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Relative quantum yields for O¹D production in the photolysis of ozone between 301 and 336 nm: evidence for the participation of a spin-forbidden channel

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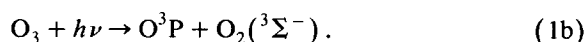
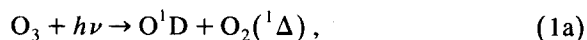
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Abstract

Relative quantum yields for the formation of O¹D from the photolysis of ozone have been measured between 301 and 336 nm. O¹D was monitored indirectly, using laser induced fluorescence detection of vibrationally excited OH. The OH was produced by the reaction of O¹D with H₂. The observation of 'blue-shifted' laser induced fluorescence provided high detection sensitivity and eliminated probe laser interference effects. The results confirm that there is a significant quantum yield for O¹D production at wavelengths longer than 320 nm. A measurable yield is observed out to 336 nm providing evidence for spin-forbidden production of O¹D.

1. Introduction

While photolysis in the peak of the Hartley (200–300 nm) bands is important in the stratospheric chemistry of ozone, absorption in the weak tail (300–350 nm) dominates the photochemical activity of ozone in the troposphere. Throughout most of the Hartley bands, ozone photolysis occurs through two spin-allowed processes. The major channel reaction 1a is thought to have a quantum yield of 0.9–0.95, producing O¹D [1–3].



The region, > 300 nm, in which the Hartley continuum passes into the more structured Huggins bands,

is responsible for the production of tropospheric O¹D, and hence the production of OH via the process



The O¹D production rate is a product of the actinic flux, ozone absorption cross-section and the quantum yield for O¹D production. The actinic flux is rising rapidly and both the ozone absorption cross-section and O¹D quantum yield, $\Phi_{\text{O}^1\text{D}}$, are falling rapidly in this region. Ozone absorption cross-sections, σ_{O_3} , are thought to be known with an uncertainty of 1% [1–3], however the uncertainty in the O¹D quantum yield is much greater, particularly in the long wavelength tail of the spectrum. The NASA evaluation [2] recommends an uncertainty of 1.3 in the region 305 nm < λ < 320 nm and suggests that $\Phi_{\text{O}^1\text{D}} = 0$ at

wavelengths longer than 320 nm. This recommendation is based on a series of experiments performed by Moortgat and coworkers [4–6]. Subsequently there have been several studies [1] using laser photolysis which have measured a significant $\Phi_{\text{O}^1\text{D}}$ at $\lambda_{\text{photolysis}} > 320$ nm. Nevertheless the two widely used evaluations of atmospheric rate constants, NASA [2] and CODATA [3] consider the long wavelength ‘tail’ in $\Phi_{\text{O}^1\text{D}}$ to be an artifact, while also acknowledging the need for further experiments. More recent field and laboratory measurements have raised new questions about the NASA/IUPAC recommendation [7–9]. In addition a recent photofragment-LIF study of jet-cooled ozone in the 317–327 nm region provides strong evidence for the spin-forbidden formation of O^1D [10].

One of the major difficulties in determination of the $\Phi_{\text{O}^1\text{D}}$ is the difficulty in monitoring O^1D , coupled with the dynamic range required, i.e. the product $\{\sigma_{\text{O}_3} \times \Phi_{\text{O}^1\text{D}}\}$ varies by a factor of $> 10^3$ between 300 and 330 nm. Laser based techniques offer the only reasonable approach to this determination but it is critical to ensure that non-linear phenomena or other artifacts associated with high photon densities do not perturb the measurements. In this work we present results based on the detection of vibrationally excited OH as a spectroscopic marker for O^1D . We find a long wavelength tail in the O^1D quantum yield which is suggestive of the participation of spin-forbidden production of O^1D .

