Quantum yields for production of O(\(^1\)D) in the ultraviolet photolysis of ozone:

Recommendation based on evaluation of laboratory data

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Abstract

The quantum yield for O($^1\text{D}$) production in the photolysis of ozone in the ultraviolet region as a function of wavelength and temperature is a key input for modeling calculations in the atmospheric chemistry. To provide the modeling community with the best possible information, the available data are critically evaluated and the best possible recommendation for the quantum yields are presented. Since the authors of this paper are the principal investigators of the groups which have provided the most of the recent experimental data for the O($^1\text{D}$) quantum yields, the basic assumptions made by each group, the input parameters used in obtaining the quantum yields, and possible sources of systematic errors are well examined. The fitting expression of the O($^1\text{D}$) yield as a function of photolysis wavelength $\lambda$ and temperature $T$ is presented in the ranges of $306 \text{ nm} \leq \lambda \leq 328 \text{ nm}$ and $200 \text{ K} \leq T \leq 300 \text{ K}$. The recommendation values of the O($^1\text{D}$) quantum yield for $290 \text{ nm} \leq \lambda \leq 306 \text{ nm}$ and $328 \text{ nm} \leq \lambda \leq 350 \text{ nm}$ are also presented. The formation mechanisms of O($^1\text{D}$) in the photolysis of ozone which result in the wavelength and temperature dependence of the O($^1\text{D}$) yields are interpreted.
Introduction

In general, electronically excited species do not play a major role in the chemistry of the Earth's lower atmosphere (i.e., below about 40 km), since they are short-lived due to collisional deactivation by N\(_2\) and O\(_2\). For this reason other competing chemical reactions are normally unimportant for such species in the atmosphere. The most notable exception is the first electronically excited state of oxygen atom, O\(^{1}\)D. O\(^{1}\)D is not only metastable (radiative lifetime ~ 148 s) but also highly reactive towards a number of atmospheric trace gases. The primary reason for the extreme importance of this very low abundant species is that O\(^{1}\)D reactions create highly reactive species from highly unreactive species. Specifically, the OH radical in the stratosphere and troposphere and NO (and eventually all nitrogen oxides) in the stratosphere are produced due mostly from the reactions of O\(^{1}\)D with inert H\(_2\)O and N\(_2\)O.

\[
\begin{align*}
O^{1}\text{D} + H_{2}\text{O} & \rightarrow 2\text{OH} \quad \text{(R1)} \\
O^{1}\text{D} + N_{2}\text{O} & \rightarrow 2\text{NO} \quad \text{(R2)}
\end{align*}
\]

The reactive species created by these reactions, OH and NO, are immensely important in the atmosphere. 1) OH is the most important initiator of the degradation of the majority of natural and anthropogenic emissions entering the atmosphere. 2) OH reactions provide the pathways that convert chemicals in the atmosphere, some times from active to inactive forms, and at other times from inactive to active forms. 3) OH is a major catalyst for lower stratospheric ozone removal. 4) Nitric oxide is a crucial ingredient of the stratosphere. Reaction (R2) leads to NO\(_x\) (NO + NO\(_2\)), which is the most important catalyst for ozone destruction in most of the stratosphere. 5) NO\(_x\) also suppresses the ozone by halogens by sequestering them in unreactive forms such as ClONO\(_2\).

The major source of O\(^{1}\)D in the lower atmosphere is the photolysis of ozone in the
Hartley and Huggins bands. The strong increase in the ozone absorption cross section below 330 nm and the consequent absorption by overhead ozone leads to the sharp decrease of the solar actinic flux becoming practically zero below 290 nm, in the lower stratosphere and troposphere. Since the photolysis of atmospheric ozone depends on the overlap of the wavelength dependent actinic flux and on the ozone absorption cross section, the opposing wavelength dependence of these two quantities essentially restricts the photodissociation to 290 ~ 330 nm \cite{Hofzumahaus et al., 1999}. This is precisely the wavelength region where \( \text{O}(^1\text{D}) \) production increases from near zero values around 330 nm to near unit values around 290 nm. Therefore, the calculated atmospheric \( \text{O}(^1\text{D}) \) production rate is very sensitive to changes in the quantum yield for its production in the photolysis of ozone in this wavelength range. It is also this region where the UV absorption cross sections of ozone and the quantum yields for \( \text{O}(^1\text{D}) \) production are highly sensitive to temperature. Thus, accurate definition of the quantum yields for \( \text{O}(^1\text{D}) \) production in ozone photolysis as a function of wavelength and temperature is essential for atmospheric chemistry.

Until a few years back, based on many previous data sets, it was suggested that the \( \text{O}(^1\text{D}) \) production drops monotonically from near unity value at ~290 nm to zero by ~310 nm \cite{DeMore et al., 1994}, the threshold for the energetically allowed channel:

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}(^1\text{D}) + \text{O}_2(a^1\Delta_g). \quad (\text{R3})
\]

It was assumed that the spin conservation would require that the co-product of \( \text{O}(^1\text{D}) \) is \( \text{O}_2(a\Delta) \), since the upper state of ozone accessed by absorption in the strongly allowed transition is a singlet. There were, however, some laboratory data that indicated the presence of a "tail" in \( \text{O}(^1\text{D}) \) quantum yield (i.e., a non-zero quantum yield) beyond this threshold \cite{Brock and Watson, 1980b; Trolier and Wiesenfeld, 1988}. Adler-Golden and Steinfeld \cite{1982} had pointed out that vibrationally excited ozone could generate \( \text{O}(^1\text{D}) \) via the
spin-allowed channel (R3) well beyond the 310 nm energetic threshold calculated for the
ground state of ozone. Ball et al. [1993] reported quantum yield measurements of \( \text{O}_2(a^1\Delta) \)
(the \( \text{O}(^1\text{D}) \) co-product from the spin-allowed photodissociation of ozone) showing a tail that
is very similar to the one for \( \text{O}(^1\text{D}) \) reported previously. Michelsen et al. [1994] further
developed the concept of Adler-Golden and Steinfeld [1982] and presented a model
calculation that described well the measured tail of the room-temperature \( \text{O}(^1\text{D}) \) quantum
yield reported by Brock and Watson [1980b] and Trolier and Wiesenfeld [1988] and \( \text{O}_2(a^1\Delta) \)
by Ball et al. [1993] up to ~320 nm. Their model assumes that the tail is due only to
photolysis of vibrationally excited ozone; it did not take into account the spin-forbidden
process, which was not known at that time. Their mathematical expression became the basis
for the NASA/JPL recommendation 1997 [DeMore et al., 1997]. Field experiments that
compared J(\( \text{O}(^1\text{D}) \)) photolysis frequencies measured directly by chemical actinometer with data
obtained from solar actinic spectra and \( \text{O}(^1\text{D}) \) quantum yield spectra [Müller et al., 1995;
Shetter et al., 1996] were also consistent with the tail. Inclusion of the tail led to a much
better agreement between measurements and calculations, as a function of solar zenith angle
and total overhead ozone column.

