O(\(^1\)D) quantum yields from O\(_3\) photolysis in the near uv region between 305 and 375 nm

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Photolysis of ozone in Huggins bands at $\lambda > 300$ nm, is responsible for the production of tropospheric O\(1^D\), and hence the production of OH via the rapid reaction of O\(1^D\) with water vapor. OH is the primary oxidant in the troposphere and accurate values of the wavelength dependence of the ozone absorption cross section and the quantum yield for O\(1^D\) production are critical components of any model of tropospheric chemistry [1]. The mechanism of ozone photolysis in the Huggins bands has been a subject of some controversy which has been rekindled by a flurry of recent studies [2-8]. In this work we present the first detailed study of the production of O\(1^D\) in the highly structured portion of the Huggins bands between 325 and 375 nm. We have observed the formation of O\(1^D\) at wavelengths between 305 and 375 nm and relative quantum yields for O\(1^D\) production have been determined. Relative O\(1^D\) yields were measured from 305 to 375 nm at 295 K and from 305 to 340 nm at 273 K. In the wavelength range from 310 to 325 nm a temperature dependent yield was observed, consistent with production of O\(1^D\) from the photolysis of vibrationally excited ozone, beyond 325 nm the yield is constant reflecting production via an exclusively spin-forbidden process and consistent with absorption to a single excited state.

While photolysis in the peak of the Hartley (200-300 nm) bands is important in the stratospheric chemistry of ozone, absorption at wavelengths longer than 300 nm dominates the photochemical activity of ozone in the troposphere. This reflects the absence of any significant tropospheric actinic flux below 300 nm. This region, in which the Hartley continuum passes into the more structured Huggins bands, is primarily responsible for the production of tropospheric O\(1^D\), and hence the production of OH via the process [9]:

$$\text{O}_3 + h\nu \rightarrow \text{O}^1\text{D} + \text{O}_2$$  \hspace{1cm} (1)
\[ O^1D + H_2O \rightarrow 2OH \quad (2) \]

The O\(^1\)D production rate is given by the product of the photolysis frequency, \( J(O^1D) \) and the ozone concentration. The photolysis frequency is given by the product of the actinic flux, \( F_\lambda \), the absorption cross section, \( \sigma \), and the quantum yield for O\(^1\)D production, \( \Phi_{O1D} \), all of which are wavelength dependent. Hence \( J(O^1D) \) is given by [10]:

\[
J(O^1D) = \int F_\lambda(\lambda) \sigma(\lambda) \Phi_{O1D}(\lambda)
\]

There are five thermodynamically allowed photolysis reactions at \( \lambda > 300 \) nm, shown below with their 0 K thermodynamic thresholds [11].

\[
O_3 + h\nu \rightarrow O^1D + O_2(^1\Delta) \quad (1a) \quad 310 \text{ nm}
\]

\[
\rightarrow O^3P + O_2(^3\Sigma^-) \quad (1b) \quad 1180 \text{ nm}
\]

\[
\rightarrow O^1D + O_2(^3\Sigma^-) \quad (1c) \quad 411 \text{ nm}
\]

\[
\rightarrow O^3P + O_2(^1\Delta) \quad (1d) \quad 611 \text{ nm}
\]

\[
\rightarrow O^3P + O_2(^1\Sigma^+) \quad (1e) \quad 463 \text{ nm}
\]

Throughout most of the Hartley continuum, ozone photolysis is thought to occur via the two spin-allowed processes (1a) and (1b). The major channel reaction (1a) is thought to have a quantum yield of 0.9-0.95, producing O\(^1\)D [12,13,14]. For many years the most widely accepted atmospheric data evaluations produced by NASA [13] and IUPAC [14] panels recommended a \( \Phi_{O1D}(\lambda) \) with a sharp cut off slightly beyond the 0 K thermodynamic threshold for reaction (1a) at 310 nm. This contrasted with a recommendation [12] based primarily on two sets of experiments which utilized laser photolysis and found a tail in \( \Phi_{O1D}(\lambda) \) which stretched out to at least 325 nm.
The most recent NASA panel recommendation [13] incorporated the tail in $\Phi_{\text{O}^1D}(\lambda)$ essentially adopting the wavelength and temperature dependence proposed by Michaelson et al. [17]. This assumes that the quantum yield at wavelengths greater than 310 nm is due exclusively to the excitation of vibrationally excited ozone molecules. As a consequence the threshold for $\text{O}^1D$ production lies at 325 nm at 300 K and moves to shorter wavelengths as the temperature decreased. In a recent study we measured $\text{O}^1D$ quantum yields out to 336 nm, concluded that the spin-forbidden production via reaction (1c) was the most likely explanation and noted that the threshold for $\text{O}^1D$ production appeared to be to the red of 336 nm [4]. In this work we present relative $\text{O}^1D$ yields which were measured from 305 to 375 nm at 295 K and from 305 to 340 nm at 273 K. The quantum yields were converted to absolute values using a yield of 0.79 at 308 nm and 0.77 at 273 nm [18,19]. A number of measurements were made at sufficiently high resolution, typically 0.1 nm steps, to allow the dependence of the quantum yield on the structure in the absorption spectrum of the Huggins bands to be determined.