2. Experimental

Our experimental studies used detection of $X^2\Pi$ OH ($\nu = 1$) as a ‘spectroscopic marker’ for O^1D . The experiments utilized pulsed, tunable laser photolysis of an $\text{O}_3/\text{O}_2/\text{H}_2$ gas mixture between 301 and 336 nm. OH ($\nu = 1$) was detected by a second pulsed tunable laser, using laser induced fluorescence (LIF) on the OH A–X (0–1) Q_1 transition at 347 nm. Fluorescence was detected in the (0–0) band at 308 nm. All experiments were performed under slow flow conditions. Ozone was generated by passing O_2 through a commercial ozonizer. The O_2/O_3 mixture was combined with a flow of H_2 and passed through a jacketed Pyrex cell. The total pressure was 55 Torr, the ozone concentration was determined photometrically and was 2×10^{15}

molecules cm^{-3} . The partial pressure of H_2 was 10 Torr and the balance of the mixture was O_2 . The photolysis laser was a frequency doubled, Nd–YAG pumped dye laser with an estimated UV bandwidth of 0.5 cm^{-1} . By using several dyes or dye mixtures it was possible to continuously tune the UV output between 300–336 nm. The probe laser output was obtained by mixing the fundamental of an injection seeded Nd–YAG laser with the output of a dye laser, the estimated bandwidth of the probe laser was 0.06 cm^{-1} . The energies of the photolysis and probe pulses were measured using photodiodes. The response of the diode which monitored the photolysis laser was corrected for the change in sensitivity as a function of wavelength by comparison with a thermoelectric power meter. In a typical experiment the photolysis laser fired and after a fixed delay of two microseconds the probe laser fired. The LIF and photodiode signals were monitored using a 500 MHz digital oscilloscope, typically averaging 100 shots. The ‘noise’, i.e. the signal due to scatter from the photolysis and probe beams, was also measured but was negligible until close to the longest wavelength, 336 nm, at which an OH LIF signal was observable. The photolysis laser wavelength was then incremented by 1 nm and the experiment repeated. The LIF signal was found to be linear with photolysis laser power over the range of laser powers available with our system. The LIF signal was linear with probe power at lower powers and showed characteristics of partial saturation at higher powers. The normalized LIF signal, i.e. the relative yield of OH ($\nu = 1$), is shown as a function of wavelength in Fig. 1. This is the product of the O_3 absorption coefficient, σ_{O_3} , and $\Phi_{\text{O}^1\text{D}}$. Relative values of $\Phi_{\text{O}^1\text{D}}$ were obtained by dividing this product by the absorption cross-sections of Molina and Molina [11]. They were then placed on an absolute basis by normalizing to a value of $\Phi_{\text{O}^1\text{D}} = 0.95$ at 302 nm^2 . The total pressure, partial pressures of H_2 and O_3 and the probe laser power were essentially constant over the course of an experiment. As shown in Fig. 1, the photolysis energy varied by a significant factor. The only other experimental variable which was adjusted was the pmt detection sensitivity which was altered by adjusting the pmt high voltage. In these cases common data points were taken at each voltage and the data normalized appropriately.

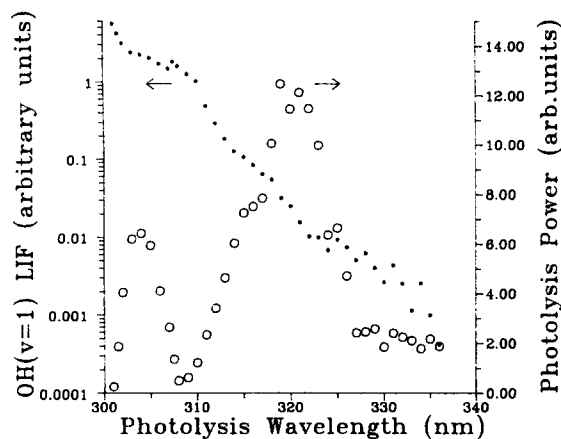


Fig. 1. The relative yield of OH ($\nu = 1$), shown as a function of wavelength between 301 and 336 nm. This yield has been normalized for variations in the photolysis laser power. The relative photolysis laser power is also shown.