Intensive laboratory work by the groups represented in this paper has yielded new
measurements of the \( \text{O}(^1\text{D}) \) quantum yield as a function of wavelength and temperature with
direct and indirect detection methods, showing clearly that the tail exists [Armerding et al.,
1995; Takahashi et al., 1996a, 1998a; Ball et al., 1997; Silvente et al., 1997; Talukdar et al.,
1998; Bauer et al., 2000; Smith et al., 2000]. More interestingly, some of these new
measurements also show that the quantum yield does not go to zero even at wavelengths as
long as ~330 nm when the temperature is cold enough to eliminate the existence of significant
fraction of ozone in its vibrationally excited level. This non-zero yield has been attributed to
the spin-forbidden channel for $O(^1D)$ production:

$$O_3 + h\nu \rightarrow O(^1D) + O_2(X^3\Sigma_g^-)$$

(R4)

and has now been clearly demonstrated via recent laboratory measurements [Takahashi et al., 1996b; Denzer et al., 1997, 1998].

The significance of these changes in $O(^1D)$ quantum yields is very important to atmospheric calculations. Müller et al. [1995] have indicated that the tail contributes at least 30% of the noon-time $J(O^1D)$ in summer in Jülich (solar zenith-angle = 28°) and that total integrated $O(^1D)$ production is enhanced by 1.38 due to the tail. Furthermore, there are many situations in the atmosphere where the available wavelengths are restricted to greater than 310 nm. Such situations include high solar zenith angles and large overhead ozone columns, both common at high latitudes during late-Fall to early-Spring time. Of course, high solar zenith angles occur every day at all sunlit locations at least for a short period. Talukdar et al., [1998] suggested that the contributions of the tail and the spin-forbidden dissociation process can make the $J(O^1D)$ value 5 times larger at solar zenith-angle of 85° than the value estimated without them.

Currently, a good evaluated data set for the quantum yields for $O(^1D)$ production in ozone photolysis at wavelengths between ~308 and ~330 nm is not available. This is because the changes in the quantum yields have been reported only recently and because there still exist significant quantitative differences in the reported values even though all the recent studies qualitatively substantiate the "tail" and the existence of the spin-forbidden photodissociation pathway.

To rectify the lack of a good recommendation for the quantum yields for $O(^1D)$ in ozone photolysis, a panel of laboratory scientists and one field measurements scientist working in the area of ozone photodissociation was brought together as a part of the joint
SPARC/IGAC activity on Laboratory Studies. This paper is a result of this activity. The aim of this paper is to critically evaluate the data available to date and to develop the best possible data set for atmospheric modeling. To enable in-depth evaluation of the data, the principal investigator(s) from each data set belong to this panel and are authors of this paper. The panel discussed the basic assumptions made by each group, the input parameters such as the absorption cross sections used in obtaining the quantum yields, and possible sources of systematic errors. In addition, a clear choice of a reasonable "anchor" point for the quantum yields allowed renormalization of the data to specific wavelengths. Trends in wavelength dependence of the quantum yields were examined for possible sources of systematic errors and differences. Such critical evaluations are not possible by an outside data panel, which would not have access to many of the needed, but unpublished, information. Each principal investigator provided such information for this evaluation and enabled a better evaluation where some data could be discarded, corrected, and/or re-normalized. The paper below lists all the steps and reasons for the choice of data is used in this recommendation and the physical basis for the generation of both ground and electronically excited oxygen atoms. Further, a comprehensive, easy-to-use equation is employed to represent the best possible data set for atmospheric modeling.

2. Experimental Considerations

The difficulties connected with the measurement of O(1D) quantum yields from the photolysis of ozone are primarily associated with the need for a narrowband, widely tunable source of photolysis radiation, the difficulty of directly monitoring O(1D) spectroscopically and the very large dynamic range (especially in ozone cross section) that the measurements span. For a similar photolysis fluence and ozone concentration, the concentration of O(1D)
produced varies by six orders of magnitude between 250 and 350 nm. In addition, the lifetime of \( \text{O}(^1\text{D}) \) with respect to either reaction or quenching is extremely short in most common gases; exceptions are gases such as He, Ne, Ar, SF\(_6\), and CF\(_4\).

All of the experimental data used in producing this evaluation, except for the recent study reported by Smith et al. [2000], used some type of pulsed tunable laser as the photolysis source. Such lasers provide a relatively high power, narrow bandwidth source of tunable radiation. However, the variation in photolysis laser fluence, i.e., energy per unit area, (or at least the relative values at different wavelengths) needs to be monitored accurately as the wavelength of the laser changes and this measurement is not trivial. Since these lasers operate in the visible and require harmonic generation techniques to reach the UV, some changes in beam profile are unavoidable as the lasers are tuned.

Smith et al. [2000] used a combination of a monochromator and a Xe arc lamp for the photolysis light source. They also indicated the presence of a "tail" in \( \text{O}(^1\text{D}) \) quantum yield beyond the threshold of the dissociation process (R3). As described above, a few years before there were two different types of experimental results: some experiments with monochromators and lamps indicated that the \( \text{O}(^1\text{D}) \) quantum yield monotonically decreases to zero by \( \sim 310 \) nm, while the others with laser light dissociation indicated that the presence of the "tail" in \( \text{O}(^1\text{D}) \) quantum yield beyond this threshold. The JPL '94 recommendation book stated that "the tail sometimes seen in the laser experiments at longer wavelengths has been eliminated, on the grounds that it is not reproduced in the monochromator experiments and may be artifacts." The results reported by Smith et al. demonstrate that the "tail" is not artificially produced by a high peak power of laser light pulse (e.g. multiphoton effects) but clearly present even in the cw light photolysis experiments. However, they used large bandwidths for the photolysis light (0.1 - 3.6 nm fwhm) probably to obtain signal intensity.
enough for the measurements, while the bandwidths in the laser experiments are much narrower (< 0.01 nm). The high resolution data of the O(^1D) quantum yield with narrow bandwidth laser photolysis [Takahashi et al. 1996a, 1998a; Bauer et al., 2000] show variations on a much finer scale than the bandwidths used by Smith et al. [2000]. This implies that the yield values for the specific wavelengths presented by Smith et al. [2000] can have a problem.

Experimentally O(^1D) monitoring techniques are conveniently divided into techniques which monitor O(^1D) directly via spectroscopy, or indirectly via approaches which allow the O(^1D) to interact with another gas to produce a species that is more conveniently monitored as a “spectroscopic marker” for O(^1D).

