Recommendations of quantum yields for production of O(1D) in the ultraviolet photolysis of ozone

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Abstract

The quantum yield for O(\(^{1}\)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(\(^{1}\)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(\(^{1}\)D) yield as a function of photolysis wavelength \(\lambda\) and temperature \(T\) is presented in the ranges of 306 nm \(\leq\lambda \leq 328\) nm and 200 K \(\leq T \leq 300\) K. The recommendation values of the O(\(^{1}\)D) quantum yield for 290 nm \(\leq\lambda \leq 306\) nm and 328 nm \(\leq\lambda \leq 350\) nm are also presented. The formation mechanisms of O(\(^{1}\)D) in the photolysis of ozone which result in the wavelength and temperature dependence of the O(\(^{1}\)D) yields are interpreted.
**Introduction**

In general, excited species do not play a major role in the chemistry of the Earth's lower atmosphere (i.e., below about 40 km), since excited atoms are very short-lived (nanoseconds) due to fast radiative transitions, or eventually due to collisional deactivation by air molecules (N\(_2\), O\(_2\)). For this reason, competing chemical reactions are normally unimportant for excited atoms 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 highly 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).

\[
\begin{align*}
    \text{O}(^1\text{D}) + \text{H}_2\text{O} & \rightarrow 2\text{OH} \quad \text{(R1)} \\
    \text{O}(^1\text{D}) + \text{N}_2\text{O} & \rightarrow 2\text{NO} \quad \text{(R2)}
\end{align*}
\]

The OH radical is immensely important in the atmosphere. 1) OH is the most important initiator of the degradation of the majority of natural and anthropogenic emissions into 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 component of stratospheric ozone loss process. Similarly, nitric oxide is a crucial ingredient of the stratosphere. Once formed via the O(\(^1\)D)) reaction, it takes part in direct ozone destruction, suppress the ozone destruction by halogens, and convert species from one form to another. Because of the importance of reactions (R1) and (R2), O(\(^1\)D)) is a critical reactant in the Earth's atmosphere.

The major source of O(\(^1\)D) in the lower atmosphere is the photolysis of ozone in the
Hartley and Huggins bands. Because of absorption by overhead ozone, the strong increase of
the ozone absorption cross-section below 330 nm towards shorter wavelength leads to the
sharp decrease of the solar actinic flux which becomes practically zero below 290 nm in the
lower stratosphere and troposphere. Since the photolysis of atmospheric ozone depends on
the overlap of the actinic flux spectrum and on the ozone absorption cross-section, the
diametrical wavelength dependence of both quantities restricts the photodissociation to 290 ~
330 nm [Hofzumahaus et al., 1999]. This is precisely the wavelength region where O(^1D)
production increases from near zero values around 330 nm to near unit values around 290 nm.
Therefore, the calculated atmospheric O(^1D) production rate is very sensitive to changes in
the quantum yield for its production in the photolysis of ozone as a function of wavelength in
this wavelength range. It is also this region where the UV absorption cross sections of ozone
and the quantum yields for O(^1D) production are highly sensitive to temperature.

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

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

It was assumed that the spin conservation would require that the co-product of O(^1D) is
O_2(^1\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 indicate the presence of
a "tail" in O(^1D) quantum yield (i.e., a non-zero quantum yield) beyond this threshold [Brock
and Watson, 1980b; Trolier and Wiesenfeld, 1988]. Adler-Golden and Steinfeld [1982] had
pointed out that vibrationally excited ozone could give O(^1D) via the spin allowed channel
(R1) well beyond the 310 nm energetic threshold calculated for the ground state of ozone.

Ball et al. [1993] reported quantum yield measurements of O_2(a^{1}\Delta) (the O(^1D) co-product
from the spin-allowed photodissociation of ozone) showing a tail that is very similar to the one of O(^1D) reported previously. Michelsen et al. [1994] followed the concept of Adler-Golden and Steinfeld [1982] and presented a model calculation that described well the measured tail of the room-temperature O(^1D) quantum yield reported by Brock and Watson [1980b] and Trolier and Wiesenfeld [1988] and O_2(a^1Δ) by Ball et al. [1993] up to ~320 nm. Their model presented assumes that the tail is due to photolysis of vibrationally excited ozone; it does not account for spin-forbidden processes. Their mathematical expression became the basis for the NASA/JPL recommendation 1997 [DeMore et al., 1997]. Further evidence for the tail came from field experiments that compared J(O(^1D)) photolysis frequencies measured directly by chemical actinometer with data obtained from solar actinic spectra and O_3 → O(^1D) photodissociation spectra [Müller et al., 1995; Shetter et al., 1996]. The quantum yield data that include the tail give much better agreement and a more consistent description of the observed J(O(^1D)) data, in particular as a function of solar zenith angle and total ozone column.

