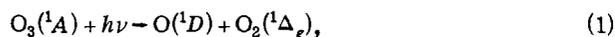
Ozone photolysis studies have been performed in both the liquid^{17,18} and gaseous^{2–9} phases by several groups utilizing a variety of techniques. However, the scope of this investigation has been limited to photolytic processes occurring only in the gaseous phase. Jones and Wayne,³ at 313 nm, measured the variation in O₃ disappearance, $\Phi(\text{O}_3)$, as a function of the O₃ concentration

in pure O₃ and O₃/H₂ mixtures. These authors concluded that the quantum yield for O(¹D) production had a value of 0.1 relative to a value of unity at wavelengths shorter than 300 nm. Castellano and Schumacher,² however, have reported a ϕ value of 1.0 at 313 nm, their results coming from an experiment very similar to that of Jones and Wayne. Simonaitis *et al.*,⁴ Kuis *et al.*,⁹ and Kajimoto and Cvetanovic⁵ photolyzed ozone at 313 nm in the presence of N₂O, and from the amount of N₂ formed, deduced ϕ to be 0.35 (modified⁹ downward from their original report of 0.5), 0.29, and 0.44, respectively. The latter two groups^{5,9} also studied the variation of ϕ O(¹D) with temperature. Moortgat and Warneck⁷ and Martin *et al.*⁸ also photolyzed ozone at 313 nm in the presence of N₂O and deduced ϕ to be 0.29 and 0.32, respectively. In these studies, ϕ was established by monitoring the infrared chemiluminescence associated with the formation of electronically excited NO₂*. Lin and DeMore⁶ measured the yield of isobutanol from the photolysis of O₃ with isobutane at 233 K and reported a value of ≤ 0.08 for ϕ O(¹D), again at 313 nm.

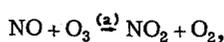
To be reported here is a new investigation on the photochemical production of O(¹D) in the spectral region of 293.0–316.5 nm. Of considerable importance in this study was the wavelength of the light source employed. In this investigation, a tunable dye laser was employed having a spectral width of ~ 0.15 nm.

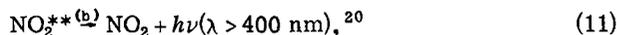
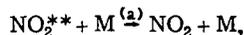
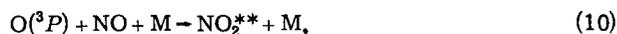
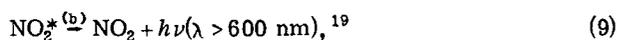
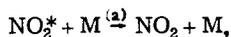
EXPERIMENTAL

The chemical scheme which describes the photochemical degradation of pure ozone can be written:



In the presence of N₂O, the following additional reactions can occur:





It will be shown later that Processes (10)–(12) are of no importance under the experimental conditions employed in the present study. Therefore, the amount of O(¹D) produced in Process (1) can be quantitatively monitored via the infrared chemiluminescence (9b) which is associated with the production of the excited electronic state of NO₂* in Reaction 8b. The intensity of emission, $I(\lambda)$, can be expressed as:

$$I(\lambda) = \beta \phi(\lambda) N_{\text{abs}}(\lambda) \gamma, \quad \text{I}$$

where $\phi(\lambda)$ is the quantum yield for O(¹D) production, β is the geometrical collection efficiency of the chemiluminescence detector, $N_{\text{abs}}(\lambda)$ is proportional to the number of quanta of the photolysis radiation absorbed by ozone in the region of the reaction cell as viewed by the chemiluminescence detector, and γ is given by:

$$\gamma = \frac{2(k_{9b}/k_{9a})k_{7b}(N_2O)k_{9b}}{[k_7(N_2O) + k_4(O_3)][k_{9a}(N_2O + O_3) + k_{9b}]}. \quad \text{II}$$