**Direct techniques:** O(^1D) can be monitored by its emission O(^1D) → O(^3P) at 630 nm. This emission is both spin and electric dipole forbidden with a lifetime of 150 s; nevertheless direct emission was used to monitor relative O(^1D) quantum yields between 221 and 243.5 nm [Cooper et al., 1993]. It is also possible to monitor O(^1D) in absorption via the 3s ^1D_2 - 2p ^1D_2 transition at 115.2 nm and this technique has found limited, and controversial, use in kinetic studies [Heidner and Husain, 1973]. It has not been applied to quantum yield measurements. Three approaches using laser excitation have also been published. Pratt et al. [1991] reported (2+1) resonance enhanced multiphoton ionization detection of O(^1D) using the 3p ^1F_3 and 3p ^1P_1 transitions at 203.5 and 205 nm. Richter and Hynes [1996] reported observation of (3+1) REMPI transitions to the 3d ^1F_3 and several other closely spaced levels at ~ 276 nm. Both sets of REMPI transitions lie within the wavelength region where O_3 absorbs strongly; hence the focused REMPI probe laser generates an interference signal because it produces O(^1D) which it then detects. The (2+1) excitation wavelength lies in a minimum in the UV absorption spectrum of O_3 and requires generation of deep UV radiation:
however Hancock and coworkers [Ball et al., 1997; Denzer et al., 1997, 1998] have successfully applied it to O(\(^1\)D) yield measurements between 305 and 330 nm. The (3+1) wavelength, 276 nm, is easily generated using currently available tunable lasers but this excitation wavelength lies close to the peak in the ozone absorption cross section. Hence background interferences are sufficiently severe that this detection scheme has little utility for yield studies at long wavelengths. Finally, laser induced fluorescence (LIF), using single photon excitation of the 3s \(^1\)D\(_2^0\) - 2p \(^1\)D\(_2^0\) transition has been demonstrated by Takahashi et al. [1996a, 1996b, 1997, 1998a]. This is technically the most demanding approach requiring sum frequency generation of VUV radiation with two tunable lasers. Nevertheless it appears to offer high sensitivity, specificity and no significant interference effects.

Potential complications from the use of direct laser based detection techniques can arise when they are used in conjunction with another laser to photolyze ozone. The first of these arises because a polarized detection laser excites a subset of the magnetic sublevels of O(\(^1\)D). In the absence of an electric or magnetic field these levels are degenerate and equally populated. However, a polarized laser may produce a preferential population in some of these sublevels; thus “an orbital alignment effect” can occur. If the “alignment effect” varies as the photolysis wavelength is changed, the probe laser signal may not reflect the overall atomic production rate. A second complication occurs when the atom is produced with a large amount of translational energy such that its Doppler linewidth exceeds that of the probe laser. Again the laser excites only a subset of the atoms, those whose velocities match the excitation laser profile. It is important to note that the presence of these effects will not necessarily cause errors in a relative yield measurement and may also be inherent in the indirect detection schemes. However, if the population of the levels which are monitored changes in a manner which does not reflect the total change in population as a function of
photolysis wavelength, errors will occur. Orbital alignment effects have been seen in the production of O(\(^1\)D) from the photolysis of N\(_2\)O \cite{Suzuki et al., 1996, Ahmed et al., 1999; Neyer et al., 1999}, however such effects seem to be either absent, or not to effect yield measurements, in O\(_3\) photolysis. Effects of changes in the Doppler profile of O(\(^1\)D) will depend on the bandwidth of the excitation laser. \textit{Takahashi et al.} \cite{1998a} found that it was necessary to correct their O(\(^1\)D) yield measurements by up to 50% to compensate for Doppler broadening at the longest wavelengths at which they made measurements whereas \textit{Ball et al.} \cite{1997} concluded that their measurements were unaffected by such effects.

\textbf{Indirect Techniques:} Because of the difficulties associated with direct observation of O(\(^1\)D), many studies have utilized indirect detection, allowing the O(\(^1\)D) to react with another molecule which is more easily monitored. Clearly the disadvantage of this approach is that it is indirect and that O(\(^1\)D) production is inferred. In this case a knowledge of the detailed chemistry associated with production of the “spectroscopic marker” is desirable; however, they can be obtained by careful variations in experimental conditions. Several studies have photolyzed O\(_3\) in the presence of N\(_2\)O. The reaction of O(\(^1\)D) with N\(_2\)O produces NO which then undergoes further reaction with ozone, producing electronically excited NO\(_2^*\) that can be detected by its chemiluminescence. It is very difficult to quench vibrationally hot NO by bath gases that do not also quench O(\(^1\)D). The kinetics of this system are complicated by the fact that NO is produced with a great deal of vibrational excitation and this appears to enhance the rate of its reaction with ozone. This approach was used in several of the early studies \cite{Kuis et al., 1975; Moortgat and Warneck, 1975; Philen et al., 1977; Arnold et al., 1977; Fairchild and Lee, 1978}, including two which used tunable laser photolysis, and which failed to report the “tail” in the O(\(^1\)D) yield. \textit{Brock and Watson} \cite{1980b} also used this approach in the first published study which reported the existence of the “tail”; thus, this
source of compilation may not be the reason for not observing the tail in some studies. A single study by *Trolier and Weisenfeld* [1988] used energy transfer from O(^1D) to CO₂ followed by detection of the infrared emission from vibrationally excited CO₂. More recently, three groups have monitored the OH produced by the reaction of O(^1D) with water, H₂ or methane. O(^1D) reacts at close to gas kinetic rates with hydrides with a well understood chemistry. Furthermore, H₂O is very efficient at quenching vibrationally excited OH and does not “react” with vibrationally excited OH. Each study utilized LIF to monitor the OH although they used different excitation schemes. *Armerding et al.* [1995] monitored the formation of OH in its ground vibrational level exciting the A-X (0-0) transition at 308 nm while *Talkudar et al.* [1998] checked the (1-0) transition at 282 nm. Since both transitions lie within the absorption spectrum of ozone, the probe beam generates some O(^1D) atoms which can react within the time frame of the probe pulse to generate an interfering OH LIF signal. This is not really a problem since it merely enhances the ‘Background’ relative to which OH produced by the photolysis laser is measured. The reaction of O(^1D) with H₂ and CH₄ produces OH with a substantial amount of vibrational excitation. *Silvente et al.* [1997] and *Bauer et al.* [2000] monitored OH (v=1) by exciting the A-X (0-1) transition at 351 nm and monitoring blue shifted fluorescence at 308 nm. This approach minimizes noise and OH interference effects and allowed Bauer et al. to monitor O(^1D) yields out to 375 nm. However, the possibility of translationally hot O(^1D) yielding differing levels of OH (v=1) may be a problem. *Smith et al.* [2000] used a chemical ionization mass spectrometry (CIMS) technique for the detection of the O(^1D) atoms produced by the photolysis of O₃. The mixture of O₃ and N₂O (O₃: N₂O = 1:100) was irradiated with the photolysis light. The reaction between O(^1D) and N₂O produces 2NO or N₂ + O₂. The NO molecule reacts with the O₃ and then produces NO₂. The NO₂ is ionized by an ion-molecule reaction with O₃⁻.
Finally, the NO$_2^-$ ion is detected with a quadrupole mass spectrometer. This method can distinguish O($^1$D) from O($^3$P) without using any laser system.

