

Photodissociation of HNO_3 at 193, 222, and 248 nm: Products and quantum yields

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Photodissociation of HNO₃ at 193, 222, and 248 nm: Products and quantum yields

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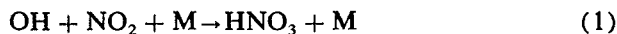
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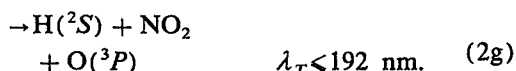
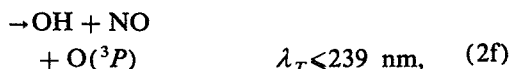
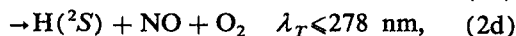
The quantum yields for OH, O(³P), O(¹D), and H(²S) from the photolysis of HNO₃ have been determined at 248, 222, and 193 nm at 298 K. The quantum yield for OH was observed to be near unity at 248 [$\Phi(\text{OH}) = 0.95 \pm 0.09$] and 222 nm [$\Phi(\text{OH}) = 0.90 \pm 0.11$]. However, at 193 nm the quantum yield for OH was found to be 0.33 ± 0.06 . The quantum yield for O atoms [O(³P) + O(¹D)], $\Phi(\text{O})$, was observed to be 0.031 ± 0.010 , 0.20 ± 0.03 , 0.81 ± 0.13 , at 248, 222, and 193 nm, respectively. Both O(³P) and O(¹D) were observed at 222 and 193 nm, but only O(³P) was detected at 248 nm. It was observed that 40% of the O atoms formed at both 193 and 222 nm were O(¹D) atoms. The upper limits for H(²S) quantum yields: $\Phi(\text{H}) < 0.002$ at 248 nm, < 0.01 at 222 nm, and < 0.012 at 193 nm were also determined. This present work quantifies the photolysis channel producing HONO + O and show that it accounts for a large fraction at HNO₃ photolysis at 193 nm.

INTRODUCTION

Nitric acid is an important reservoir in the stratosphere for both HO_x and NO_x species. It is formed by the termolecular reaction



and destroyed primarily by photolysis and also via reaction with hydroxyl radicals.¹ In the lower stratosphere, cloud processes and downward transport to the troposphere all contribute to loss of HNO₃. Photolysis of nitric acid can occur through a variety of channels



(Threshold wavelengths are at 0 K.) Early studies by Johnston *et al.*² between 200 and 300 nm found that reaction (2a) was the dominant process occurring with a primary quantum yield of unity. However, this measurement was based on simulations of a complex chemical system including several heterogeneous reactions. A later study of Jolly *et al.*,³ mea-

sured the OH yield directly by laser photolysis/resonance absorption at 222 nm and found that $\Phi(\text{OH}) = 0.89 \pm 0.08$ in relatively good agreement with the yield of unity reported by Johnston *et al.* As a result, many studies have employed HNO₃ as a photolytic precursor of OH radicals, assuming that OH and NO₂ are the only photofragments produced.⁴⁻⁸ Margitan and Watson⁸ have reported a quantum yield of 0.03 for O(³P) atoms and < 0.002 for H atoms at 266 nm. However, more recently, several studies have shown evidence for other photoproduct channels. At 193 nm, Kenner *et al.*⁸ have shown that photolysis of HNO₃ produced a long lived intermediate ($\tau > 20 \mu\text{s}$) which could absorb a second photon and produce OH ($A^2\Sigma^+$). This intermediate was hypothesized to be HONO by spin conservation and energy considerations.⁹ Since the beginning of this work, we have been aware of the detection of HONO from the photolysis of HNO₃ at 193 nm in a supersonic jet expansion,¹⁰ and the recent work by Schiffman and Nesbitt.¹¹ Schiffman and Nesbitt indicate that the OH yield at both 248 and 193 nm is significantly less than unity [$\Phi(\text{OH}) = 0.75$ at 248 and $\Phi(\text{OH}) = 0.47$ at 193 nm].

In this study, we report the quantum yields for OH, O [O(³P) + O(¹D)] and H atoms at 248, 222, and 193 nm measured in pulsed laser photolysis systems. Atomic resonance fluorescence detection was used for O(³P) and H(²S), while pulsed laser induced fluorescence was used for OH(^X²Π) detection. The primary quantum yield for OH was determined relative to that of the hydrogen peroxide which has been measured in our laboratory at both 248 nm [$\Phi(\text{OH}) = 2.0$]¹² and at 193 nm [$\Phi(\text{OH}) = 1.5$].¹³ The quantum yield for OH at 222 nm was then measured relative to the OH yield obtained at 248 nm. In all of these experiments the total yield of OH, including OH(^A³Σ) and any vibrationally excited OH(^X²Π), is measured by quenching

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the excited species to OH($X^2\Pi$, $v'' = 0$). The primary quantum yield of O atoms [$O(^3P) + O(^1D)$] was measured relative to O atoms produced in ozone photolysis in N₂ bath gas which is unity at 222 and 248 nm and 1.2 at 193 nm.¹⁴ Photolysis of HNO₃ in He with added N₂ or H₂ allowed us to distinguish between O(3P) and O(1D) formation. Yields of atomic hydrogen were measured relative to the H atom yield in the photolysis of O₃/H₂ mixtures where the quantum yield for O(1D) production in O₃ photodissociation and the yield for H atom in the reaction of O(1D) + H₂ are known.