As can be seen from Eq. II, the magnitude of γ depends upon the values of several rate constants as well as the concentrations of N₂O and O₃. Consequently, if the initial concentrations of N₂O and O₃ are kept constant, and the consumption of ozone during photolysis is limited to <1%, then the value of λ is constant. However, it can be shown that the intensity of fluorescence (I_F) is relatively insensitive to the chemical composition of the photolysis mixture as it is directly proportional to (O₃ + N₂O) through Processes (1) and (7) and inversely proportional to (O₃) and (N₂O) through Process (9a), the electronic quenching of NO₂*. Calculations based on recent rate constant data²¹ for Reactions (4) and (7) predict that under our experimental conditions ~82% of the O(¹D) produced in Process (1) reacts with N₂O to produce an equal concentration of NO. $N_{\text{abs}}(\lambda)$ can be calculated using the Beer–Lambert expression of $\ln(I_0/I_t) = \sigma(\lambda)(O_3)l$, and knowledge of the incident photolysis flux [$N_0(\lambda)$]. $\sigma(\lambda)$ is the absorption cross section for ozone.

The experimental arrangement employed in this study utilized a frequency doubled, flashlamp pumped, tunable dye laser as the photolytic source of radiation in the region of 293–316 nm (see Fig. 1). This dye laser system was operated with Rhodamine 6G, Rhodamine B, or a mixture of both dyes to provide continuous tunable output from 586 to 633 nm in the fundamental. Doubled uv radiation was obtained by use of three different temperature tuned crystals (ADA, 293–306 nm; ADP, 305–315 nm; RDP, 313–316.5 nm). Temperature tuning was used in favor of angle turning so as to minimize beam “walk off” (i. e., it is essential that the photolysis beam

traverse the reaction cell in exactly the same position at all wavelengths) and thus maintain the geometric cell factor, β , constant. The linewidth of the doubled output was ~0.15 nm. The combination of three doubling crystals and different dyes provided continuous tuning over the entire photolysis region. The output wavelength of the dye laser was calibrated to within ±0.1 nm for the fundamental frequency relative to the He/Ne laser line at 632.8 nm. The latter was achieved with the use of a $\frac{3}{4}$ meter spectrograph. The uv photon flux incident on the reaction cell was monitored using an RCA-935 calibrated photodiode which was traceable to an NBS standard. In an effort to eliminate any saturation problems on the 935 photodiode, the intensity of the laser pulse was reduced by two quartz beam splitters (see Fig. 1).

The NO₂* fluorescence was monitored, through a cut-off filter (λ transmitted >610 nm) by a cooled EMI-9658 R photomultiplier (extended S20 response) positioned at right angles to the incident uv radiation. In order to prevent dye laser fundamental radiation scattering into the reaction cell, two UG-5 filters were placed on the output end of the frequency doubling crystal. Both the fluorescence and the incident radiation signals were stored on a Textronix dual trace storage oscilloscope, and the ratio of their intensities taken. A short series of experiments was also performed where the oscilloscope was replaced by a Northern 610 multichannel analyzer (discussed later).

In all experiments, the reaction cell was evacuated to a vacuum of 1×10^{-6} torr or lower before each experiment, using a liquid N₂ trapped oil diffusion pump system. Mixtures of 0.9 torr of O₃ and 9.1 torr of N₂O were used for all data points to give a total mixture of 1 : 10 O₃ to N₂O. Each mixture was frequently changed to minimize any possibility of ozone destruction by homogeneous gas phase reactions, or by heterogeneous decomposition on the cell walls.

The nitrous oxide was Matheson Research Grade having a stated purity of 98%. Ozone was prepared using a commercial ozonizer, and then stored on silica gel at 193 K. Before each experiment, the ozone was purified by vacuum pumping on the silica gel while at 193 K. Frequent tests of the O₃ purity showed levels of at least 95% (95% O₃; 5% O₂).

RESULTS

At each wavelength, several sets of experiments were performed where the ratio of the infrared fluorescence,

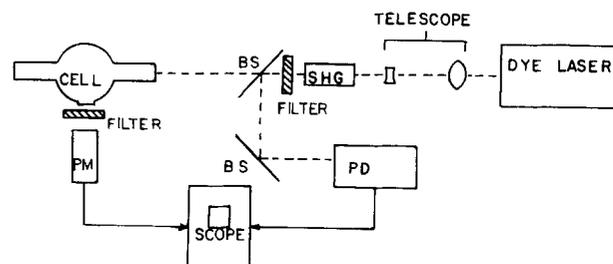


FIG. 1. Experimental arrangement of ozone photolysis experiment using a frequency doubled dye laser.