As in our previous study [4] we used detection of $\text{X}^2\Pi$ OH (v=1) as a "spectroscopic marker" for $\text{O}^1D$. However in this work our photolysis source was a tunable optical parametric oscillator pumped by the third harmonic of an injection seeded Nd-Yag laser. The visible output of the OPO was frequency doubled or summed with the 1064 nm fundamental of the Nd-Yag pump laser generating tunable radiation between 305 and 375 nm with a bandwidth of 0.4 cm$^{-1}$. This was used to photolyze $\text{O}_3$ / $\text{H}_2$ / He or $\text{O}_3$ / $\text{CH}_4$ / He gas mixtures. Any $\text{O}^1D$ produced by photolysis reacts rapidly with $\text{H}_2$ or $\text{CH}_4$ producing OH in a range of vibrational levels. In our experiments OH (v=1) was detected by a second Nd-Yag pumped tunable dye laser, which fired a few microseconds after the photolysis laser. Detection utilized laser excitation of the OH A-X (0-
1) transition while the observation of "blue-shifted" lif on the OH A-X (0-0) band provided high
detection sensitivity and eliminated probe laser interference effects. The delay between the
photolysis and detection lasers was fixed at, typically, 15 microseconds and the OH signal
monitored as the wavelength of the photolysis laser was varied. The OH concentration was
sufficiently low that radical-radical reactions were insignificant and all production and loss
processes were pseudo-first-order. This was confirmed by the OH signal varying linearly as a
function of both photolysis and probe laser powers. Under these conditions the concentration of
OH is directly proportional to the concentration of O¹D produced by the photolysis pulse. The
measured OH lif signal was corrected for variations in the photolysis and probe laser powers, and
small drifts in [O₃]. The variation in this normalized signal as a function of wavelength gives an
O¹D photofragment yield spectrum. It shows the relative variation in the production of OH and
hence O¹D as a function of wavelength and is proportional to the product of the O₃ absorption
coefficient, σₒ₃, and Φₒ₁D. We subsequently refer to this spectrum as PYₒ₁D(λ) where:

\[ \text{PY}_\text{o₁D}(\lambda) = \sigma_\text{o₃}(\lambda) \times \Phi_\text{o₁D}(\lambda) \]