EXPERIMENT

All experiments reported here were carried out by pulsed laser photolysis of H₂O₂, HNO₃, and other photo-lytes, followed by detection of O(3P), H(2S), or OH($X^2\Pi$, $v'' = 0$). The atomic species, O(3P) and H(2S), were measured using an apparatus equipped with resonance fluorescence detection, and OH was detected via a pulsed laser induced fluorescence apparatus. Both of the apparatuses used in this study have been described in detail elsewhere,^{14–16} and only brief descriptions necessary to understand the present experiments will be given here. The photolytic light sources in both experiments were excimer lasers at 193 nm (ArF, 0.14–5.6 mJ pulse⁻¹ cm⁻², 2–10 Hz, pulse width of ~20 ns), 222 nm (KrCl, 0.14–4.2 mJ pulse⁻¹ cm⁻², 2–10 Hz, pulse width of ~20 ns) and 248 nm (KrF, 0.14–45 mJ pulse⁻¹ cm⁻², 2–10 Hz, pulse width of ~20 ns). In the time-resolved atomic resonance fluorescence experiments, the O(3P) resonance lamp consisted of a microwave discharge through a flow of high-purity He. O(3P) atoms were detected by fluorescence in the $3^3S_1^0 \rightarrow 2^3P_J$ transitions at 130.2, 130.5, and 130.6 nm. The resonance radiation was admitted to the reaction cell through a calcium fluoride window which filters out Lyman- α radiation (121.6 nm). Resonance fluorescence was collected perpendicular to both the photolysis and fluorescence excitation beams by a magnesium fluoride lens and imaged onto the photocathode of a solar blind photomultiplier tube. The volume between the MgF₂ lens and the phototube was flushed with N₂. For H atom detection, the same resonance lamp was used, but the CaF₂ window and the MgF₂ lens were replaced with magnesium fluoride windows which transmit the Lyman- α line at 121.6 nm. An oxygen flush (~1200 Torr cm) was used between the lamp and the reactor cell and between the reactor cell and the PMT to eliminate the O atom light at 130–131 nm. By this choice of flush gases and windows we could detect O(3P) without any interference from H(2S) and vice-versa. Signals were obtained by photon counting using multichannel scaling techniques, and using dwell times of 2–200 μ s/channel. For 1 s integration, the detection limit, defined as $f^0/B^{1/2} = 1$, where f^0 is the signal immediately after photolysis and B is the background radiation, was determined to be 2×10^8 cm⁻³ for O atoms and 3×10^8 cm⁻³ for H atoms in the present study. Typically, 300–5000 laser shots were averaged to produce a well defined O(3P) or H(2S) temporal profile. All experiments were carried out at room temperature (298 ± 3 K) in an excess of N₂ or He (20–100 Torr).

In the pulsed laser photolysis/pulsed laser induced-flu-

orescence experiments, OH was detected by exciting the Q₁(1) ($A^2\Sigma \leftarrow X^2\Pi$) line by a beam from a frequency-doubled Nd:YAG pumped dye laser at a right angle to the photolysis beam. The resulting OH fluorescence was collected perpendicular to both the photolysis and probe beams by a photomultiplier tube, whose signal was fed to a gated charge integrator and then sent to a computer for data analysis. The [OH] was measured at several different delay times after the photolysis pulse to generate a temporal profile. All experiments were carried out at 298 ± 3 K and in ~100–300 Torr N₂ and ~1 Torr H₂O.

Both the atomic resonance fluorescence and LIF experiments were carried out under "slow flow" conditions (linear velocity = 10–20 cm/s). Since the photolysis laser (~0.5 cm beam diameter) traversed the reactor cell perpendicular to the gas flow direction, a fresh reaction mixture was provided for each laser flash under the conditions of laser repetition rate and gas flow rates that were used. This replenishment avoided accumulation of photolysis or reaction products, but allowed the system to kinetically behave like a static one. HNO₃ was prepared by the reaction of NaNO₃ with H₂SO₄ and collected and stored in the dark at 197 K. An NO₂ impurity of <0.3% was estimated from the measured O(3P) decay rates (due to the O + NO₂ reaction) in the O(3P) resonance fluorescence experiments. HNO₃ was added to the reactor cell by bubbling a small flow of He or N₂ through the trap held at 273–288 K. The nitric acid concentration was measured either prior to or just after the reaction cell by uv absorbance at either 184.9 or 213.9 nm using 50 to 150 cm long absorption cells. Ozone concentrations were similarly measured by uv absorbance at 253.7 nm and the concentration of H₂O₂ was determined by uv absorbance at 213.9 nm. The absorbance cross sections used in this study are listed in Table I. The use and preparation of O₃, H₂O₂, and H₂O in our laboratory are described elsewhere.^{12–14} Concentrations of other species were determined by adding known flows, measured by calibrated flow meters, to the reaction cell and measuring the pressure with a capacitance manometer. Commercial gases used in this study included He (>99.9999%, Bureau of Mines), N₂ (>99.9995%, Scientific Gas Prod.), O₂ (>99.99%, Scientific Gas Prod.), and H₂ (>99.999%, Scientific Gas Prod.).