While the convergence of recent measurements is gratifying, significant and puzzling discrepancies remain even between the various studies which are the input to this recommendation. No obvious single experimental factor seems to emerge as the culprit. The discrepancies which remain are significant and further studies to resolve them are required. In the opinion of the authors the variation of the photolysis fluence coupled with changes in beam profile with changes in wavelength remains a significant potential source of systematic error in such measurements.

In an attempt test if the measurements of relative laser fluence as a function of wavelength was a source of error, the power meters used by the Japanese and NOAA group were intercompared at the NOAA laboratories. They showed no systematic differences. See Appendix 1 for details.

3. Data treatment and recommendations

The recommendations for the O($^1$D) quantum yields in the photolysis of O$_3$ were derived using the following procedures. First, we based on data from the studies considered here the quantum yield of O($^1$D) at 298 K at 308 nm was set to 0.79. Second, we derived a wavelength dependence of quantum yields at 298 K between 306 and 328 nm, by checking and renormalizing the experimental data presented by several groups and then averaging them. The wavelength dependence at 298 K is also anchored at 308 nm. Third, we determined the parameters in the chosen expression (see below) for 306 nm < $\lambda$ < 328 nm and 200 K < T < 320 K, by fitting the experimental data of the temperature dependence as well as the yields at 298 K obtained above to this expression.
3-1. Absolute quantum yield at 308 nm at room temperature

There are several absolute measurements of $O(^1D)$ quantum yields in the photolysis of ozone at 248, 266 and 308 nm [Talukdar et al., 1997; Takahashi et al., 1996a, 1998a; Greenblatt and Wiesenfeld, 1983; Amimoto et al., 1980]. Since the photolysis of ozone at wavelengths longer than 300 nm is of importance in atmospheric chemistry, the absolute measurements at 308 nm is most important among those studies. Table 1 lists the results of the absolute measurements at 308 nm. Two types of experimental method were used for the measurements of the absolute yield. Talukdar et al. [1997] and Greenblatt and Wiesenfeld [1983] measured the time profile of $O(^3P)$ resonance fluorescence after the pulsed laser photodissociation of $O_3$. The temporal profile of $O(^3P)$ initially jumps due to the direct formation in the photolysis of $O_3$, followed by an exponential rise controlled by the following reactions of $O(^1D)$ and a slow decay due to diffusion.

$$O(^1D) + O_3 \rightarrow 2O_2 \quad k_5 \quad (R5)$$
$$O(^1D) + O_3 \rightarrow 2O(^3P) + O_2 \quad k_6 \quad (R6)$$

Based on the experimental results that the two rate coefficients are equal ($k_5/k_6 = 1.0$) [DeMore et al., 1997; Talukdar et al., 1997]. The absolute $O(^1D)$ quantum yield value was calculated from amounts of the initial jump and the exponential rise of the $O(^3P)$ signal.

Although both groups used XeCl excimer laser light as a light source at 308 nm, we estimate that the difference is less than 1 % from the usage of a monochromatic light at 308.0 nm. On the other hand, Takahashi et al. [1996a, 1998a] measured photofragment yield spectra of both $O(^3P)$ and $O(^1D)$ after the photolysis of $O_3$ by scanning the photolysis laser wavelength between 308-326 nm and monitoring the $O(^3P)$ and $O(^1D)$ concentration with a vacuum-uv laser induced fluorescence technique. The sum of the photofragment yield spectra for both
O(^1D) and O(^3P) atoms with absolute scales should correspond to the absorption spectrum of the O_3 molecule.

\[ \sigma_{\text{abs}}(\lambda) = s_{1D} \ Y_{1D}(\lambda) + s_{3P} \ Y_{3P}(\lambda), \]  

(1)

where \( \sigma_{\text{abs}}(\lambda) \) is the absorption cross section of O_3 at wavelength \( \lambda \), \( Y_{1D}(\lambda) \) and \( Y_{3P}(\lambda) \) are the experimentally obtained photofragment yield spectra of O(^1D) and O(^3P), and \( s_{1D} \) and \( s_{3P} \) are the detection sensitivity factors for O(^1D) and O(^3P), respectively. Since the yield spectra of O(^1D) and O(^3P) are not parallel in the wavelength range of 308-328 nm, a pair of the \( s_{1D} \) and \( s_{3P} \) values were determined so that the sum of \( s_{1D} Y_{1D}(\lambda) \) and \( s_{3P} Y_{3P}(\lambda) \) reproduced the absorption spectrum \( \sigma_{\text{abs}}(\lambda) \). The absolute value of O(^1D) quantum yield is calculated as \( \Phi(\lambda) = s_{1D} Y_{1D}(\lambda) / \sigma_{\text{abs}}(\lambda) \).

As listed in Table 1, the published absolute values for the O(^1D) quantum yield at 308 nm are in good agreement with each other, in spite of using the two different experimental techniques. We adopted the value of 0.79 for the O(^1D) yield at 308 nm at room temperature as a standard (“anchor”) point. The quoted uncertainty is in the range of 0.02-0.12 from the value at this point (Table 1) from the different studies. The value of 0.02 for the uncertainty estimated by Greenblatt and Wiesenfeld [1983] seems to be too small, because the uncertainty of the assumption of \( k_5/k_6 = 1.0 \) should be larger than 2-3 %. Additional work to determine more accurately the absolute value of O(^1D) quantum yield at 308 nm is needed, since this value affects the overall accuracy of the yields at other wavelengths.

3-2. O(^1D) quantum yield at 298 K in the wavelength range of 306-328 nm

There are many studies on the quantum yields between 306 and 328 nm at room temperature (298K). To obtain a wavelength dependence of the O(^1D) yield at 298 K in the wavelength range of 306-328 nm, the recent experimental data sets reported by 8 groups are used, Talukdar et al. [1998], Takahashi et al. [1996a], Ball et al. [1997], Armerding et al.
In these studies, the existence of the "tail" around 315 nm is obvious. The wavelength dependencies measured by the different laboratories look quite similar, but there are some differences among the reported values of the quantum yields. In these studies, the relative O(\(^1\)D) concentration were measured at various wavelengths for O\(_3\) photolysis, for example, by detecting the laser induced fluorescence intensity of OH radical produced by the reaction of O(\(^1\)D) + H\(_2\)O → 2OH. Then, the relative O(\(^1\)D) concentration obtained at each photolysis wavelength was divided by a value of the published absorption cross section. In most of the recent studies, Talukdar et al. [1998], Ball et al. [1997], Armending et al. [1995], and Bauer et al. [2000], the absorption cross sections reported by Malicet et al. [1995] were used to calculate absolute quantum yields. Trolier and Wiesenfeld [1988] used the absorption data reported by Molina and Molina [1986] and Smith et al. [2000] used the data by Molina and Molina [1986] with unpublished high resolution data. Brock and Watson [1980b] used their own measurements for the absorption cross sections. The difference between the two sets of absorption data, Malicet et al. [1995] and Molina and Molina [1986], is small (<2 %) in the wavelength range of 306 - 316 nm, and less than 6 % between 317 and 328 nm. The choice between the two absorption data does not lead to a large error in the calculation of the O(\(^1\)D) quantum yields. However, we have recalculate the quantum yield data obtained from relative measurements by Brock and Watson [1980b] using the absorption cross sections by Malicet et al. [1995], since their original absorption cross sections differ from the recent two absorption data.