3. Results

Fig. 2 shows Φ_{O^1D} , obtained by dividing the LIF signal by the O_3 absorption cross-section and normalizing to a value of 0.95 at 302 nm. The error bars are 1σ measures of the precision of the measurements and do not include an estimate of systematic errors. There is a considerable degree of scatter in the values around 301 nm and 310 nm, including two points with values (including 1σ errors) of Φ_{O^1D} which exceed 1. This is suggestive of some systematic error in the normalization procedure at the very low photolysis laser powers that were available around these wavelengths. The 'tail' in Φ_{O^1D} is clearly evident and the threshold for O^1D production appears to be to the red of 336 nm.

The elimination of experimental artifacts associated with the use of the high photon fluxes is a significant concern in this type of experiment. Some of the potential problems associated with this type of experiment are as follows:

3.1. Is OH ($\nu = 1$) a true spectroscopic marker for O^1D ?

The reaction of O^1D with H_2 to produce vibrationally excited OH is well characterized [12] and is extremely fast with a rate coefficient [2] of $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The product OH is

formed with a high degree of vibrational and rotational excitation with greater than 50% being formed in $\nu = 1$ or higher levels [12]. After photolysis we expect rapid rotational thermalization together with relatively fast vibrational deactivation via collisions with O_2 . Rensberger et al. [13] reported a rate coefficient for O_2 vibrational deactivation of OH ($\nu = 2$) of $2.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with the deactivation rate with H_2 being immeasurably slow. The formation of OH, population of $\nu = 1$ via collisions from $\nu > 1$ and the deactivation of $\nu = 1$ are pseudo-first order in H_2 or O_2 . Hence, for a fixed delay between the pump and probe lasers, the relative OH ($\nu = 1$) LIF signal should accurately reflect relative O^1D formation.

If, as we suggest below, the mechanism of photodissociation involves both spin-allowed and spin-forbidden channels the translational energy disposed into the O^1D fragments is likely to be very different in the two cases. If O^1D is produced with significant translational energy and this affects the energy disposal in the OH product of its reaction with H_2 then a significant artifact could be introduced into this work.

The only other potential sources of OH ($\nu = 1$) would require a hot atom reaction of O^3P with H_2 . We consider 'hot atom' artifacts to be unlikely,

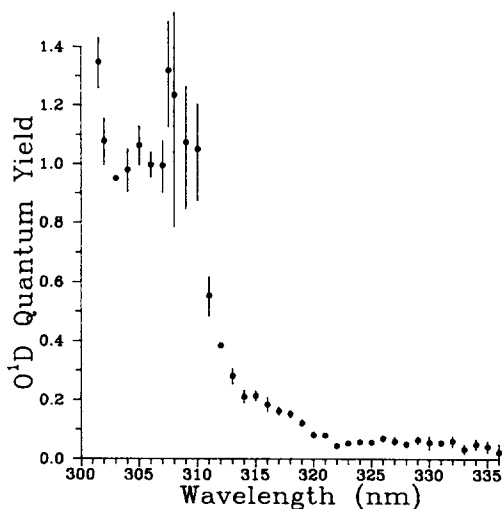


Fig. 2. Quantum yields for O^1D production as a function of wavelength between 301 and 336 nm. Yields were placed on an absolute scale by normalizing to a value of 0.95 at 302 nm.

particularly at the pressures used here, but we plan to examine the pressure dependence of Φ_{O^1D} in a bath gas which has a low efficiency for O^1D deactivation, i.e. He or Ar, but which will efficiently thermalize atoms with excess translational energy.

3.2. Multiphoton photolysis of O_3

Even if the observed OH LIF signal is indeed due to O^1D , multiphoton dissociation of O_3 could produce an artifact. Such a process would produce a non-linear dependence of the LIF signal with photolysis power, experimentally, however, a linear dependence was observed.

3.3. Probe laser photochemical effects

If the probe laser photolyzed electronically excited O_2 to produce O^1D , this could react to produce OH ($v=1$) within the 6 nsec duration of the probe pulse. Such a photolytically generated signal would initially show a quadratic dependence on the probe laser power. The experimentally observed probe power dependence of the LIF signal was linear at lower powers, showing the 'roll-off' characteristic of partial saturation at higher powers.