TABLE I. Absorbance cross sections used in the present study.

λ (nm)	HNO ₃ ^a	$\sigma(10^{-20}$ cm ² molecule ⁻¹) H ₂ O ₂ ^b	O ₃ ^c
184.9	1630
193	1330	60.6	43.4
213.9	45.6 ^d	33.0	...
222	12.0	...	220
248	1.98	9.0	1080
253.7	1150

^a Taken from Refs. 17 and 18.

^b Taken from Ref. 17.

^c Taken from Refs. 19 and 17.

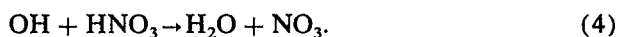
^d Measured in the present work relative to 184.9 nm.

RESULTS

All photolyses were carried out under optically thin conditions so that attenuation of the photolysis laser beam in passing through the reactor was mostly $<1\%$; but at the highest concentrations of HNO₃ in 193 nm experiments, the attenuation of the laser beam was $\sim 5\%$. This was only for a few experiments and no corrections were made for this change. The experiments for the measurement of the quantum yield for each species [O(³P), H(²S), or OH(²Π)] at the different wavelengths is similar. However, for each species detected, a different reference system (which had different subsequent chemistry) was used. Therefore, our results will be presented in three subsections (one for each species measured) for ease of presentation.

Primary quantum yield of OH

The quantum yield for OH from HNO₃ photolysis was measured relative to that in H₂O₂ which has been measured to be $\Phi_{\text{H}_2\text{O}_2}(\text{OH}) = 1.51 \pm 0.18$ at 193 nm¹³ and 2.00 ± 0.05 at 248 nm.¹² The initial OH signals were obtained from the $t = 0$ intercept of $\ln(S_t - B)$ vs time, t , plots (where B is the background excited by the probe laser and S_t is the signal at time t). The temporal profile of OH produced upon photolysis is governed mainly by its reaction with the photolyte, H₂O₂ or HNO₃, which is in large excess over OH



In addition, the OH is lost via diffusion out of the detection zone and reaction with impurities. This first order loss process has a rate coefficient k_d . Therefore, the OH temporal is given by the equation: $[\text{OH}]_t = [\text{OH}]_0 \exp(-k't)$, where $k' = k_d + k_3[\text{H}_2\text{O}_2]$ or $k' = k_d + k_4[\text{HNO}_3]$. By variation of either [H₂O₂] or [HNO₃], the rate coefficients k_3 and k_4 were measured. The obtained values of k_3 were $(1.88 \pm 0.04) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the 193 nm and $(2.01 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the 248 nm experiments. The rate coefficient for reaction (4) was found to be $k_4 = (1.50 \pm 0.16) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (at 193 nm, 100 Torr N₂, 1 Torr H₂O) and $(1.48 \pm 0.07) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (at 248 nm, 310 Torr N₂, 1 Torr H₂O). All of these measurements were at 298 K and the errors reported are 2σ (precision only). The values of k_3 are in excellent agreement with those measured previously by us¹² and in good agreement with recommended values.¹⁷ The accuracy of these rate coefficients are estimated to $\pm 10\%$. The measured value of k_4 is $\approx 15\%$ higher than the recommended value.¹⁷ It is possible that this small discrepancy is due to the presence of $<0.3\%$ of NO₂. These rate coefficient measurements served as a check of the measured concentrations of the photolytes, and the absence of secondary production/consumption of OH.

Hydrogen peroxide was first photolyzed and the initial signal, $S_{\text{H}_2\text{O}_2}^0$, was determined. The H₂O₂ was then replaced by HNO₃ and photolysis was repeated to obtain $S_{\text{HNO}_3}^0$. Under optically thin conditions, back to back photolysis runs of HNO₃ and H₂O₂ can be ratioed to obtain

$$\frac{S_{\text{HNO}_3}^0}{S_{\text{H}_2\text{O}_2}^0} = \frac{\Phi_{\text{HNO}_3}(\text{OH})\sigma_{\text{HNO}_3}E_{\text{HNO}_3}[\text{HNO}_3]}{\Phi_{\text{H}_2\text{O}_2}(\text{OH})\sigma_{\text{H}_2\text{O}_2}E_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]}. \quad (I)$$