To convert the measured relative quantum yields to absolute values, different anchor wavelengths have been used in different studies. We have re-normalized the data sets to reduce the systematic error before averaging them. The re-normalization factors for the data...
sets were not determined so that their yield values at one specific wavelength coincide to a standard value, but so that their yield dependence curves fit each other in the wide wavelength range (ca. 307-320 nm). The average of the renormalized data set was scaled to have the value of 0.79 at 308 nm which is the standard point we employed. Table 2 lists the renormalization factors, the renormalized O(1^D) yield data sets of the 8 groups and their average values. It should be noted that the data set reported by Takahashi et al. [1996a] is not renormalized since they used an absolute method to obtain the yield value as described in the preceding section. The highly wavelength resolved data of Takahashi et al. [1996a] was binned into 1-nm intervals in this calculation. In the averaging of the values at 308 nm, the extremely large value reported by Ball et al. [1997] was excluded. We have checked experimental results reported by others in addition to the 8 groups. Since those results had exceedingly different wavelength dependence from the data sets by 8 groups, we omitted those data in the calculation to obtain the quantum yields at 298 K in the wavelength range of 306 - 328 nm. The renormalized values of the data sets reported by 8 groups and their average values are plotted in Figure 1. The absorption cross sections at 295 K reported by Malicet et al. [1995] are also listed in Table 2, which were used to calculate the absolute quantum yields from the relative measurements of O(1^D) concentrations in the studies by Talukdar et al.[1998], Ball et al.[1997], Armending et al. [1995], and Bauer et al. [2000].

We used 1.0-nm intervals for the derived quantum yields at 298 K and later we also used 1.0-nm intervals in the calculation of the fitting expression for the temperature dependence. The 1.0-nm intervals seem insufficient to resolve the fine structures in the ozone absorption spectrum. There is some evidence for structure between 312 and 320, which can be seen the high-resolution quantum yield spectrum of O(1^D) reported by Takahashi et al. [1996a] The 1-nm intervals are also insufficient to resolve the structure in a
solar actinic flux spectrum. However, Hofzumahaus et al. [1999] have shown that the
calculation of J(O\(^1\)D) (photolysis frequency of O\(_3\) to form O(\(^1\)D) ) using 1 nm resolution is
less than 2% different from the higher resolution calculation even at solar zenith angles below
80°. Therefore, we believe that the 1 nm resolution is sufficient for current atmospheric
calculations.

The accuracy of the photolysis wavelength should be also considered. It has been
indicated that a wavelength shift of only 0.1 nm would add another systematic difference of
2-3% in the calculated J(O\(^1\)D) even if the actinic flux spectrum is recorded with a bandpass of
1.0 nm [Hofzumahaus et al., 1999]. Wavelengths in this work are expressed by the values in
air (not in vacuum) as wavelength values in air were used in the reports of the O\(_3\) absorption
cross section [Molina and Molina, 1986; and Malicet et al., 1995].

3-3. Temperature dependence of the quantum yield

To obtain the parameters for the expression to calculate the recommended values in
the ranges of T = 200-320 (K) and \(\lambda\) = 306 - 328 (nm), we have used the experimental data of
the temperature dependence reported by Talukdar et al. [1997, 1998], Takahashi et al.[1998a],
Ball et al. [1997], Bauer et al. [2000] and Smith et al. [2000] as well as the averaged data at
298 K described above. First, the temperature dependence of the O(\(^1\)D) yield at 308 nm was
examined. In the first approximation, it was assumed that the O(\(^1\)D) quantum yield linearly
depends on the temperature of O\(_3\) gas. The linear least square fitting to the detailed
experimental results at 308 nm under the condition of the fixed point of 0.79 at 308 nm leads
to the equation:

\[
\Phi(308\text{ nm}, T) = 6.10 \times 10^{-4} T + 0.608
\]

(2)
Figure 2 shows the plots of experimental results of the O(1^D) quantum yield at 308 nm versus temperature, and also shows the fitting results of Eq. (2).

The experimental data at temperatures other than 298 K, reported by the above 5 groups, is normalized to $\Phi(308 \text{ nm})$ calculated from this expression. Again, the data at 228 K by Takahashi et al. [1998a] was not renormalized since they used an absolute method to obtain the yield value.

For the fitting expression, an equation containing three Gaussians and a constant term is used,

$$
\Phi(\lambda, T) = \left( \frac{q_1}{q_1 + q_2} \right) \times A_1 \times \exp\left\{ \frac{\left( X_1 - \lambda \right)}{\omega_1} \right\}^4 + \left( \frac{q_2}{q_1 + q_2} \right) \times A_2 \times \left\{ \frac{T}{300} \right\}^2 \times \exp\left\{ \frac{\left( X_2 - \lambda \right)}{\omega_2} \right\}^2 + A_3 \times \left\{ \frac{T}{300} \right\}^{1.5} \times \exp\left\{ \frac{\left( X_3 - \lambda \right)}{\omega_3} \right\}^2 + c
$$

(3)

where

$$q_i = \exp\left\{ \frac{-v_i}{RT} \right\}$$

(4)

and $X_{1-3}$, $A_{1-3}$, $\omega_{1-3}$, $v_2$ and $c$ are valuable fitting parameters, $\lambda$ is in nm and $T$ is in K, and values of $v_1$ and $R$ are 0 (cm$^{-1}$) and 0.695 (cm$^{-1}$/K), respectively. This expression has some physical basis. The constant term, $c$, is included to represent the spin-forbidden channel and is assumed to be wavelength and temperature independent. It is assumed to be temperature independent since we expect this channel to be occurring from the ground state of O$_3$. It is assumed to be wavelength independent because there is no data to support either wavelength-dependent structure or variation. The first rapidly dropping function is supposed to represent the spin-allowed channel from the ground vibrational state of O$_3$. The second and third terms represent the dissociation from the vibrationally excited states. The need for two
terms is clear in reproducing observed quantum yields. It should be noted that once the
complete mechanism for ozone photodissociation and UV absorption by ozone are understood,
a more physically based model can be derived. Evidence for these processes and the possible
reasons for their origin are given in a later section.