TABLE I. Experimentally determined quantum yields for $O(^1D)$.

Wavelength (nm)	$O(^1D)$
293.5	0.968 ± 0.07
294.0	1.050 ± 0.09
296.5	0.970 ± 0.11
297.0	1.006 ± 0.07
298.0	1.093 ± 0.07
298.5	1.077 ± 0.07
299.0	0.950 ± 0.091
300.0	1.004 ± 0.065
301.5	0.943 ± 0.068
302.0	0.986 ± 0.067
302.5	1.009 ± 0.073
303.0	1.069 ± 0.053
304.0	0.917 ± 0.11
305.0	0.871 ± 0.086
305.5	0.760 ± 0.057
306.0	0.883 ± 0.11
306.2	0.916 ± 0.078
306.5	0.906 ± 0.096
307.0	0.684 ± 0.114
308.0	0.592 ± 0.07
309.0	0.484 ± 0.086
309.5	0.364 ± 0.028
310.0	0.344 ± 0.068
311.0	0.224 ± 0.032
311.5	0.185 ± 0.022
312.5	0.154 ± 0.024
313.0	0.121 ± 0.029
313.5	0.080 ± 0.017
314.0	0.090 ± 0.026
315.0	0.035 ± 0.02
316.5	0.022 ± 0.015

I_F , and incident uv laser radiation, N_0 , signals were measured. The ratio was measured for at least ten individual laser pulses within each set of experiments, and then averaged. The resulting ratios, corrected for the ozone absorption cross section and the photodiode response curve, gave the desired relative quantum efficiency for $O(^1D)$ production as a function of wavelength. The quantum yield, ϕ , has been tabulated (Table I) and plotted (Fig. 2) as a function of wavelength from 293.0 to 316.5 nm. The expressed uncertainties represent the 90% confidence limits on the data. At wavelengths shorter than 300 nm, the quantum yields were normalized to unity. Above 302.5 nm the quantum yield was observed to deviate from unity with the maximum rate of decrease appearing at 308 nm. At the wavelengths 313.5 and 316.5 nm, it can be seen that ϕ decreased to 0.1 and 0.02, respectively. Determinations of ϕ at still longer wavelengths were precluded due to experimental difficulties. Further improvements in the experimental technique could yield more data in this region, if needed. It should be noted that while the absolute value of the uncertainty in Fig. 2 appears to decrease as one goes to longer wavelengths the relative error associated with each point (that is, the uncertainty divided by the mean value of the quantum yield) remains approximately constant over the spectral region of interest.

A series of experiments was also performed to show that there were no unrecognized sources of detectable

radiation which could have resulted in an erroneous interpretation of the data. These included (a) eliminating the 610 nm cut-off filter, or replacing it with a 540 nm cut-off filter, (b) a variation in the incident uv photolysis flux by a factor of ~ 10 , and (c) a variation in chemical composition. The most likely source of unwanted fluorescence would have been associated with the formation of electronically excited NO_2^* via Reaction (10) followed by Process (11b). In this case, the fluorescence associated with the formation of NO_2^* is shifted to shorter wavelengths (relative to that associated with NO_2) due to the increased exothermicity of Reaction (10) compared to Reaction (8). However, the observation that the intensity of detected fluorescence was (a) invariant to the type of cut-off filter employed, and (b) varied linearly with the incident flux, strongly indicates that Reaction (10) was of no significance. If Process (10) had been important, the resulting fluorescence intensity would have been (a) dependent upon the choice of cut-off filter, and (b) varied with the square of the photolytic flux. These experiments, therefore, confirmed our calculations which showed that Process (10) should not have been important. Preliminary experiments conducted at wavelengths shorter than 305 nm, with a chemical composition of 0.25 torr each of N_2O and O_3 , resulted in similar results for ϕ , again indicating that Reaction 10 was unimportant. As expected, there was no observable fluorescence signal when pure O_3 or pure N_2O was photolyzed within the spectral region of interest. Fluorescence due to the $O(^3P) - O(^1D)$ electronic transitions at 630 nm was not important due to the long radiative lifetime²² associated with this spin-forbidden process.