In Eq. (1), E_{HNO_3} and $E_{\text{H}_2\text{O}_2}$ are the laser fluences for the HNO₃ and H₂O₂ runs, respectively, and σ_{HNO_3} and $\sigma_{\text{H}_2\text{O}_2}$ are the respective absorption cross sections of HNO₃ and H₂O₂ at the photolysis wavelength. A constant excess of water vapor (≈ 1 Torr) was added to the reactor during both runs to insure that electronic quenching of OH(⁴Σ⁺) remains constant and thus to keep the detection sensitivity the same in both runs, and to quench any vibrationally excited OH that is produced. Production of OH from the photolysis of H₂O at 193 nm was found to be $<25\%$ of the total OH signal, and was accounted for by measuring the OH produced in a third run with only H₂O present. The primary quantum yield is then obtained from a plot of the ratio of the initial signals (normalized for the laser fluence) vs [HNO₃]/[H₂O₂]. One such plot is shown in Fig. 1 for 193 nm photolysis. From the slope of these plots, quantum yields of $\Phi_{\text{HNO}_3}(\text{OH})$ were measured to 0.95 ± 0.09 at 248 nm and 0.33 ± 0.06 at 193 nm [The quoted errors are 2σ , and in-

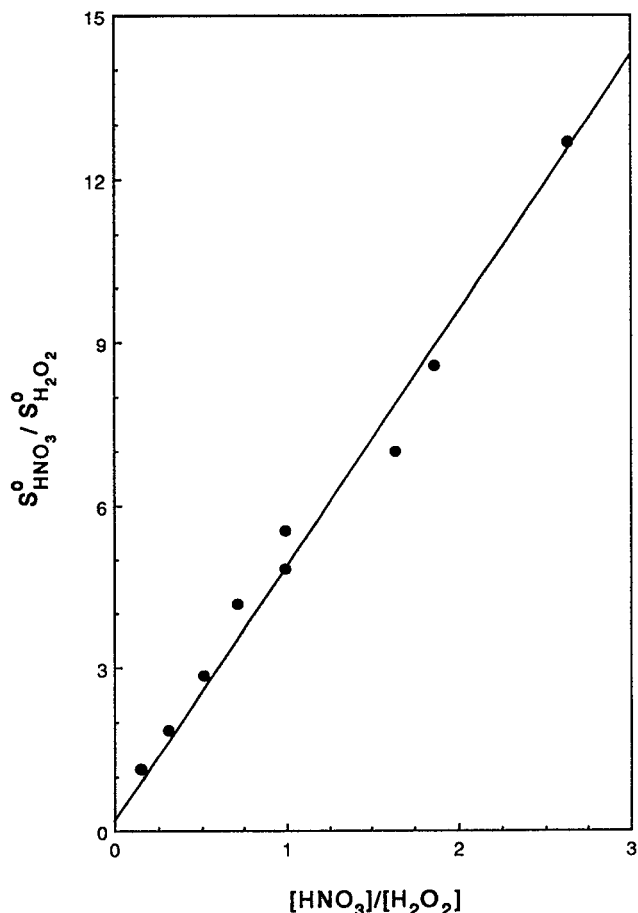


FIG. 1. Plot of the ratio of the initial OH signals from the photolysis of HNO₃, $S_{\text{HNO}_3}^0$, and H₂O₂, $S_{\text{H}_2\text{O}_2}^0$, vs the ratio of the concentrations obtained at 193 nm. The initial signals are normalized for laser fluence. Total pressure of 100 Torr N₂ with 1 Torr of H₂O. The slope of this line is equal to $\Phi_{\text{HNO}_3}(\text{OH})\sigma_{\text{HNO}_3}/\Phi_{\text{H}_2\text{O}_2}(\text{OH})\sigma_{\text{H}_2\text{O}_2}$.

clude precision, and an estimated 2% error for σ_{HNO_3} , 5% error for $\sigma_{\text{H}_2\text{O}_2}$, as well as the error in $\Phi_{\text{H}_2\text{O}_2}(\text{OH})$. These values are listed in Table II.

Once the primary quantum yield for OH at 248 nm was determined, it was possible to use this value to obtain the OH quantum yield at 222 nm. A steady concentration of HNO₃ was flowed through the photolysis cell (in 100 Torr N₂, 1 Torr H₂O) and photolyzed at 248 nm. An initial signal, S_{248}^0 , was obtained [from a $\ln(S_t - B)$ vs t plot], and then the photolysis was carried out using 222 nm light, and a second initial signal, S_{222}^0 , was measured. Extreme care was taken to insure that the overlap between the photolysis beam and the probe beam were identical for both the 248 and 222 nm beams. This was accomplished by allowing the photolysis beam to completely fill apertures on both the front and back of the photolysis cell. The ratio of the initial signals is then described by

$$\frac{S_{222}^0}{S_{248}^0} = \frac{\Phi_{\text{HNO}_3}^{222}(\text{OH})\sigma_{222}E_{222}N_{222}[\text{HNO}_3]}{\Phi_{\text{HNO}_3}^{248}(\text{OH})\sigma_{248}E_{248}N_{248}[\text{HNO}_3]}, \quad (\text{II})$$