The values of the parameters were obtained by fitting the expression to the data using
a non-linear least square method. In the least square calculation, the weight of the average
data at 298 K was set to be 8, while those of the other individual data were one. The
obtained best-fit parameters are listed in Table 3. We recommend the values calculated using
the expression (3) and parameters in Table 3 for the O(1D) quantum yields in the wavelength
range of 306 nm < \lambda < 328 nm and in the temperature range of 200 K < T < 320 K. Table 4
lists the calculated quantum yields at various temperatures and various wavelengths using the
fitting expression (3) and the parameter values in Table 3. The comparisons of the values
calculated at 298 K using the expressions in this work, JPL '94 [DeMore et al., 1994], JPL '97
[DeMore et al., 1997] and JPL 2000 [Sander et al., 2000] recommendations are shown in
Figure 3. Between 307 and 325 nm the results of this work and JPL 2000 recommendation at
298 K are in good agreement with each other. It should be noted that the JPL 2000
recommendations were based partly on the previous discussions of our panel in progress.
The O(1D) quantum yield values calculated using the expression (3) and parameters in Table
3 for 298 K, 253 K and 203 K are plotted in Figure 4.

We also tried to use linear polynomial functions up to 6th order for temperature and 6th
order for wavelength in a similar way used in the JPL '94 recommendation [DeMore et al.,
1994]. However, even the 6th \times 6th orders function with 49 adjustable parameters did not
reproduce the experimental results as well as the above expression in the wavelength range of
306-328 nm.
The primary uncertainties of our recommendation values come from the absolute value at 308 nm which we employed an ‘anchor’ point (Table 1). Then, the relative measurements for the wavelength and temperature dependence give some errors. The fitting of the expression (3) to the experimentally obtained values also produces some errors. At room temperature (298 K) we estimate the uncertainties of the quantum yield values calculated with the expression (3) is $\pm 10\%$ ($1\sigma$) for $\Phi(\lambda, 298 \text{K}) \geq 0.4$, while the uncertainties is estimated to be $\pm 0.04$ in the absolute value for $\Phi(\lambda, 298 \text{K}) < 0.4$. At temperatures other than room temperature, the uncertainties of the yield is estimated to be $\pm 15\%$ for $\Phi(\lambda, T) \geq 0.4$ and $\pm 0.06$ for $\Phi(\lambda, T) < 0.4$.

3-4. Quantum yields at the wavelengths shorter than 305 nm

For the wavelength range of 290-305 nm, the value of 0.95 has been recommended by JPL ’97 [DeMore et al., 1997] and JPL 2000 [Sander et al., 2000]. However, recent two experimental studies reported by Talukdar et al. [1998] and Taniguchi et al. [2000] have indicated that the O($^1\text{D}$) yield values in the wavelength range of 290-305 nm is around 0.90, using the standard point value of 0.79 at 308 nm. The yield values of Trolier and Wiesenfeld [1988] and Ball et al. [1997] which we renormalized above also indicated values around 0.90. Talukdar et al. [1998] have reported the yield values do not depend on the temperature of O$_3$ in this wavelength range. The results of no dependence on the temperature can be explained by the small contribution of the hot band excitation in this wavelength range as will be described later. The averaged value of the O($^1\text{D}$) quantum yield is 0.90 over this wavelength range. Although it is likely that there is structure in the quantum yield spectrum in this wavelength range, the amplitude of the structure is less than 0.05. Therefore, we recommend the yield of 0.90 in the range of 290-305 nm, which is independent of the temperature. The
uncertainties of our recommended values in the 290 nm < \lambda < 305 nm is estimated to be \pm 0.09.

For the wavelength range of 220-290 nm, the absolute yield at 248 nm is reported to be 0.91 \pm 0.06 by *Talukdar et al.* [1998] and 0.94 \pm 0.01 by *Greenblatt and Weisenfeld* [1983], while the yield at 266 nm is 0.88 \pm 0.02 by *Brock and Watson* [1980a]. The yield value in the wavelength range of 220-290 nm should be 0.85-0.95. However, the contribution from these wavelengths to O(^1D) production in the stratosphere and troposphere is not significant. Our understanding of ozone photochemistry would benefit from a better definition of the O(^1D) quantum yields in this region.

### 3-5. Quantum yields at the wavelengths longer than 328 nm

The O(^1D) quantum yield does not drop to zero even at the wavelength longer than 328 nm. The formation of O(^1D) is attributed to the spin-forbidden dissociation to O(^1D) + O_2(X^3Σ_g^+), (R4), as will be described later. The energetic threshold for this spin-forbidden process (R4) is around 411 nm. This implies that the formation of O(^1D) can continue to 411 nm. *Bauer et al.* [2000] have measured the relative O(^1D) yield up to 370 nm. They have proposed the O(^1D) yield of 0.064 \pm 0.006 between 325 nm and 375 nm. *Smith et al.* [2000] have reported the quantum yields are nearly constant (~0.12) and independent of temperature between 328 and 338 nm. In the wavelength range of 329-340 nm we recommend the value of 0.08 \pm 0.04, which is independent of the temperature. The J(O(^1D)) value is still sensitive to the O(1D) quantum yields around 330 nm at large solar zenith-angles. Therefore, more measurements are needed with various experimental techniques around 330 - 340 nm. The O(^1D) formation in the atmosphere above 340 nm is not significant due to the small absorption coefficient of O_3.
4. Formation mechanisms of $\text{O}^1(\text{D})$ in the photolysis of $\text{O}_3$

There are five energetically possible fragmentation pathways in the UV/VIS photolysis of $\text{O}_3$:

$$\text{O}_3 + h\nu (\lambda < 310 \text{ nm}) \rightarrow \text{O}^1(\text{D}) + \text{O}_2(a^1\Delta_g) \quad (\text{R3})$$

$$\text{O}_3 + h\nu (\lambda < 411 \text{ nm}) \rightarrow \text{O}^1(\text{D}) + \text{O}_2(X^3\Sigma_g^-) \quad (\text{R4})$$

$$\text{O}_3 + h\nu (\lambda < 463 \text{ nm}) \rightarrow \text{O}^3(\text{P}) + \text{O}_2(h^1\Sigma_g^+) \quad (\text{R7})$$

$$\text{O}_3 + h\nu (\lambda < 612 \text{ nm}) \rightarrow \text{O}^3(\text{P}) + \text{O}_2(a^1\Delta_g) \quad (\text{R8})$$

$$\text{O}_3 + h\nu (\lambda < 1180 \text{ nm}) \rightarrow \text{O}^3(\text{P}) + \text{O}_2(X^3\Sigma_g^-) \quad (\text{R9}),$$

where the long wavelength limits given in parentheses indicate the thermodynamic thresholds for the fragmentations at 298 K when the parent $\text{O}_3(X^1\text{A}_1)$ molecule is excited from its vibrationless level ($v'' = 0$) [Atkinson et al., 1997]. For photodissociation in the Hartley band at $\lambda < 300 \text{ nm}$, it has generally been accepted that channels (R4) and (R9) are predominant, with reported quantum yields of ca. 0.9 and 0.1, respectively, [Alder-Golden et al., 1982].