Several experiments were performed where a multi-channel analyzer was used in the single photon counting mode to accumulate the NO_2^* fluorescence emitted from 10–20 laser pulses. Typical concentrations of O_3 and N_2O were 0.25–0.5 torr. The resulting fluorescence

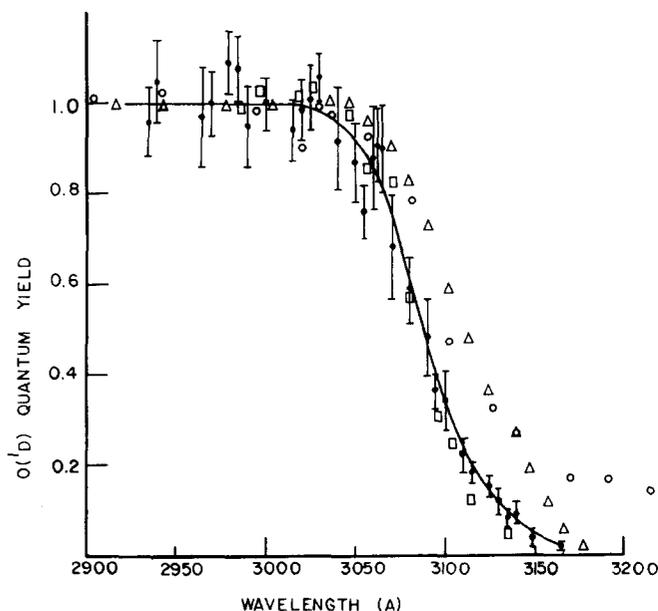


FIG. 2. Experimental quantum yield of $O(^1D)$; \square , Lin-DeMore; Δ , Moortgat *et al.*; \circ , Martin *et al.*; \bullet , this work.

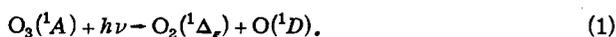
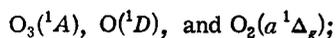
TABLE II. Summary of O(¹D) quantum yields.

Investigator	ϕ O(¹ D)	Temp(°K)	Technique	Photolytic source
Castellano, Schumacher	0.75	248	Gas phase O ₃ ;	cw lamp
	1.0	298	decrease in O ₃ pressure	
Kajimoto, Cvetanovic	0.53	313	Gas phase O ₃ , N ₂ O;	cw lamp Chemical filter
	0.21	198	Increase in N ₂	
Simonaitis, Braslavsky, Heicklen, Nicolet	0.35	298	Gas phase O ₃ , N ₂ O;	cw lamp Chemical filter
			Increase in N ₂	
Martin, Girman, Johnston	0.32	298	O ₃ , N ₂ O; N ₂ O chemi- luminescence	cw lamp
Moortgat, Warneck	0.29	298	O ₃ , N ₂ O; NO ₂ chemi- luminescence	cw lamp
Kuis, Simonaitis, Heicklein	0.29	293	Gas phase O ₃ , O ₂ ,	cw lamp Chemical filter
	0.22	258	N ₂ O; Increase	
	0.11	221	in N ₂	
Jones-Wayne	0.1	298	Decrease in O ₃	cw lamp
Lin-DeMore	0.08	235	O ₃ , Isobutane	cw lamp
This work	0.12	298	O ₃ , N ₂ O; NO ₂ chemi- luminescence	Pulsed dye laser

