

*Atmospheric Chemistry of Ozone Photolysis at High Latitudes :
Laboratory and Modeling Studies (Extended Abstract)*

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The near ultraviolet photochemistry of ozone remains a topic of great contemporary interest. The quantum yield for O(¹D) production in the photolysis of ozone (O₃) in the ultraviolet (uv) region as a function of wavelength and temperature is a key input for modeling calculations in the atmospheric chemistry.



The primary reason for the extreme importance of the quantum yield for O(¹D) production in the photolysis of ozone is that 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(1D) with inert H₂O and N₂O :



The overwhelming route to OH formation in the Earth's lower atmosphere is through the reaction of an electronically excited oxygen atom, O(¹D), which is formed from the solar photolysis of ozone. The highly reactive OH radical is nature's atmospheric detergent; it cleanses pollutants by initiating oxidation and hence removing them from the atmosphere. Ozone in the stratosphere itself screens the atmosphere below from most solar UV radiation needed to produce O(¹D). It is the weaker part of the ozone absorption spectrum at longer wavelengths ($\lambda > 310$ nm) which controls how much O(¹D) is produced. Therefore, how ozone dissociates when it absorbs this long wavelength radiation is a crucial piece of information. At high latitude regions, the solar radiation reaching the troposphere has passed through large slant columns of ozone, resulting in a solar spectrum attenuated most at wavelengths less than around 310 nm. Thus, the remaining solar radiation is relatively redder than it would be at lower latitudes. This spectral shift causes an increased sensitivity to quantum yield values for wavelengths > 310 nm in high latitude O(¹D) production models as compared to lower

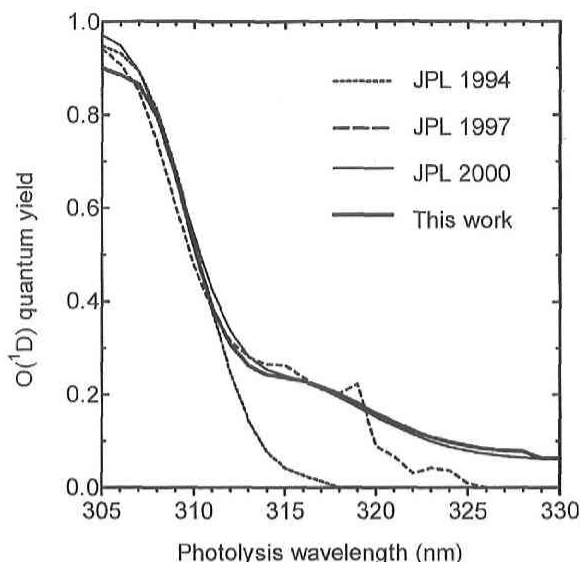


Figure.1. Comparison of the recommendation values of $O(^1D)$ quantum yields at 298 K in the wavelength range 305–330 nm : this work, JPL 1994 [DeMore *et al.*, 1994], JPL 1997 [DeMore *et al.*, 1997], and JPL 2000 [Sander *et al.*, 2000].

latitude $O(^1D)$ production.

We have determined the $O(^1D)$ quantum yield in the photolysis of ozone at ultraviolet wavelengths ($305 \text{ nm} < \lambda < 330 \text{ nm}$) by the laboratory experiments. The $O(^1D)$ and $O(^3P_j)$ photofragments produced in the photodissociation of ozone in the wavelength range 305–329 nm both at 295 K and 227 K have been detected directly using a technique of laser induced fluorescence (LIF) in the vacuum ultraviolet (vuv). Photofragment excitation (PHOFEX) spectra for both species have been measured by scanning the photodissociation laser wavelength while monitoring vuv-LIF at 115 nm [$O(^1D)$] and 130 nm [$O(^3P_j)$]. After applying suitable corrections for the relative detection sensitivities, suitably weighted combinations of these PHOFEX spectra are found to provide a quantitative match to the parent O_3 absorption spectrum both at 295 K and 227 K, thereby providing a method of determining both the wavelength and temperature dependence of the absolute $O(^1D)$ quantum yield, $\Phi_{1D}(\lambda, T)$. The results of the absolute $O(^1D)$ quantum yield at room temperature between 305 and 330 nm are shown in Fig.1. Hot band excitation of internally excited O_3 molecules and dissociation via the spin-allowed channel yielding $O(^1D) + O_2(^1\Delta_g)$ products makes the dominant contribution to the quantum yield $\Phi_{1D}(\lambda, T)$ in the wavelength range 310–320 nm. For $\lambda > 320 \text{ nm}$, the $O(^1D)$ atoms must arise predominantly via the spin-forbidden channel yielding $O(^1D) + O_2(X^3\Sigma_g^-)$. The analysis allows the determination of the absolute branching to this channel ($\Phi \sim 0.07\text{--}0.08$) following O_3 photolysis in the wavelength range 318–329 nm. The quantum yield values for $O(^1D)$ formation in the ozone photolysis between 230 and 308 nm are also