The literature shows evidence for all the spin-forbidden channels, (R4), (R7) and (R8), as well as spin-allowed channels (R3) and (R9) occurring in the uv region above 300 nm, generally referred to as the Huggins band [Wayne, 1989]. Production of the $\text{O}^1(\text{D})$ atoms above 310 nm has been attributed to both channel (R3) via the photodissociation of internally excited $\text{O}_3$, and the spin-forbidden dissociation channel (R4) [Alder-golden et al., 1982; Michelsen et al., 1994; Takahashi et al., 1996a, 1996b, 1997, 1998a; Ball et al., 1997; Denzer et al., 1997, 1998; Talukdar et al., 1998]. The contributions made by these excitation processes to the quantum yields for $\text{O}^1(\text{D})$ atoms from $\text{O}_3$ photolysis are indicated in Figure 4. These excitation processes are schematically shown on an energy level diagram in Figure 5, and are now discussed in turn. This section shows the origin of the processes, which together, lead
to the complex variations of O($^1$D) quantum yield as a function of wavelength and temperature. This discussion also justifies, to first order, the expression for the quantum yield that is adopted in this evaluation.

The transition responsible for the Hartley band takes the molecule from its ground X$^1$A$_1$ state to an electronically excited $^1$B$_2$ state [Wayne, 1989] and the angular distribution of the fragments is consistent with this being a mainly parallel dissociation (the transition dipole moment lying in the molecular plane and perpendicular to the C$_2v$ axis), with dissociation of the bent O$_3$ molecule dominantly in process (R3) being rapid in comparison with molecular rotation [Fairchild et al., 1978; Suits et al., 1993; Thelen et al., 1995; Blunt and Suits, 1997; Takahashi et al., 1998b; Hancock et al., 1999]. The origin of the structured part of the Huggins band at wavelengths above about 310 nm however has been the subject of some debate. Transitions are seen which support vibrational structure, but no distinct rotational lines can be observed, and the electronic parentage has been assigned as transitions to the same $^1$B$_2$ state as for the Hartley band which supports bound vibrational levels below the threshold to process (R3) [Katayama, 1979] or to bound vibrational levels of a $^1$A$_1$ state reached in a two electron transition from the ground $^1$A$_1$ (0,0,0) state but with an odd quantum number change in the antisymmetric stretch mode $\nu_3$, making the overall symmetry $^1$B$_2$ [Joens, 1994], and presumably gaining intensity from the nearby one photon $^1$B$_2$ state. Measurements of the rotational contours of the Huggins bands have been carried out [Sinha et al., 1986; Takahashi et al., 1997], with the most recent measurements favouring the rotational constants which are calculated for the 2$^1$A$_1$ state [Takahashi et al., 1997]. Translational anisotropy measurements are unable to distinguish the two possibilities but are consistent with both, as positive values of the translational anisotropy factor $\beta$ are both predicted and measured [Denzer et al., 1997, 1998; Hancock et al., 1999].
a) Photolysis of internally excited ozone

The most recent experimental approach to determine the bond energy for the dissociation of jet-cooled O$_3$ into O$(^1D) +$ O$_2$(a$^1\Delta_g$) yields a value of 386.59 ± 0.04 kJ/mol, and the standard heat of formation of O$_3$ at 0 K is calculated to be $\Delta H^0(0K) = -144.31 \pm 0.14$ kJ/mol [Taniguchi et al., 1999]. This corresponds to a wavelength limit at 0 K of 309.44 ± 0.02 nm for channel (R3). Formation of the O$(^1D)$ atoms at $\lambda > 309.45$ nm , however, was observed in the flow cell experiments at 200 - 320 K, and we attribute the temperature dependent part of the quantum yield to the photodissociation of vibrationally excited parent O$_3$. The energy difference in the threshold energies for the cold and hot band was measured to be 1056±20 cm$^{-1}$ from the difference in the threshold photolysis wavelengths [Takahashi et al., 1997]. The vibrational spacing for the antisymmetric stretching $v_3$ vibration of O$_3$(X$^1A_1$), 1042 cm$^{-1}$ [Barbe et al., 1974], is equal to this within experimental error (the $v_1$ and $v_2$ levels are at 1103 and 701 cm$^{-1}$) and therefore the active vibrational mode in the hot band excitation is assigned to the antisymmetric vibration. The thermal population in the $v_3$''=1 level of O$_3$(X$^1A_1$) is calculated to be only 0.6% of that of the $v$''=0 level at room temperature, but the Franck-Condon factor for the vibrational transition is suggested to several tens of times, or more, larger for the $v_3$''=1 level than for the $v$''=0 level because of preferential overlap of the potential surfaces of the ground and excited states [Michelsen et al., 1994; Taniguchi et al., 2000]. Thus, the contribution of the hot band is non-negligible in the near uv region.

b) Spin-forbidden processes

In the Huggins band region there is clear evidence for the existence of a spin-forbidden channel forming O$(^1D)$. Measurements of the translational energy distributions of the O$(^1D)$ fragments have shown that they contain contributions from species formed with
kinetic energies well above those possible on energetic grounds from process (R3), and are entirely consistent with those expected from process (R4) [Takahashi et al., 1996b; Denzer et al., 1997, 1998]. We attribute the temperature independent part of the quantum yield above 320 nm to this process. At shorter wavelengths it can still be distinguished from the spin-allowed step-photofragment spectroscopy experiments have shown it to be observable at 313 nm [Denzer et al., 1998] and the approximate constancy of the quantum yield for the lowest temperature data above 313 nm suggests that there is a persistent spin-forbidden yield at about the 6-8% level above this wavelength at all temperatures. There is no evidence at present for a contribution of this magnitude at shorter wavelengths, where only the spin-allowed processes (R3) and (R9) have been observed.

We now consider the parentage of the spin-forbidden products. The assignments of both Joens [1994] and Katayama [1979] suggest that the initial absorption in the structured region is to a singlet state, so that absorption would be followed by a curve crossing to a dissociative triplet state. Lifetimes of the states reached by absorption in the structured bands are seen to increase with increasing wavelength in measurements of both linewidths [Takahashi et al., 1997] and translational anisotropies [Hancock et al., 1999]. This observation is consistent with an energy dependent intersystem crossing rate, and would not be expected for direct absorption to a dissociative triplet state. We thus favour singlet to triplet crossing following spin-allowed absorption in this region, although we cannot rule out a contribution from any (as yet unassigned) singlet to triplet absorption.