intensity-time profiles were recorded and observed to be logarithmic with typical $1/e$ decay times (I_F maximum occurs at $t \approx 10^{-5}$) of $\sim 3 \times 10^{-4}$ s. An analysis of the reaction scheme reveals that the only process involved in the formation of NO₂* which has a lifetime exceeding a few microseconds is Reaction (8). Therefore, the time profile of I_F is equivalent to monitoring the rate of removal of NO [$(I_F)_t \propto (\text{NO})_t$]. The predicted reaction lifetime for NO was expected to be typically 5×10^{-3} [$\tau = 0.7 / (\text{O}_3)k_8$], assuming the accepted value²³ for k_8 of 1.8×10^{-14} cm³ molecule⁻¹ s⁻¹ at 298 K. Therefore, it can be seen that the predicted lifetime is approximately an order of magnitude longer than that observed experimentally. This observation is most easily rationalized by invoking the production of vibrationally excited NO in Process (7b) which reacts with O₃ at a rate 10–20 times greater than that of NO($\nu=0$) + O₃(0, 0, 0). This hypothesis is strongly supported by the quantitative observations of Chamberlain *et al.*²⁴ where NO($\nu'' = 1, 2, 3$) were observed as products of Reaction (7b).

DISCUSSION

The wavelength limit for Process (1) can be determined from the basic thermodynamic properties of



The electronic excitation energies of O(¹D) and O₂(¹Δ_g) are 45.4 and 22.5 kcal mol⁻¹, respectively, and the bond dissociation energy of O₃ at 0 K is 24.3 ± 0.4 kcal mol⁻¹. Therefore, the calculated energy limit for Process (1) is 92.2 ± 0.4 kcal mol⁻¹, which corresponds to a wavelength limit of 310.3 ± 1.3 nm.

Table II summarizes the reported values for ϕ O(¹D) at 313 nm. It can be seen that there is significant disagreement with values ranging from 0.1 to 1.0 at 298 K. It should be noted, however, that a significant difference between this and previous studies which have measured ϕ O(¹D) as a function of wavelength is the utilization in this investigation of a narrow line (0.15 nm) dye laser as the photolytic source. Hence, this investigation should have exhibited a higher degree of definition in the fall-off region than has heretofore been possible where cw arc lamps have been coupled to scanning monochromators for wavelength selectivity.^{6–8} Experiments performed with the latter type of photolysis source might have been subject to overestimating the values of ϕ O(¹D) in the fall-off region due to the transmission of a small quantity of short wavelength light where both ϕ O(¹D) and $J(\text{O}_3)$ are greater. However, in several of the earlier studies involving the determination of ϕ O(¹D) at 313 nm, a medium pressure mercury lamp was employed having two spectral lines of near equal intensity at 313.16 and 312.57 nm. These lines were isolated from others using special chemical filters which *should* have insured the spectral purity of the photolysis radiation. Consequently, if these lamps did provide spectrally pure radiation at ~ 313 nm, then no explanation can, at present, be forwarded for the large discrepancies reported for ϕ O(¹D) between these earlier studies and the present work.

The value determined in this study for ϕ O(¹D) at 313 nm is in good agreement with that reported by Jones and Wayne³ and Lin and DeMore⁶ (after a correction for the temperature dependence—to be discussed), but a factor of 2–3 lower than Kuis *et al.*,⁹ Kajimoto and Cvetanovic,⁵ Martin *et al.*,⁸ and Moortgat and Warneck.⁷ Al-

though Jones and Wayne³ reported high values for the quantum yield for the loss of O_3 (probably due to HO_x impurities), this should not have invalidated their results for ϕ , $O(^1D)$. Indeed, their results were unchanged when using the H_2/O_3 system.