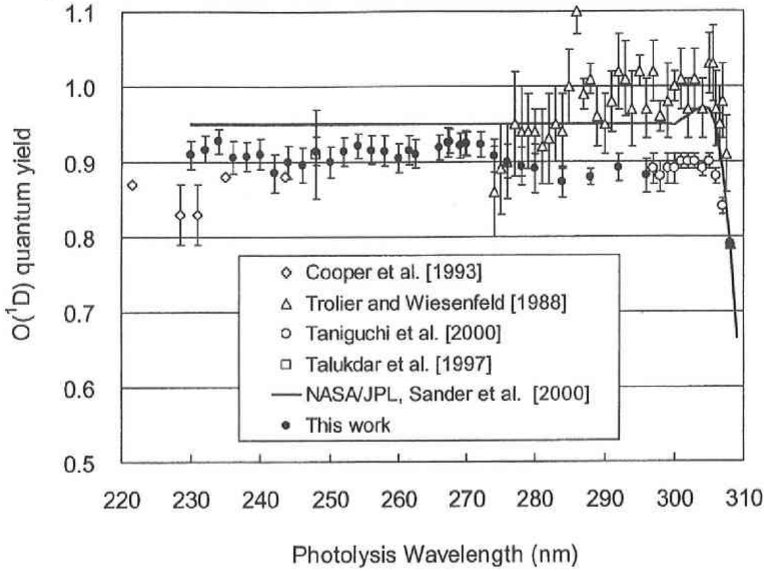


Fig. 2. The quantum yield for $O(^1D)$ formation in the Hartley band photolysis of O_3 at $297 \pm 2K$ as a function of photolysis wavelength. For comparison, the yield values reported by other groups are also shown. Solid line indicates the yield values recommended by NASA/JPL panel [Sander *et al.*, 2000], which are constant (0.95) between 240 and 300 nm.

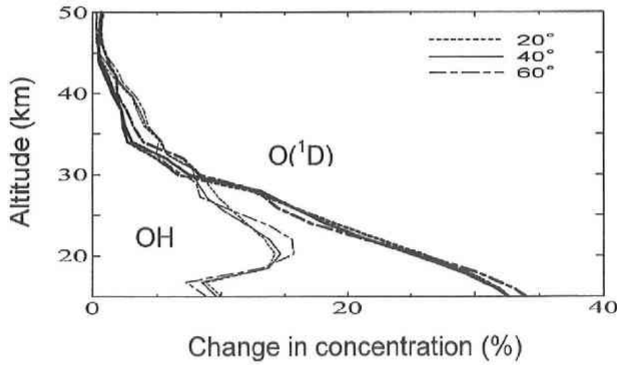


Fig. 3. Calculated percentage change in the concentrations of $O(^1D)$ (thick lines) and OH (thin lines) for the solar zenith angles of 20, 40, and 60 degrees in March as a function of altitude using the new $O(^1D)$ quantum yield values measured in this study, relative to the NASA/JPL 1994 recommendation [DeMore *et al.*, 1994].

determined as a function of the photolysis wavelength. The $O(^1D)$ quantum yield values obtained are found to be almost independent of the photolysis wavelength over the Hartley band (~ 0.91) as shown in Fig. 2. The results are compared with the values measured previously using various experimental techniques, and also with the recom-

mentation values for use in atmospheric modeling.

We have also examined the effects of our O(¹D) quantum yield values on the atmospheric chemistry at high latitudes using a one-dimensional dynamical-photochemical model. We have found that the O(¹D) production rates in the photolysis of O₃ are sensitive to the O(¹D) quantum yield values in the photolysis of ozone especially at high latitudes. Figure 3 shows the calculated percentage change in O(¹D) and OH concentrations for the solar zenith angles of 20, 40, and 60 degrees in March as a function of altitude using the new O(¹D) quantum yield values measured in this study, relative to the NASA/JPL 1994 recommendation [DeMore *et al.*, 1994].

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