Intensive laboratory work by the groups participating in this paper has yielded new measurements of the O(^1D) 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]. More interestingly, some of these new measurements 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:

\[ \text{O}_3 + h\nu \rightarrow \text{O}^{(1)D} + \text{O}_2(X^{3}\Sigma_g^-), \quad (R4) \]
and has now been demonstrated to occur 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(^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(^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 are 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 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 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 information. Each PI 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

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 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 O(1D) with respect to either reaction or quenching is extremely short in all gases except ultrahigh purity, rare gases.

All of the experimental data used in producing this evaluation 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, ie power per unit, area 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. In addition, since the lasers typically have a high peak power, it is essential to avoid multiphoton effects. Problems in monitoring the change in laser fluence as a function of wavelength probably account for most of the systematic error in the studies reported here.

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 which 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 1D2 0 - 2p 1D2 transition at 115.2 nm and this technique has found limited, although controversial, use in kinetic studies [Heidner and Husain, 1973]. It has not been applied to quantum yield measurements. Three approaches using laser excitation have been published. Pratt et al. [1991] reported (2+1) resonance enhanced multiphoton ionization detection of O(1D) using the 3p 1F3 and 3p 1P1 transitions at 203.5 and 205 nm. Richter and Hynes [1996] reported observation of (3+1) REMPI transitions to the 3d 1F3 and several other closely spaced levels at ~ 276 nm. Both sets of REMPI transitions lie within the absorption spectrum of O3 hence
the focused REMPI probe laser generates an interference signal because it produces \( \text{O}(^1\text{D}) \) which it then detects. The (2+1) excitation wavelength lies in a minimum in the UV absorption spectrum of \( \text{O}_3 \) 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 \( \text{O}(^1\text{D}) \) yield measurements between 305 and 330 nm. The (3+1) wavelength, 276 nm, is easily generated using currently available tunable lasers, however this excitation wavelength lies close to the peak in the ozone absorption cross section and probe background interferences are sufficiently severe that it has little utility for yield studies at long wavelengths. Finally, laser induced fluorescence (LIF), using single photon excitation of the \( 3s^1\text{D}_2^0 - 2p^1\text{D}_2 \) 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 techniques can arise when they are used in conjunction with another laser as the ozone photolysis source. The first of these arises because a polarized laser excites a subset of the magnetic sublevels of the atom it interacts with. In the absence of an electric or magnetic field these levels are degenerate and equally populated. However, if the atom is produced by photolysis using another polarized laser then it is possible to produce a preferential population in some of these sublevels, “an orbital alignment effect”. If the “alignment effect” varies as the photolysis wavelength is changed then 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. 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(^1D) from the photolysis of N_2O, 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(^1D) will depend on the bandwidth of the excitation laser. Takahashi et al. [1998a] found that it was necessary to correct their O(^1D) yield measurements by up to 50% to compensate for Doppler broadening at the longest wavelengths at which they made measurements whereas Ball et al. [1997] concluded that their measurements were unaffected by such effects.

Indirect Techniques: Because of the difficulties associated with direct observation of O(^1D), many studies have utilized indirect detection, allowing the O(^1D) to react with another molecule which is more easily monitored. Clearly the disadvantage of this approach is that it is indirect and that O(^1D) production is inferred. In this case a knowledge of the detailed chemistry associated with production of the “spectroscopic marker” is desirable. Several studies have photolyzed O_3 in the presence of N_2O. The reaction of O(^1D) with N_2O produces NO which then undergoes further reaction with ozone, producing electronically excited NO_2* which can be detected by its chemiluminescence. 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 [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(^1D) yield. Brock and Watson [1980b] also used this
approach in the first published study which reported the existence of the “tail”. A single study by Trolier and Weisenfeld [1988] used energy transfer from O(\(^{1}\)D) to CO\(_{2}\) followed by detection of the infrared emission from vibrationally excited CO\(_{2}\). More recently, three groups have monitored the OH produced by the reaction of O(\(^{1}\)D) with water, H\(_{2}\) or methane. O(\(^{1}\)D) reacts at close to gas kinetic rates with hydrides with a well understood chemistry. 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] monitored the (1-0) transition at 282 nm. Since both transitions lie within the absorption spectrum of ozone, the probe beam generates some O(\(^{1}\)D) atoms which can react within the time frame of the probe pulse to generate an interfering OH LIF signal. This interference is one of the major limitations on the use of LIF to monitor tropospheric OH. The reaction of O(\(^{1}\)D) with H\(_{2}\) and CH\(_{4}\) 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(\(^{1}\)D) yields out to 375 nm.