An example of the signal-to-noise which characterizes these experiments is shown in Fig. 3. In this case the signal averager was used as a digital boxcar integrator set to a ten shot exponential average of the LIF signal which was recorded in 'strip chart' form. The points were sampled at 5 Hz, hence each point corresponds to an instantaneous average of two laser shots, smoothed by the ten shot exponential average. The full scale of 1200×2 shots corresponds to a 4 min measurement period. It can be seen that at 329 nm the observed LIF signal greatly exceeds the background noise and disappears when the photolysis laser is blocked, the H_2 flow is turned off or the ozonizer is switched off. The total signal is a factor of six larger than the background and the ratio of the signal to the 1σ standard deviation in the background is 35. At 336 nm a small OH signal is observable above the background. We estimate that our signal-to-noise ratio can be improved significantly by increasing $[O_3]$, switching to He buffer gas which does not quench the A state of OH and increasing averaging times. This experimental ap-

proach is well suited to determining the form of the long wavelength tail for O^1D production as well as the temperature dependence and threshold.

4. Discussion

Our data are shown in Fig. 4, together with the recent results of Amerding et al. [8] Also shown are the currently recommended NASA/IUPAC evaluation, the recommendation of Steinfeld et al. [1] and the model calculations of Michelsen et al. [14]. The Michelsen et al. model assumes that the long wavelength tail is solely due to dissociation of vibrationally excited molecules. Early experiments on the yield of O^1D were reviewed by Steinfeld et al. [1]. Those workers recommended a 'tail' in Φ_{O^1D} based on the laser photolysis experiments of Brock and Watson [15] and Troler and Weisenfeld [16]. However, both the NASA and IUPAC panels have continued to regard this tail as an artifact. In addition to our work and that of Amerding et al. [8], Takahashi et al. [9] have recently reported values of Φ_{O^1D} between 308 and 325 nm using VUV LIF to directly observe the O^1D photofragment. They do not tabu-

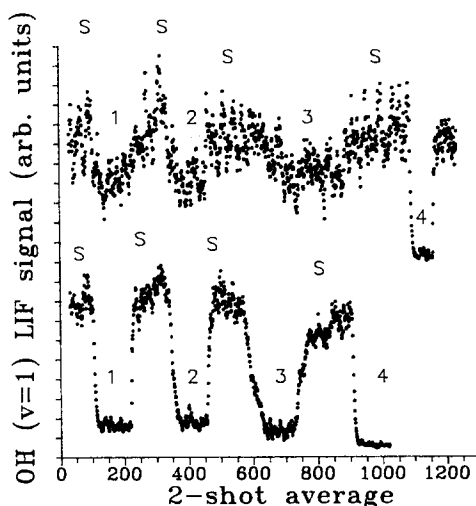


Fig. 3. Examples of the signal-to-noise ratio obtained using detection of 'blue-shifted' fluorescence at 329 and 336 nm photolysis wavelengths. Each point corresponds to the average of 2 laser shots. (S) total signal (LIF of OH ($v=1$)+ background); (1) photolysis laser blocked; (2) H_2 flow off; (3) ozonizer off; (4) probe and photolysis beams blocked.

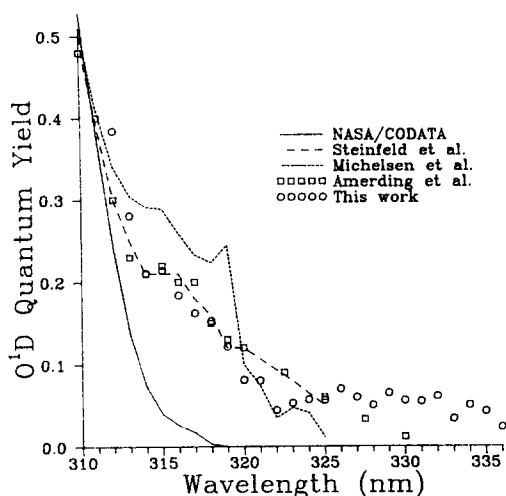


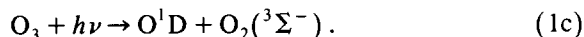
Fig. 4. Comparison of our results with the work of Amerding et al. [8]. Also shown are the currently recommended NASA/IUPAC evaluation, the recommendation of Steinfeld et al. [1] and the model calculations of Michelsen et al. [14].

late their results but their reported yields are in very close agreement with the yields of Trolrier and Weisenfeld [16]. Recent measurements of Ball and coworkers [17–19] show that the yield of $O_2(^1\Delta)$ is significant out to 325 nm. In recent, unpublished data [20] they report O^1D yields which broadly agree with the $O_2(^1\Delta)$ yields. In this work a (2 + 1) REMPI technique is used to directly monitor O^1D .