where E_{222} and E_{248} are the laser fluences at the two wavelengths, N_{222} and N_{248} are the number photons per unit energy at each wavelength, and σ_{222} and σ_{248} are the respective absorption cross sections of HNO₃. The value of $N_{222}/N_{248} = 0.895$. The HNO₃ concentration remains constant in both runs, as evidenced by the observation that the pseudo-first-order rate coefficient varied <5% between the two back-to-back runs. Using $\Phi_{\text{HNO}_3}^{222}(\text{OH}) = 0.95 \pm 0.09$ (measured in the previous experiment), the primary quantum yield for OH was found to be $\Phi_{\text{HNO}_3}^{222}(\text{OH}) = 0.90 \pm 0.11$ (2σ , precision only), and is included in Table II. Variation of the [HNO₃] allowed for the measurement of the rate coefficient of reaction (4) as in the previous experiment. The obtained value of k_4 was $(1.32 \pm 0.08) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ (2σ , precision only, data from both 222 and 248 nm runs) in good agreement with recommended values.¹⁷

TABLE II. Summary of results and experimental conditions.

Species, X	λ , (nm)	[HNO ₃] (10 ¹⁴ molecule cm ⁻³)	$\Phi_{\text{HNO}_3}(\text{X})^a$
OH	248	10–40	$0.95 \pm 0.09(14)$
	222	8.9–32	$0.90 \pm 0.11(10)$
	193	0.7–4.0	$0.33 \pm 0.06(9)$
O ^b	248	11–16	$0.031 \pm 0.010(9)$
	222	7.0–50	$0.20 \pm 0.03(25)$
	193	0.7–5.3	$0.81 \pm 0.13(21)$
H	248	10	$<0.002(2)$
	222	10	$<0.01(2)$
	193	3.9–11.5	$<0.012(11)$
O(³ P)/O _{tot}	248	32	$0.93 \pm 0.07(4)$
	222	6.0	$0.60 \pm 0.04(4)$
	193	1.5–4.0	$0.65 \pm 0.11(14)$

^a Errors are reported as 2σ and are described in the text. Number of measurements are shown in parentheses.

^b Defined as $\text{O} = \text{O}(\text{}^3\text{P}) + \text{O}(\text{}^1\text{D})$.

Primary quantum yield for O atoms

Ozone was used as the reference compound to determine the oxygen atom quantum yield from HNO₃. In an excess of nitrogen (25 or 100 Torr), O(¹D) produced is rapidly quenched ($<1 \mu\text{s}$) to O(³P) and thus the measured O(³P) is the sum of O(¹D) and O(³P). The quantum yields for O atom [O(³P) and O(¹D)] production from O₃ photolysis at both 248 and 222 nm are known to be unity. At 193 nm, the quantum yield for O atom production from ozone has been observed to be $\Phi_{\text{O}_3}(\text{O}) = 1.20 \pm 0.15$.¹⁴ At both 248 and 193 nm, the temporal profile of O(³P) in the photolysis of O₃ was measured. At 248 nm, plots of $\ln(f_t - B)$ vs time (where f_t is the signal at time t and B is the background fluorescence signal measured prior to the laser flash) were linear after 1 μs and were extrapolated to $t = 0$ to obtain the initial signal, $f_{\text{O}_3}^0$. At 193 nm, the temporal profile of O(³P) shows a slow rise (rise time = 1 ms for [O₃] = 5×10^{13} molecule cm⁻³) and then a decay. The rise is due to the production of O(³P) from the reaction of O₂(^b¹Σ), which is produced in the O₃ photolysis, with O₃ (Ref. 14) and the decay is due to diffusive and reactive loss. The initial signal was obtained by fitting the data to a double exponential function using a nonlinear least squares fitting routine,¹⁴ and extrapolating to $t = 0$. Ozone was then replaced by HNO₃ and a second temporal profile was obtained to determine $f_{\text{HNO}_3}^0$ [from a $\ln(f_t - B)$ vs t plot]. To account for absorption of the resonance radiation by HNO₃, the initial signals were normalized to the background to obtain $S_{\text{O}_3}^0 = f_{\text{O}_3}^0/B_{\text{O}_3}$ and $S_{\text{HNO}_3}^0 = f_{\text{HNO}_3}^0/B_{\text{HNO}_3}$. (The validity of this normalization was checked by photolyzing O₃ at 248 and adding various amounts of HNO₃, under conditions where >95% of the observed O(³P) was produced from O₃. The normalized initial signal, $S^0 = f^0/B$, was found to be independent of [HNO₃] as expected.) Then the initial signals can be ratioed

$$\frac{S_{\text{HNO}_3}^0}{S_{\text{O}_3}^0} = \frac{\Phi_{\text{HNO}_3}(\text{O})\sigma_{\text{HNO}_3}E_{\text{HNO}_3}[\text{HNO}_3]}{\Phi_{\text{O}_3}(\text{O})\sigma_{\text{O}_3}E_{\text{O}_3}[\text{O}_3]} \quad (\text{III})$$