It can be seen from Fig. (2) that the value of $\phi O(^1D)$ decreases from unity at wavelengths significantly shorter than the thermodynamically allowed limit. This observation has been previously⁶⁻⁸ reported and is not at all unexpected. Process (1) probably involves a vertical transition from the 1A_1 ground state to the 1B_2 bound state,²⁵ which correlates to $O(^1D) + O_2(^1\Delta_g)$, while Processes (3a) or (3b) involve the same vertical transition followed by curve crossing to a repulsive potential surface. The exit channel of the process may have a low energy barrier, which would be expected to decrease the value of $\phi O(^1D)$ below unity prior to the thermodynamic energy cut off. Therefore, if there is an energy barrier to dissociation, any value of $O(^1D)$ greater than zero at the thermodynamic limit must be explained by certain available rotational states supplying energy to overcome this barrier. This availability of rotational energy for overcoming the energy barrier for dissociation also explains the long wavelength ($\lambda > 310$ nm) tail. An alternate and more likely explanation for the fall off in $\phi O(^1D)$ above the thermodynamic limit is that there exists a curve crossing to a repulsive potential surface in the vicinity of the thermodynamic limit for $O(^1D) + O_2(^1\Delta_g)$ production, thus decreasing the value of $\phi O(^1D)$ below unity. Kuis *et al.*⁹ and Kajimoto and Cvetanovic⁵ measured $\phi O(^1D)$ as a function of temperature at 313 nm, and reported $\phi O(^1D)$ to vary from 0.29 at 293 to 0.11 at 221 K, and 0.53 at 313 to 0.21 at 198 K, respectively. Both groups calculated the population distribution of rotational states with temperature. Kajimoto and Cvetanovic⁵ assumed that all the rotational energy was available for overcoming any barrier to dissociation and it appears that when the absolute values for $\phi O(^1D)$ were calculated as a function of temperature at 313 nm, it was assumed that $\phi O(^1D)$ has a value of unity at the thermodynamic energy limit.

Kuis *et al.*⁹ performed several classical and quantum mechanical calculations, preferring that calculation where it was assumed that only two degrees of rotational freedom could contribute to overcoming the energy barrier (due to conservation of angular momentum consideration). Kuis *et al.*⁹ used their experimentally determined temperature dependency for $\phi O(^1D)$, 313 nm) to determine that the best value for $E\epsilon$ (the energy barrier for O_3 dissociation at 313 nm) was 0.86 kcal mol⁻¹. This would correspond to a value of 24.32 kcal mol⁻¹ for the dissociation enthalpy of O_3 at 0 K, provided that there were no barrier height for dissociative crossover from the excited 1B_2 electronic state of O_3 . A conclusion that one can draw from this calculation, therefore, is that $\phi O(^1D)$ should be unity at the thermodynamic energy limit.

Both of the above calculations^{5,9} assume that the rate of change of $\phi O(^1D)$ in the fall-off region is totally governed by the rotational population distribution of

ozone molecules in the ground electronic state. However, the results obtained in both the present and earlier studies⁶⁻⁸ do not support this assumption since the observed fall off is significantly slower than that calculated from the rotational distribution. (A more complete discussion of the functional dependence of $\phi O(^1D)$ with wavelength has been presented by Moortgart and Warneck.⁷)

It thus appears that these calculations may provide reasonably accurate values for the relative population distribution of rotational states lying above the theoretical energy cut off as a function of temperature. If so, this would enable one to predict the rate of change of $\phi O(^1D)$ with temperature at any wavelength beyond that set by the thermodynamic limit, but would not permit the assignment of absolute values of $\phi O(^1D)$ without further knowledge of the potential energy surfaces of O_3 .

As noted earlier in the text, the absolute values of $\phi O(^1D)$ predicted from the two sets of calculations are significantly different due to the different number of degrees of rotational freedom which were assumed to be required to overcome the energy barrier [i. e., $\phi O(^1D)$ at 298 K = 0.26, Kuis *et al.*⁹ and 0.42 Kajimoto and Cvetanovic⁵]. By comparison, Moortgart and Warneck⁷ calculated that 44% of the ozone molecules had sufficient rotational energy (278 cm⁻¹) to photodissociate to produce $O(^1D)$ atoms at 313 nm. These calculations once again took the thermodynamic limit for the production of $O(^1D)$ from ozone photolysis to be 310 nm.

The calculated ratios reported for $\phi O(^1D)_{298 K} / \phi O(^1D)_{233 K}$ were 1.42 (Kuis *et al.*⁹) and 1.65 (Kajimoto and Cvetanovic⁵) resulting in a mean ratio of 1.54. Therefore, modifying the data of Lin and DeMore⁶ $\phi O(^1D) = 0.08$ at 233 K) leads to a value of 0.123 at 298 K, in excellent agreement with that reported in the present study. As stated earlier, no explanation can be forwarded for the disagreement with other studies.