Fig. 1 shows the relative PYₒ₁D(λ) at 1 nm intervals, normalized to \( \sigma_\text{o₃}(345 \text{ nm}) \), together with
the \( \sigma_\text{o₃}(\lambda) \). Our measured PYₒ₁D(λ) varies by more than four orders of magnitude over the 305-
375 nm wavelength interval and this variation is much larger than the dynamic range of our
detection system. Hence measurements were made in a series of overlapping segments which
were then normalized relative to each other. In the 305-350 nm region the reported values are the
average of five sets of measurements. We performed only one set of relative measurements
between 350 and 375 nm hence the scatter in this data is rather larger than in the measurements
below 350 nm. Relative values of \( \Phi_\text{o₁D} \), the fractional yield per photon absorbed, were obtained
by dividing $\text{PY}_{\text{O1D}}(\lambda)$ by $\sigma_{\text{O3}}(\lambda)$ and these yields were then placed on an absolute basis by normalizing to a value of $\Phi_{\text{O1D}} = 0.79$ at 308 nm. At wavelengths below 345 nm the agreement between the literature values of $\sigma_{\text{O3}}(\lambda)$ is good and we used the data of Malicet et al. [20]. Above 345 nm the values of the available $\sigma_{\text{O3}}(\lambda)$ data sets, Brion et al. [21], and Voigt et al. [22] differ significantly as shown in Fig. 1 and values for $\Phi_{\text{O1D}}(\lambda)$ between 345 and 375 nm were calculated using both sets of cross sections. Fig. 2 shows $\Phi_{\text{O1D}}(\lambda)$ at 295 and 273 K. Since the quantum yield was independent of temperature between 325 and 340 nm we did not extend the 273 K measurements beyond 340 nm. In the wavelength range from 310 to 325 nm $\Phi_{\text{O1D}}$ varies as a function of wavelength becoming wavelength independent at $325 \text{ nm} < \lambda < 345 \text{ nm}$. These differences are more obvious at higher resolution when we compare $\text{PY}_{\text{O1D}}(\lambda)$ with $\sigma_{\text{O3}}(\lambda)$. Fig. 3a shows $\text{PY}_{\text{O1D}}(318.5-324 \text{ nm})$ together with $\sigma_{\text{O3}}(318.5-324 \text{ nm})$ with the relative photofragment yield signal normalized to the absorption spectrum at 324 nm. It is clear that $\text{PY}_{\text{O1D}}(318.5-324 \text{ nm})$ is not directly correlated with $\sigma_{\text{O3}}(318.5-324 \text{ nm})$ although the structure in the spectrum is reflected in the experimentally observed signal to some extent. Hence dividing $\text{PY}_{\text{O1D}}(318.5-324 \text{ nm})$ by $\sigma_{\text{O3}}(318.5-324 \text{ nm})$ and normalizing to $\Phi_{\text{O1D}} = 0.79$ at 308 nm gives a $\Phi_{\text{O1D}}(\lambda)$ shown in Fig. 3b, which increases in distinct steps from 0.085 at 324 nm to 0.22 at 319 nm. This contrasts strongly with observations between 329.6 and 336.2 nm. Fig. 4a shows $\text{PY}_{\text{O1D}}(329.6-336.2 \text{ nm})$ together with $\sigma_{\text{O3}}(329.6-336.2 \text{ nm})$ with the relative photofragment yield signal normalized to the absorption spectrum at 336.2 nm. In this case the structure in the experimentally observed $\text{PY}_{\text{O1D}}(\lambda)$ is well correlated with the structure in $\sigma_{\text{O3}}(\lambda)$. Hence $\Phi_{\text{O1D}}(\lambda)$, shown in Fig. 4b is constant within experimental error. This is the case throughout the 325 - 345 nm region hence we obtain a constant quantum yield, $\Phi_{\text{O1D}}(325-345 \text{ nm}) = 0.064 \pm 0.002 (\pm 2\sigma)$. If we take the
of Voigt et al. we obtain a $\Phi_{\text{O}1\text{D}}(345-375 \text{ nm}) = 0.080 \pm 0.008 \ (\pm 2\sigma)$. In both cases the quoted error is a measure of precision only, with the increased scatter reflecting the smaller number of measurements in the 345-375 nm region. The accuracy of $\Phi_{\text{O}1\text{D}}(325-345 \text{ nm})$ is related to the uncertainty in the value used to normalize the relative data, $\Phi_{\text{O}1\text{D}} = 0.79$ at 308 nm, and any systematic errors in the normalization process. We estimate that the overall error is less than 10%. In the 350-375 nm region we performed one set of measurements hence the potential for some systematic error in the normalization process is greater and the uncertainty in the cross sections is also greater. Use of the cross sections of Brion et al. gives a $\Phi_{\text{O}1\text{D}}(\lambda)$ which rises from 0.065 at 350 nm to 0.38 at 375 nm as shown in Fig. 2.

The observation of a significant “tail” beyond 310 nm in the quantum yield has been seen by several groups and confirms the early observations of Brock and Watson [15] and Trolier and Weisenfield [16] that the quantum yield is significant out to at least 325 nm. Our observation of a temperature dependent quantum yield in the 310-325 nm region confirms the recent work of Talukdar et al. [7] and Takahashi et al. [6] and these observations together with studies of the internal energy of the O1D photofragment suggest that between 310 and 325 nm, photolysis occurs via both spin allowed and spin forbidden processes. The experimental manifestation of this is that $\Phi_{\text{O}1\text{D}}(\lambda)$ is not directly correlated with $\sigma_{\text{O}3}(\lambda)$. Other than our preliminary yields out to 336 nm there is no previous data on the long wavelength structured portion of the Huggins bands. This work demonstrates that photodissociation in the region between 325 and 350 nm produces O1D with a constant quantum yield of 0.064. In this region the major photodissociation process is thought to be the spin allowed reaction (1b), giving O3P and $O_2$ ($^3\Sigma^-$). The production of O1D in this region necessarily requires that the spin-forbidden channel (1c) rather than a vibrationally
enhanced reaction (1a) is responsible. The fraction of vibrationally excited molecules with the energy to produce O\textsuperscript{1}D by reaction (1a) at photolysis wavelengths beyond 330 nm is too small to be of any significance. The correlation between the highly structured absorption spectrum and the O\textsuperscript{1}D photofragment yield which gives the constant quantum yield indicates that the initial step in the photodissociation process is the same for both the major and minor channels. This must involve excitation from the same levels of the O\textsubscript{3} ground state populating an excited singlet state which either predissociates via reaction (1b) or crosses to a triplet state and then dissociates via reaction (1c). Our results indicate that the competition between direct predissociation and intersystem crossing is constant as a function of wavelength between 325 and 350 nm. The agreement between \( \Phi_{O1D}(325-345) \) and \( \Phi_{O1D}(345-375) \) obtained using the \( \sigma_{O3}(345-375) \) of Voigt et al. suggests that this is also true out to 375 nm and suggests that the O\textsuperscript{1}D quantum yield may be constant out to the thermodynamic threshold at 411 nm. We believe that the 25\% difference in the absolute values reflects systematic errors in the measurements both of the yields and of the absorption cross sections in this region and that \( \Phi_{O1D}(325-375 \text{ nm}) = 0.064 \pm 0.006 \) is the preferred value. Use of the \( \sigma_{O3}(350-375) \) of Brion et al. gives a \( \Phi_{O1D}(\lambda) \) which rises steeply and implies that the spin-forbidden process accounts for \( \approx 40\% \) of the total cross section at 375 nm. This seems counter-intuitive although resolution of the discrepancies in \( \sigma_{O3}(\lambda) \) is required to resolve this issue.