in a similar fashion as before. A plot of the ratio of the normalized initial signals vs [HNO₃]/[O₃] at 193 nm is shown in Fig. 2 from which the quantum yield, $\Phi_{\text{HNO}_3}(\text{O}) = 0.81 \pm 0.13$ [2σ , precision + 2% error from σ_{O_3} , σ_{HNO_3} , + error in $\Phi_{\text{O}_3}(\text{O})$] is obtained. At 248 nm, the quantum yield was observed to be $\Phi_{\text{HNO}_3}(\text{O}) = 0.036 \pm 0.009$ (2σ , precision + errors in cross sections). At 193 nm the effect of O atom production from the photolysis of the NO₂ impurity is negligible. At 248 nm, photolysis of the NO₂ impurity leads to a small overestimate of the O atom quantum yield (<14%), which, when corrected for, leads to a final value of $\Phi_{\text{HNO}_3}(\text{O}) = 0.031 \pm 0.010$.

At 222 nm, the experiments were carried out in a different way. HNO₃ was photolyzed to obtain a temporal profile and an initial signal, $S_{\text{HNO}_3}^0$. A mixture of the same concentration of HNO₃ and a known small concentration of O₃ was then photolyzed (at a constant laser fluence) to obtain an initial signal, $S_{\text{O}_3}^0$. The ratio of initial signals in this situation becomes¹²

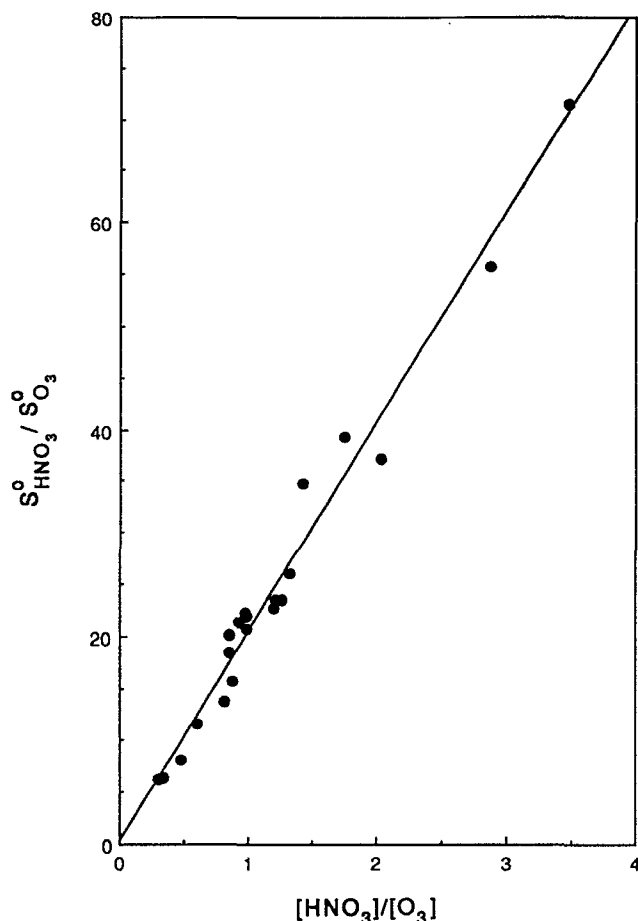


FIG. 2. Plot of the ratio of initial O atom signal from the photolysis of HNO₃, $S_{\text{HNO}_3}^0$, and O₃, $S_{\text{O}_3}^0$, vs the ratio of the concentrations obtained at 193 nm. The initial signals are normalized for laser fluence and changes in the background. Total pressure is 25–100 Torr N₂. The slope of this line is equal to $\Phi_{\text{HNO}_3}(\text{O}) \sigma_{\text{HNO}_3} / \Phi_{\text{O}_3}(\text{O}) \sigma_{\text{O}_3}$.