In recent field experiments, Muller et al. [7] simultaneously measured spectrally resolved actinic fluxes between 280 and 330 nm and $J(O^1D)$ using a chemical actinometer. They compared calculated and measured O^1D formation rates using both the NASA recommended Φ_{O^1D} , and one that included a long wavelength tail. Their results are consistent with a significant long wavelength tail.

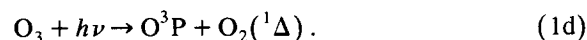
It is clear that there is a significant body of laboratory and field evidence which supports the existence of a long wavelength tail in Φ_{O^1D} although its precise form and magnitude is not well defined and there is little data on its temperature dependence. The thermodynamic threshold for the spin-allowed channel 1a is 310 nm, and two mechanisms provide likely explanations for a significant Φ_{O^1D} at longer wavelengths. Each quantum of excitation in the (001) or (100) vibrational modes decreases the photolysis threshold by $\approx 1000 \text{ cm}^{-1}$. This shifts the photoly-

sis threshold by $\approx 10 \text{ nm}$ to the red. Photolysis of vibrationally excited O_3 could be responsible if the absorption spectrum of these levels is significantly red shifted.



The participation of the spin-forbidden channel 1c, which has a thermodynamic threshold of 411 nm, would also be consistent with long wavelength O^1D production.

The measurements of Ball and coworkers [17–19] on the wavelength and temperature dependence of the yield of $O_2(^1\Delta)$ seem consistent with an $O_2(^1\Delta)$ yield which has a temperature dependent spin-allowed component, together with a temperature independent spin-forbidden component, channel 1d.



The temperature independent channel provides strong evidence for the participation of the spin-forbidden channel and time of flight measurements on the kinetic energy of $O_2(^1\Delta)$ produced in long wavelength (> 320 nm) photolysis are consistent with this. However, if $O_2(^1\Delta)$ is produced from both spin-allowed and forbidden channels then it is not possible to infer O^1D yields from these measurements.

Data on Φ_{O^1D} beyond 325 nm is limited to the recent data of Amerding et al. [8] and the results reported here, both of which determined relative yields using OH as a spectroscopic marker for O^1D . The agreement between these results is reasonable up to 328 nm, however we find a measurable OH yield out to 336 nm. Amerding et al. [8] use an extrapolation to place the threshold for O^1D formation between 331 and 333 nm. They claim that this makes the participation of a spin-forbidden channel unlikely. They cite an unpublished communication from Banichevich [22] reporting calculations which suggest that reaction 1c is the least likely dissociation channel for electronically excited O_3 .

The most significant differences between the experimental approaches are our use of H_2 , rather than H_2O , as the co-reactant and the use of the A–X (0–1) transition to pump vibrationally excited OH, followed by detection of blue shifted fluorescence. Frost and Vaida [21] have recently suggested that

$\text{H}_2\text{O}-\text{O}_3$ complexes may photolyze at long wavelengths to produce OH directly. If their calculations are correct, such a complex would have been present at significant concentrations in the experiments of Amerding et al. [8] and would have contributed to the observed OH ($\nu = 0$) LIF signal. In order to avoid such complications we used H_2 . If photolysis of such a complex was significant, the $\Phi_{\text{O}^1\text{D}}$ measured by Amerding et al. [8] would have been larger than ours and should have been measurable at longer wavelengths. The agreement between the results suggests that photolysis of $\text{H}_2\text{O}-\text{O}_3$ complexes is not a significant source of OH. Our detection scheme has two major advantages over excitation of the A–X (0–0) transition at 308 nm. Observation of blue shifted fluorescence allows for very effective discrimination against scattered probe laser light. In addition, since the O_3 absorption cross section and $\Phi_{\text{O}^1\text{D}}$ are small at 347 nm, the probe beam produces a negligible OH LIF background signal. This is in strong contrast to the use of 308 nm excitation which produces a strong background OH LIF signal with the same laser pulse producing O^1D and detecting the OH reaction product. This noise signal is a two-photon process and scales quadratically with laser power.