While the convergence of recent measurements is gratifying, significant and puzzling discrepancies remain even between the various studies which make up this recommendation. No obvious single experimental factor seems to emerge as the culprit. Examples are: 1) the failure of early studies to observe the “tail” which is incorporated in this recommendation and 2) the divergence which occurs at 300 nm amongst the various studies, a wavelength at which signal levels should be large. 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 variations in beam profile remains the largest potential source
of systematic error in such measurements.

3. Data treatment and recommendations

The recommendations for the O(1D) quantum yields in the photolysis of O₃ have been derived with the following procedures. First, we have checked experimental studies on the absolute quantum yield of O(1D) and set a standard value at 298 K at a specific wavelength (0.79 at 308 nm). Second, we have obtained an authentic wavelength dependence of quantum yields at 298 K in the wavelength range 306-328 nm, by checking and renormalizing the experimental data presented by several groups and then averaging them. The wavelength dependence at 298 K is anchored at the above standard point. Third, we have determined the parameters in an expression which provides recommendation values for the ranges of 306 nm < λ < 328 nm and 200 K < T < 320 K, by fitting the expression to experimental data of the temperature dependence as well as the yields at 298 K obtained above.

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 wavelength of 308 nm should be used as a standard point for the O(1D) yield. 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] have measured the time profile of O(3P) resonance fluorescence after the pulsed laser
photodissociation of O\textsubscript{3}. The temporal profile of O(\(^3\text{P}\)) initially jumps due to the direct formation in the photolysis of O\textsubscript{3}, followed by an exponential rise controlled by the following reactions of O(\(^1\text{D}\)) and a slow decay due to diffusion.

\[
\text{O}(^1\text{D}) + \text{O}_3 \rightarrow 2\text{O}_2 \quad \quad k_5 \quad \quad (\text{R5})
\]

\[
\text{O}(^1\text{D}) + \text{O}_3 \rightarrow 2\text{O}(^3\text{P}) + \text{O}_2 \quad \quad k_6 \quad \quad (\text{R6})
\]

Based on the experimental results that the two rates are equal (\(k_5/k_6 = 1.0\)), the absolute O(\(^1\text{D}\)) quantum yield value is calculated from amounts of the initial jump and the exponential rise of the O(\(^3\text{P}\)) 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(\(^3\text{P}\)) and O(\(^1\text{D}\)) after the photolysis of O\textsubscript{3} by scanning the photolysis laser wavelength between 308-326 nm and monitoring the O(\(^3\text{P}\)) and O(\(^1\text{D}\)) concentration with a vacuum-uv laser induced fluorescence technique. The sum of the photofragment yield spectra for both O(\(^1\text{D}\)) and O(\(^3\text{P}\)) atoms with absolute scales should correspond to the absorption spectrum of the O\textsubscript{3} molecule.

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

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

\[
\Phi(\lambda) = s_{1\text{D}} Y_{1\text{D}}(\lambda) / \sigma_{\text{abs}}(\lambda).
\]

As listed in Table 1, the published absolute values for the O(\(^1\text{D}\)) 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 point. There is some uncertainty of 0.02-0.12 for the value at this point (Table 1). Additional work for the absolute value at 308 nm is needed, since the value at this standard point affects all other yield values.

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

The wavelength range of 306-328 nm seems to be extensively important for atmospheric purposes. There are many studies on the quantum yields at room temperature (298K). To obtain a authentic 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 7 groups are taken into account, Talukdar et al. [1998], Takahashi et al. [1996a], Ball et al. [1997], Armerding et al. [1995], Bauer et al. [2000], Brock and Watson [1980b], and Trolier and Wiesenfeld [1988]. 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 discrepancies among the reported values of the quantum yields. In these studies, the relative O(1D) concentration were measured at various wavelengths for O₃ photolysis, for example, by detecting the laser induced fluorescence intensity of OH radical produced by the reaction of O(1D) + H₂O → 2OH. Then, the relative O(1D) concentration obtained at each photolysis wavelength was divided by a value of the published absorption cross section. The absorption cross sections used in those studies are data reported by two groups [Molina and Molina, 1986; and Malicet et al., 1995]. The difference between the two sets of absorption data is small (<2 %) in the wavelength range of 306 - 316 nm, and less than 6 % between 317 and 328 nm. Therefore, the choice of the absorption data causes no
serious error in the calculation of the O(1D) quantum yields.