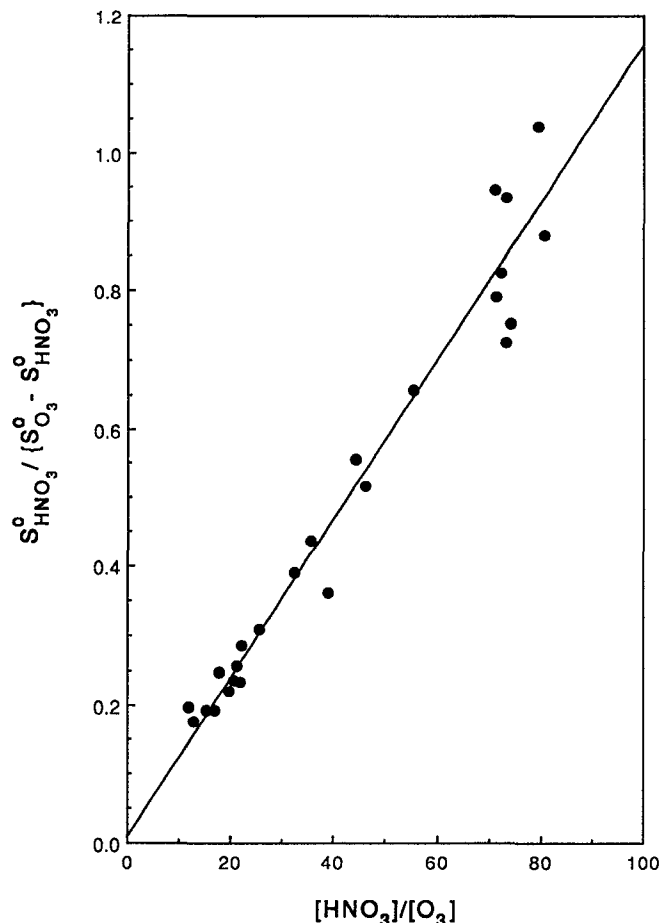


FIG. 3. Plot of $S_{\text{HNO}_3}^0 / \{S_{\text{O}_3}^0 - S_{\text{HNO}_3}^0\}$ vs $[\text{HNO}_3]/[\text{O}_3]$ measured at 222 nm, where $S_{\text{HNO}_3}^0$ is the initial signal from photolysis of HNO₃ and $S_{\text{O}_3}^0$ is the initial signal from photolysis of HNO₃ and O₃. Initial signals are normalized for small changes in laser fluence and background. Total pressure is 25–100 Torr N₂. The slope of this line is equal to $\Phi_{\text{HNO}_3}(\text{OH}) \sigma_{\text{HNO}_3} / \Phi_{\text{O}_3}(\text{OH}) \sigma_{\text{O}_3}$.

$$\frac{S_{\text{HNO}_3}^0}{S_{\text{O}_3}^0 - S_{\text{HNO}_3}^0} = \frac{\Phi_{\text{HNO}_3}(\text{O}) \sigma_{\text{HNO}_3} [\text{HNO}_3]}{\Phi_{\text{O}_3}(\text{O}) \sigma_{\text{O}_3} [\text{O}_3]}. \quad (\text{IV})$$

This method has the advantage that absorption of the resonance fluorescence light by HNO₃ is the same in both runs. A plot of $S_{\text{HNO}_3}^0 / \{S_{\text{O}_3}^0 - S_{\text{HNO}_3}^0\}$ vs $[\text{HNO}_3]/[\text{O}_3]$ is shown in Fig. 3. The slope of this plot leads to a quantum yield of $\Phi_{\text{HNO}_3}(\text{O}) = 0.21 \pm 0.02$ (2σ , precision + errors in cross sections). A small correction for O atom production from NO₂ impurity is necessary. After this correction we obtain $\Phi_{\text{HNO}_3}(\text{O}) = 0.20 \pm 0.03$. These results are included in Table II.

Since both O(¹D) and O(³P) can be produced at 222 and 193 nm, it is necessary to determine their individual quantum yields. Photolysis of HNO₃ in He (20–25 Torr) allowed us to distinguish O(³P) from O(¹D). First, an excess of N₂ (1.3×10^{17} molecule cm⁻³) was added to the photolysis mixture and an initial signal, S_1^0 , was obtained (see Fig. 4). This corresponds to the signal due to the total amount of O atoms produced in the photolysis, as O(¹D) is rapidly quenched by N₂ to O(³P). The N₂ was replaced with

H₂ (7×10^{16} molecule cm⁻³) and HNO₃ was photolyzed to obtain the initial signal, S_2^0 . In this run, O(¹D) is rapidly scavenged by H₂ and the initial signal is due only to O(³P) produced in photolysis (Fig. 4). Photolysis of only HNO₃ in He was also used for this second run since O(¹D) will be scavenged by HNO₃. The branching ratio for O(¹D) quenching by HNO₃ is not known and could be a complication. However, as shown later, it appears that O(¹D) reacts with HNO₃ and is not quenched. The fraction of O(³P) produced, (S_2^0/S_1^0), was measured to be 0.65 ± 0.11 (2σ , precision only), at 193 nm and 0.60 ± 0.04 (2σ , precision only) at 222 nm. At 193 nm there was no difference in the ratio S_2^0/S_1^0 observed by using either H₂ (0.65 ± 0.12) or HNO₃ (0.64 ± 0.09) as the O(¹D) scavenger, suggesting that quenching of O(¹D) to O(³P) by HNO₃ is not important. Using the quantum yield for the total amount of O atoms obtained earlier, the values, $\Phi(\text{O}^3\text{P}) = 0.53 \pm 0.13$ and 0.126 ± 0.022 [errors are 2σ and include the precision and error in $\Phi_{\text{HNO}_3}(\text{O})$] at 193 and 222 nm, respectively, can be derived. By difference, the quantum yields for O(¹D) production are found to be $\Phi(\text{O}^1\text{D}) = 0.28 \pm 0.07$ at 193 nm, and 0.074 ± 0.013 at 222 nm [error is 2σ and includes