Measurements of Doppler widths [Takahashi et al., 1996b] and translational energies [Denzer et al., 1998] have shown that the ratio of spin-allowed to spin-forbidden O(1D) formation is smaller on peaks in the Huggins band than in the troughs between them. If absorption on the peaks has a marked component that corresponds to transitions to bound levels
of an upper singlet state which then predissociates to form channels other than process (R3) (including formation of ground state O(^3P) atoms), whereas absorption in the troughs has a relatively larger component from the hot bands of ozone, then there is a possibility of the O(^1D) quantum yield showing some structure. Furthermore, as the absorption peaks become more pronounced at lower temperatures, any structure may be temperature dependent. Only one set of quantum yield data, that of Takahashi et al. [1996a, 1998a] shows continuous measurements over the structured region, all other data being taken at specific wavelengths. Their room temperature measurements show the photofragment yield spectrum of O(^1D) to be virtually structure free between 310 and 325 nm, and thus the quantum yield shows a small anticorrelation with the absorption spectrum [Takahashi et al., 1996a, 1998a]. At low temperatures above 320 nm there is slight structure on the photofragment yield spectrum which correlates with that in absorption [Takahashi et al., 1998a], and results at longer wavelengths show that the photofragment yield follows closely the absorption spectrum [Bauer et al., 2000]. The effect on the O(^1D) yield of taking into account any local variations in the tail will be small in comparison with the change brought about by the new recommendations, but would warrant further investigation.

Summary

To rectify the lack of a good recommendation for the quantum yields for O(^1D) in ozone photolysis, a panel of laboratory scientists and one field measurements scientist working in the area of ozone photodissociation have critically evaluated the data available to date and developed the best possible data set for atmospheric modeling. The experimental techniques used in the experiments of O(^1D) quantum yield measurements were reviewed. The quantum yield of O(^1D) at 298 K at 308 nm was set to 0.79 based on the absolute
quantum yield measurement studies. The wavelength dependence of quantum yields at 298 K between 306 and 328 nm was derived, by checking and renormalizing the recent experimental data presented by the 8 groups and then averaging them. The wavelength dependence at 298 K was anchored at 308 nm. The comprehensive, easy-to-use equation, Eq. (3), was employed for 306 nm < \lambda < 328 nm and 200 K < T < 320 K, by fitting the experimental data of the temperature dependence as well as the yields at 298 K obtained above to the equation. The formation mechanisms of O(^1D) in the photodissociation of O_3 was reviewed and the contributions of the hot band excitation and the spin-forbidden processes were clearly indicated.

**Acknowledgements**

This work was partly supported by International Joint Research Grants of the New Energy and Industrial Technology Development Organization (NEDO). ARR thanks NOAA’s Climate and Global change program and NASA’s Upper Atmospheric Research program for financial support.
**Table 1.** Experimental data of absolute O(\(^{1}\text{D}\)) quantum yield, \(\Phi(\(^{1}\text{D}\))\), in the photolysis of O\(_3\) at 308 nm at room temperature.

<table>
<thead>
<tr>
<th>(\Phi((^{1}\text{D})))</th>
<th>Uncertainty</th>
<th>Reference</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.79</td>
<td>± 0.10</td>
<td><em>Talkudar et al.</em>, [1997]</td>
<td>Time profile of O((^{3}\text{P})) resonance fluorescence intensity</td>
</tr>
<tr>
<td>0.79</td>
<td>± 0.12</td>
<td><em>Takahashi et al.</em>, [1996b]</td>
<td>Photofragment yield spectra of O((^{3}\text{P})) and O((^{1}\text{D})) by VUV-LIF.</td>
</tr>
<tr>
<td>0.79</td>
<td>± 0.02</td>
<td><em>Greenblatt and Wiesenfeld</em>, [1983]</td>
<td>Time profile of O((^{3}\text{P})) resonance fluorescence intensity</td>
</tr>
</tbody>
</table>
**Table 3.** Parameters for the expression (3) in the text to calculate recommendation values of O(\(^1\)D) quantum yields.

<table>
<thead>
<tr>
<th></th>
<th>(i = 1)</th>
<th>(i = 2)</th>
<th>(i = 3)</th>
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<tbody>
<tr>
<td>(X_i) (nm)</td>
<td>304.225</td>
<td>314.957</td>
<td>310.737</td>
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<tr>
<td>(o_i) (nm)</td>
<td>5.576</td>
<td>6.601</td>
<td>2.187</td>
</tr>
<tr>
<td>(A_i)</td>
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<td>8.9061</td>
<td>0.1192</td>
</tr>
<tr>
<td>(v_i) (cm(^{-1}))</td>
<td>0</td>
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<td>-</td>
</tr>
<tr>
<td>(c)</td>
<td>0.0765</td>
<td>-</td>
<td>-</td>
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</table>
Table 4. Recommendation values of the O(1D) quantum yields in the photolysis of O₃ at various temperatures calculated with the expression (3) in the text and the parameters in Table 3.

<table>
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<tr>
<th>nm</th>
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<th>298 K</th>
<th>273 K</th>
<th>253 K</th>
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<th>203 K</th>
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References


Arnerding, W., F. J. Comes and B. Schülke, O(¹D) quantum yield of ozone photolysis in the UV from 300 nm to its threshold and at 355 nm, J. Phys. Chem. 99, 3137-3143, 1995


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Figure 1. Wavelength dependence of the O(1D) quantum yield in the photolysis of O$_3$ at 298 K. The re-normalized values of the data sets reported by 8 groups and their average values are plotted. The recommendation values calculated with the expression (3) for 298 K is also plotted.
Figure 2  Temperature dependence of the O(¹D) quantum yield in the photolysis of O₃ at 308 nm. The experimental results reported by Talukdar et al. [1997, 1998], Takahashi et al. [1998a], Ball et al. [1997] and Bauer et al. [2000] are plotted. The straight line indicates the results of the linear least square fitting under the condition of the fixed point of 0.79 at 298 K, expression (2) in the text.
Figure 3. Comparison of the recommendation values of O(1D) quantum yields at 298 K in the wavelength range 305-330 nm: this work (expression (3) in the text with the fitting parameter in Table 3), JPL 1994 [DeMore et al., 1994], JPL 1997 [DeMore et al., 1997], and JPL 2000 [Sander et al., 2000].
Figure 4. Recommendation values of O(1^D) quantum yields calculated with the expression (3) with the fitting parameter in Table 3 for 203, 253 and 298 K in the wavelength range 305-330 nm (Solid lines). Contributions made by the various dissociation processes to the quantum yields for O(1^D) atoms from O_3 photolysis are also indicated. Region I corresponds to the O(1^D) formation following excitation of parent vibration less molecules and dissociation via channel (R3). Region II (hatched with vertical lines) indicates the contribution from the hot band excitation process leading to O(1^D) formation via channel (R3) at 298 K, while region III (hatched with slash lines) represents the contribution from the spin-forbidden process leading to O(1^D) formation via channel (R4).
Figure 5. Schematic diagram of potential curves as a function of dissociation coordinate. Some of the dissociation processes are also schematically shown. Energy is not on scale for explanation purpose of the hot and cold band excitation processes.