To convert the relative values to absolute quantum yields, various standard wavelengths and values have been used in those studies. The procedures for the calculation of the O(1D) quantum yields from the relative O(1D) concentrations could produce some distinct systematic differences due to a different scaling of the quantum yield curve. 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(1D) yield data sets of the 7 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 7 groups. Since those results had exceedingly different wavelength dependence from the data sets by 7 groups, we omitted those data in the calculation to obtain the authentic quantum yields at 298 K in the wavelength range of 306 - 328 nm. The re-normalized values of the data sets reported by 7 groups and their average values are plotted in Figure 1.

We used 1.0-nm intervals for the authentic 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 not to be sufficient 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(1D) reported by Takahashi et al. [1996a] The 1-nm intervals are not also sufficient to resolve the structure in a solar actinic flux spectrum. However, Hofzumahaus et al. [1999] have indicated that the calculation of J(O1D) (photolysis frequency of O3 to form O(1D)) with the resolution of 1 nm produces only a small systematic error of less than 2% even at solar zenith angles below 80°. Therefore, we think that this resolution is high enough for atmospheric purpose for the time being.

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 error of 2-3% in the calculation of J(O1D) 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 O3 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 recommendation values in the ranges of T = 200-320 (K) and λ = 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], and Bauer et al. [2000] as well as the averaged data at 298 K described above. First, the temperature dependence of the O(1D) yield at 308 nm was examined. In the first approximation, it was assumed that the O(1D) quantum yield linearly depends on the temperature of O3 gas. The linear least square fitting to the detailed experimental results at 308 nm leads to the equation:
Φ(308 nm, T) = 6.10 \times 10^{-4} T + 0.608 \tag{2}

where \( T \) is temperature in K. The experimental data for the temperature dependence reported by the above 4 groups is normalized at 308 nm with 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,

\[
\Phi(\lambda, T) = \left( \frac{q_1}{q_1 + q_2} \right) A_1 \times \exp \left\{ - \left( \frac{X_1 - \lambda}{\omega_1} \right)^4 \right\} + \left( \frac{q_2}{q_1 + q_2} \right) A_2 \times \left( \frac{T}{300} \right)^2 \times \exp \left\{ - \left( \frac{X_2 - \lambda}{\omega_2} \right)^2 \right\} \\
+ A_3 \times \left( \frac{T}{300} \right)^{1.5} \times \exp \left\{ - \left( \frac{X_3 - \lambda}{\omega_3} \right)^2 \right\} + c \tag{3}
\]

where

\[
q_i = \exp \left( - \frac{\nu_i}{RT} \right) \tag{4}
\]

and \( X_{1-3}, A_{1-3}, \omega_{1-3}, \nu_2 \) and \( c \) are valuable fitting parameters, \( \lambda \) is in nm and \( T \) is in K, and values of \( \nu_1 \) and \( R \) are 0 (cm\(^{-1}\)) and 0.695 (cm\(^{-1}\)/K), respectively. 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 7, 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 \( \text{O}(^1\text{D}) \) 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 2. 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 recommendation is based on the 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 3.

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 × 6th orders function with 49 adjustable parameters did not reproduce the experimental results satisfactorily in the wavelength range of 306-328 nm.

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(1D) 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 small values around 0.90. Talukdar et al. [1998] have reported the yield values do not depend on the temperature of O3 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(1D) 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.

For the wavelength range of 220-290 nm, the absolute yield at 248 nm is reported to be 0.91 ± 0.06 by Talukdar et al. [1998] and 0.94 ± 0.01 by Greenblatt and Weisenfeld [1983], while the yield at 266 nm is 0.88 ± 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.

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), as will be described later. The thermoenergetic threshold for this spin-forbidden process is around 411 nm. This implies that the formation of O(^1D) can continue to 411 nm. Recently, 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 ± 0.006 between 325 nm and 375 nm. In the wavelength range of 329-350 nm we recommend the value of 0.064, which is independent of the temperature. The O(^1D) formation in the atmosphere above 350 nm is not significant due to the small absorption coefficient of O_3.