During the revision of this paper, a preliminary report on the photolysis of jet-cooled ozone appeared which provides strong evidence for the formation of O^1D via the spin-forbidden process 1c. Takahashi et al. [10] photolyzed jet-cooled O_3 between 317–327 nm and obtained the O^1D photofragment excitation spectrum using laser induced fluorescence to monitor O^1D . At 320.05 and 323.80 nm, wavelengths which correspond to peaks in the photofragment excitation spectrum, they obtained broad O^1D Doppler profiles of 1.5 cm^{-1} . This necessarily implies spin-forbidden O^1D production if the excitation is from the vibrationless level of O_3 . It also implies that an insignificant fraction of the available energy is partitioned into vibrational excitation of O_2 ($^3\Sigma^-$). The Doppler profiles of O^1D produced by photolysis at two wavelengths in the underlying continuum are narrower and the authors identify these as being formed from vibrationally excited O_3 . However narrow profiles do not necessarily imply spin-allowed production of O^1D . Such profiles would be consistent with spin-forbidden production in which a significant

fraction of the available energy is partitioned into excitation of O_2 ($^3\Sigma^-$). The structure which the authors identify with the spin-forbidden process is apparent in the photofragment spectrum of thermalized O_3 at 227 K [10] but is not apparent at 298 K in the 317–325 nm region [9].

The model of Michelsen et al. [14] predicts spin-allowed production of O^1D out to 325 nm, although the predicted quantum yield at 325 nm is 0.01, lower than any of the experimental studies. At 324 nm approximately 0.2% of the O_3 population has sufficient internal energy to produce O^1D via a spin-allowed process. At 334 nm this fraction has dropped by greater than two orders of magnitude to 0.0014%. Our observations imply that $\Phi_{\text{O}^1\text{D}}$ is essentially constant in this region. For our observations to be consistent with production of O^1D via channel 1a the cross-section of vibrationally excited ozone molecules would have to increase dramatically with wavelength between 324 and 334 nm. At 334 nm it would require a cross section of $\approx 2 \times 10^{-17} \text{ cm}^2$. It seems more likely, in our view, that the spin-forbidden channel 1c is operative. Temperature dependent studies and the measurement of the quantum yield at longer wavelengths should shed more light on this question. As we have noted above our experimental approach should be able to address both questions. With some experimental modifications we should be able to increase our signal-to-noise ratio significantly and extend the measurements to temperatures as low as 215 K.

These results have significant implications for both tropospheric and stratospheric models. We have used a time-dependent photochemical model [23,24] to examine the effects of the increase in $\Phi_{\text{O}^1\text{D}}$ on tropospheric OH levels. The full details of these calculations will be published elsewhere [25], however we find that at 298 K and 0 km the use of our $\Phi_{\text{O}^1\text{D}}$ increases the average OH concentration by 10–20% over that computed with currently recommended NASA values. The exact value depends on latitude and is greater at higher latitudes. At 298 K the inclusion of a spin-forbidden channel with $\Phi_{\text{O}^1\text{D}} = 0.05$ for $325 \text{ nm} < \lambda < 350 \text{ nm}$ has essentially no effect on this result. At lower temperatures the effects of a spin-forbidden tail could be more significant. A preliminary assessment suggests that at a temperature of 220 K and a height of 15 km an

addition of a temperature independent ‘tail’ with $\Phi_{O^1D} = 0.05$ for $320 \text{ nm} < \lambda < 350 \text{ nm}$ would increase the calculated J_{O^1D} by 10% over the model of Michelsen et al. [14] at high zenith angles. By contrast both models predict rates which are a factor of 3 larger than those calculated using the current NASA values.

Acknowledgements

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