In our previous work [4] we suggested that the threshold for O\textsuperscript{1}D production lay to the red of 336 nm and that this could make a significant contribution to total O\textsuperscript{1}D production at high zenith angles, particularly at high altitudes. Talukdar et al. [7] calculated O\textsuperscript{1}D production rates assuming a quantum yield of 0.06 between 329 and 410 nm although their measurements
extended only to 329 nm. They concluded that an O1D yield of 0.06 between 329 and 360 nm would contribute significantly to the O1D production rate at high zenith angles. Our results show that the quantum yield is constant with a value of 0.064 between 325 and 350 nm and that this value probably extends to 375 nm. We find that the threshold for O1D production lies to the red of 375 nm and suggest that it probably extends to the thermodynamic threshold for reaction (1c) at 411 nm. For atmospheric modeling purposes we recommend a quantum yield of 0.064 between 325 and 375 nm, and suggest that calculations should consider the effect of extending this value to 410 nm.

References:


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Figure Captions:

1) The relative yield of OH (v=1), shown as a function of wavelength between 305 and 375 nm together with the absorption cross-sections of ozone as reported by Voigt et al. [22] and Malicet et al. [20]/Brion et al. [23]. The relative yield is in arbitrary units and is scaled to be equal to the ozone absorption cross section at 345 nm.

2) Quantum yield for O1D production, $\Phi_{O1D}$, between 305 and 375 nm at 298 K and between 305 and 340 nm at 273 K. The absolute yield is obtained by normalizing to $\Phi_{O1D} = 0.79$ at 308 nm.

3) a) The relative yield of OH (v=1), shown as a function of wavelength between 318.5 and 324 nm together with the absorption cross sections of ozone. The relative yield is in arbitrary units and is scaled to be equal to the ozone absorption cross section at 324 nm. b) Quantum yield for O1D production between 318.5 and 324 nm obtained by normalizing to $\Phi_{O1D} = 0.79$ at 308 nm, for comparison the ozone absorption spectrum is also shown.

4) a) The relative yield of OH (v=1), shown as a function of wavelength between 329.6 and 336.2 nm together with the absorption cross sections of ozone. The relative yield is in arbitrary units and is scaled to be equal to the ozone absorption cross section at 336.2 nm. b) Quantum yield for O1D production between 329.6 and 336.2 nm obtained by normalizing to $\Phi_{O1D} = 0.79$ at 308 nm, for comparison the ozone absorption spectrum is also shown.
Figure 1

\[
\begin{align*}
\text{wavelength [nm]} & \quad 310 \quad 320 \quad 330 \quad 340 \quad 350 \quad 360 \quad 370 \\
\text{O}_3 \text{ cross section [cm}^2\text{]} & \quad 10^{-19} \quad 10^{-20} \quad 10^{-21} \quad 10^{-22} \quad 10^{-23} \\
\text{life signal [arbitrary units]} &
\end{align*}
\]
Figure 2

$T = 295$ K ($\sigma_{O3}$: Voigt [1999])

$T = 295$ K ($\sigma_{O3}$: Malicet [1995], Brion [1998])

$T = 273$ K ($\sigma_{O3}$: Malicet [1995])
Figure 3

(a) Lif signal [arbitrary units] and cross section [10^{-20} \text{ cm}^2 \text{ molec}^{-1}].

(b) O^1D quantum yield and cross section [10^{-19} \text{ cm}^2 \text{ molec}^{-1}].
Figure 4

(a) l.i.f. signal [arbitrary units]

(b) O¹D quantum yield

- + l.i.f. signal
- \( \sigma_{O_3}: \text{Malicet [1995]} \)

- \( O^{1}D \) quantum yield
- \( \sigma_{O_3}: \text{Malicet [1995]} \)

Wavelength [nm]