3-6. Uncertainties of our recommendation on the O(^1D) quantum yields

The primary uncertainties of our recommendation values come from the absolute value at 308 nm which we employed as a standard 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. We estimate the uncertainties of the quantum yield values calculated with the expression (3) is $\pm 10\% (1\sigma)$ at 298 K and $\pm 15\%$ at other temperatures. The uncertainties of our recommendation values in the $290\,\text{nm} < \lambda < 305\,\text{nm}$ is estimated to be $\pm 10\%$, while those for $329\,\text{nm} < \lambda < 350\,\text{nm}$ are $\pm 20\%$.

**Formation mechanisms of O(1D) in the photolysis of O$_3$**

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

$$
O_3 + \text{hv} (\lambda < 309\,\text{nm}) \rightarrow O(1\text{D}) + O_2(a^1\Delta g) \quad \text{(R7)}
$$

$$
O_3 + \text{hv} (\lambda < 411\,\text{nm}) \rightarrow O(1\text{D}) + O_2(X^3\Sigma_g^-) \quad \text{(R8)}
$$

$$
O_3 + \text{hv} (\lambda < 463\,\text{nm}) \rightarrow O(^3\text{P}) + O_2(b^1\Sigma_g^+) \quad \text{(R9)}
$$

$$
O_3 + \text{hv} (\lambda < 612\,\text{nm}) \rightarrow O(^3\text{P}) + O_2(a^1\Delta g) \quad \text{(R10)}
$$

$$
O_3 + \text{hv} (\lambda < 1180\,\text{nm}) \rightarrow O(^3\text{P}) + O_2(X^3\Sigma_g^-) \quad \text{(R11)},
$$

where the long wavelength limits given in parentheses indicate the thermodynamic thresholds for the fragmentations when the parent 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 (R7) and (R11) are predominant, with reported quantum yields of *ca.* 0.9 and 0.1, respectively, [Alder-Golden et al., 1982]. and this is reflected in our recommendation for the region 290-305 nm. However, it should be noted that these values are not yet fixed. At a slightly longer wavelength, we recommend the quantum yield of O(1D) at 308 nm, $\Phi(308\,\text{nm}, 300\,\text{K}) = 0.79$ and $\Phi(308\,\text{nm},...
227 K) = 0.76, which are almost temperature independent for 300-227 K and are taken as our standard values. The literature shows evidence for all the spin-forbidden channels (R8)-(R10) as well as spin-allowed channels (R7) and (R11) occurring in the uv region above 300 nm, generally referred to as the Huggins band [Wayne, 1989]. Production of the O(^1D) atoms above 310 nm has been attributed to both channel (R7) via the photodissociation of internally excited O3, and the spin-forbidden dissociation channel (R8) [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 O(^1D) atoms from O3 photolysis are indicated in Figure 3. Energetic diagram of these excitation processes are schematically shown in Figure 4, and are now discussed in turn.

The transition responsible for the Hartley band takes the molecule from its ground X^1A_1 state to an electronically excited ^1B_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 molecule dominantly in process (R7) 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 ^1B_2 state as for the Hartley band which supports bound vibrational levels below the threshold to process (1) [Katayama, 1979] or to bound vibrational levels of a ^1A_1 state reached in a two electron transition from the ground ^1A_1 (0,0,0) state but with an odd quantum number change in the antisymmetric stretch mode ν_3,
making the overall symmetry $^1B_2$ [Joens, 1994], and presumably gaining intensity from the nearby one photon $^1B_2$ 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 $2^1A_1$ 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 $386.59 \pm 0.04$ kJ/mol, and the standard heat of formation of $O_3$ at 0 K is calculated to be $\Delta H_f^0(O_3) = -144.31 \pm 0.14$ kJ/mol. [Taniguchi et al., 1999] This corresponds to a wavelength limit at 0 K of $309.44 \pm 0.02$ nm for channel (R7). 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 $1056 \pm 20$ cm$^{-1}$ from the difference in the threshold photolysis wavelengths [Takahashi et al., 1997]. The vibrational spacing for the antisymmetric stretching $\nu_3$ vibration of $O_3(X^1A_1)$, 1042 cm$^{-1}$ [Barbe et al., 1974], is equal to this within experimental error (the $\nu_1$ and $\nu_2$ levels are at 1103 and 701 cm$^{-1}$) and therefore the active vibrational mode in the hot band excitation is thus assigned to the antisymmetric vibration. The thermal population in the $\nu_3''=1$ level of $O_3(X^1A_1)$ is calculated to be only 0.6% of that of the $\nu''=0$ level at room temperature, but the
Franck-Condon factor for the vibrational transition is suggested to be more than several tens of times 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]. 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 \( \text{O}(1\,^D) \). Measurements of the translational energy distributions of the \( \text{O}(1\,^D) \) fragments have shown that they contain contributions from species formed with kinetic energies well above those possible on energetic grounds from process (R7), and are entirely consistent with those expected from process (R8) [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 lower 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 lower wavelengths, where only the spin allowed processes (R7) and (R11) 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
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(1\text{D}) 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 (R7) (including formation of ground state O(3\text{P}) 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(1\text{D}) 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 excitation (PHOFEX) spectrum of O(1\text{D}) 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 PHOFEX spectrum which correlates with that in absorption [Takahashi et al., 1998a], and results at higher wavelengths show that the PHOFEX yield follows closely the absorption spectrum [Bauer et al., 2000]. The effect on the O(1\text{D}) 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.