A final comment on the results reported here concerns the possibility that the normalization of our Φ values to unity at wavelengths less than 3000 Å may not in the final analysis be the correct normalization factor. For example, in a recent study by Stone and Lawrence,²⁶ results were obtained which shows $\phi O(^1D)$ varying monotonically from 0.87 to 0.93 in the wavelength region 274–300 nm. If these results are later confirmed by other studies our Φ values would want to be systematically shifted downward by a small factor.

*Present Address: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103

†This author would like to acknowledge the financial support of the National Science Foundation RANN Program and the National Aeronautics and Space Administration for their support of this research.

¹R. F. Hampson, *J. Phys. Chem.*, Ref. Data 3, (1973).

²E. Castellano and H. J. Schumacher, *Z. Phys. Chem.* (Leipzig) 65, 62 (1969).

³I. T. N. Jones and R. P. Wayne, *Proc. R. Soc. Ser. A* 319, 273 (1970).

⁴R. Simonaitis, S. Braslavsky, J. Heicklen, and M. Nicolet, *Chem. Phys. Lett.* 19, 601 (1973).

⁵O. Kajimoto and R. J. Cvetanovic, *Chem. Phys. Lett.* 37,

- 533 (1976).
- ⁶C. L. Lin and W. B. DeMore, *J. Photochem.* **2**, 161 (1973–74).
- ⁷G. K. Moortgat and P. Warneck, *Z. Naturforsch Teil A* **30**, 835 (1975).
- ⁸D. Martin, J. Girman, and H. S. Johnston, 167th ACS National Meeting, spring 1974, Los Angeles.
- ⁹S. Kuis, R. Simonaitis, and J. Heicklen, *J. Geophys. Res.* **80**, 1328 (1975).
- ¹⁰K. Wanatabe, E. C. V. Inn, and M. Zelikoff, *J. Chem. Phys.* **21**, 1026 (1953).
- ¹¹E. C. V. Inn and Y. Tanaka, *J. Opt. Soc. Am.* **43**, 870 (1953).
- ¹²E. Vigroux, *Ann. Phys. (Paris)* **8**, 709, (1953).
- ¹³M. Griggs, *J. Chem. Phys.* **49**, 857 (1968).
- ¹⁴W. B. DeMore and O. F. Raper, *J. Phys. Chem.* **68**, 412 (1964).
- ¹⁵A. G. Hearn, *Proc. Phys. Soc.* **78**, 932 (1961).
- ¹⁶R. F. Hudson, *Can. J. Chem.* **52**, 1465 (1974).
- ¹⁷W. B. DeMore and O. F. Raper, *J. Chem. Phys.* **37**, 2048 (1962).
- ¹⁸W. B. DeMore and O. F. Raper, *J. Chem. Phys.* **44**, 1780 (1966).
- ¹⁹P. N. Clough and B. A. Thrush, *Trans Faraday Soc.* **63**, 915 (1967).
- ²⁰A. Fontijn, C. B. Meyer, and H. I. Schiff, *J. Chem. Phys.* **40**, 64, 1964.
- ²¹G. E. Streit, C. J. Howard, A. Schmeltekopf, J. A. Davidson, and H. I. Schiff, *J. Chem. Phys.* **65**, 4761 (1976).
- ²²W. L. Wiese, M. W. Smith, and B. N. Miles, *Natl. Stand. Ref. Data Ser. Natl. Bur. Stand.* **22** (1969).
- ²³R. F. Hampson and D. Garvin, *Natl. Bur. Stand. (U.S.) Tech. Note* (**1975**) 866.
- ²⁴G. A. Chamberlain and J. P. Simons, *J. Chem. Soc. Faraday Trans. I*, **402** (1974).
- ²⁵P. J. Hay, T. H. Dunning, Jr., and W. Goddard, III, *Chem. Phys. Lett.* **23**, 457 (1973).
- ²⁶N. Stone and G. M. Lawrence (private communication).