Acknowledgements

?
Table 1. Experimental data of absolute O(\(^1\)D) quantum yield, \(\Phi(\(^1\)D)\), in the photolysis of O\(_3\) at 308 nm at room temperature.

<table>
<thead>
<tr>
<th>(\Phi((^1)D))</th>
<th>Uncertainty</th>
<th>Reference</th>
<th>Method</th>
</tr>
</thead>
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<tr>
<td>0.79</td>
<td>± 0.10</td>
<td>Talkudar et al., [1997]</td>
<td>Time profile of O((^3)P) resonance fluorescence intensity</td>
</tr>
<tr>
<td>0.79</td>
<td>± 0.12</td>
<td>Takahashi et al., [1996b]</td>
<td>Photofragment excitation spectra of O((^3)P) and O((^1)D) by VUV-LIF.</td>
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<tr>
<td>0.79</td>
<td>± 0.02</td>
<td>Greenblatt and Wiesenfeld, [1983]</td>
<td>Time profile of O((^3)P) resonance fluorescence intensity</td>
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</table>
Table 2. $\text{O}^{(1)\text{D}}$ quantum yield in the photolysis of $\text{O}_3$ between 306 and 328 nm at 298 K.

The re-normalized values of the results reported by 7 groups and the average values are listed.

The numbers in the round brackets are renormalization factors used in this work.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>Talukdar et al. [1998] (1.00)</th>
<th>Takahashi et al. [1996a] (1.00)</th>
<th>Ball et al. [1997] (0.93)</th>
<th>Armerding et al. [1995] (1.05)</th>
<th>Bauer et al. [2000] (1.03)</th>
<th>Brock et al. [1980b] (1.05)</th>
<th>Trolier et al. [1988] (0.93)</th>
<th>Average$^a$</th>
<th>Fitting Results$^b$</th>
<th>JPL '97$^c$</th>
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$^a$ Average of the values from the 7 groups.

$^b$ Calculated value with the expression (5) and parameter values in Table 3.

$^a$ DeMore et al. [1997]

$^b$ Atkinson et al. [1997]
Table 3. Parameters for the expression (3) to calculate recommendation values of O(\(^{1}\text{D}\)) quantum yields.

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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) and the parameters in Table 3.

<table>
<thead>
<tr>
<th>nm</th>
<th>321 K</th>
<th>298 K</th>
<th>273 K</th>
<th>253 K</th>
<th>223 K</th>
<th>203 K</th>
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<td>0.876</td>
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<td>0.255</td>
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<td>0.149</td>
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<tr>
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<td>0.101</td>
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<td>0.166</td>
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<tr>
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<td>0.081</td>
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Figure Captions

Figure 1. Wavelength dependence of the O(\(^1\)D) quantum yield in the photolysis of O\(_3\) at 298 K. The re-normalized values of the data sets reported by 7 groups and their average values are plotted. The recommendation values calculated with the expression (3) for 298 K is also plotted.

Figure 2. Recommendation values of O(\(^1\)D) quantum yields at 298 K in the wavelength range 305-330 nm: this work (expression (3) 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 3. Recommendation values of O(\(^1\)D) quantum yields calculated with the expression (5) 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 (R7). Region II (hatched with vertical lines) indicates the contribution from the hot band excitation process leading to O(\(^1\)D) formation via channel (R7) 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 (R8).

Figure 4. 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.
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