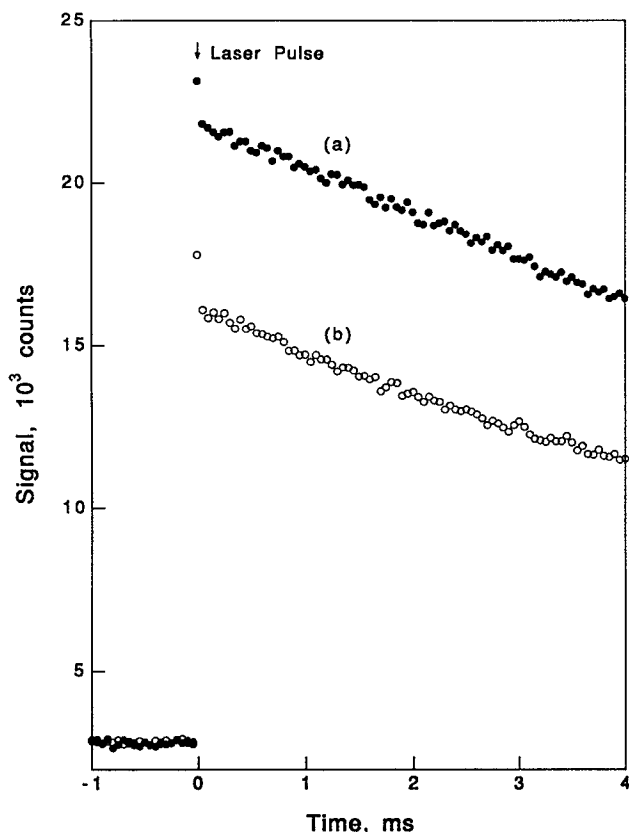


FIG. 4. Plot of the O(³P) signal vs time from the photolysis of [HNO₃] = 2.0 × 10¹⁴ molecule cm³ at 193 nm (*E* = 0.35 mJ pulse⁻¹ cm⁻²) for (a) the addition of ~3 Torr of N₂ which quenches O(¹D) to O(³P) and (b) the addition of 2 Torr of H₂ which scavenges O(¹D). Time resolution is 50 μs/channel.

precision and the error in $\Phi_{\text{HNO}_3}(\text{O})$. At 248 nm, production of O(¹D) is thermochemically prohibited. A similar experiment at 248 nm using N₂ and H₂ resulted in the O(³P)/O_{tot} ratio of nearly unity ($S_2^0/S_1^0 = 0.93 \pm 0.07$, 2σ, precision only), confirming the absence of O(¹D) production.

Primary quantum yields of H(²S) atoms

It was clear from preliminary experiments that very little or no H atoms are produced in the photolysis of HNO₃ at 222 and 248 nm. The observed hydrogen atom yields were quantified in a similar fashion to the determination of oxygen atoms, using the photolysis of O₃/H₂ in 20–25 Torr of He as a reference. H atoms are produced by the reaction sequence



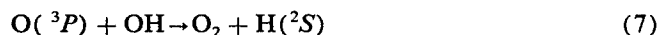
Excess H₂ ([H₂] ≈ 7 × 10¹⁶ molecule cm⁻³) was added so that complete consumption of O(¹D) occurred within the first detection channel (< 2 μs). Ozone concentrations were maintained at [O₃] ≤ 4 × 10¹³ molecule cm⁻³ to reduce any secondary chemistry. The temporal profile and initial signal in O₃/H₂ photolysis, $S_{\text{O}_3}^0$, was determined. The O₃/H₂ was then replaced with HNO₃, and the temporal profile and ini-

tial signal, $S_{\text{HNO}_3}^0$, was again obtained. The ratio

$$\frac{S_{\text{HNO}_3}^0}{S_{\text{O}_3}^0} = \frac{\Phi_{\text{HNO}_3}(\text{H})\sigma_{\text{HNO}_3}E_{\text{HNO}_3}[\text{HNO}_3]}{\Phi_{\text{O}_3}(\text{H})\sigma_{\text{O}_3}E_{\text{O}_3}[\text{O}_3]} \quad (V)$$

was used to obtain the quantum yield, $\Phi_{\text{HNO}_3}(\text{H})$. The quantum yield for H atom production in the reference system is $\Phi_{\text{O}_3}(\text{H}) = \Phi_5(\text{O}^1\text{D})\Phi_6(\text{H})$. $\Phi_6(\text{H})$, the yield of H atom in reaction (6), is known to be unity and $\Phi_5(\text{O}^1\text{D})$ has been observed to be 0.91 ± 0.03 at 248 nm,^{20,21} 0.87 ± 0.04 at 222 nm,¹⁴ and 0.46 ± 0.29 at 193 nm.¹⁴ Since the H atom yields were not measurable, we can only report upper limits for $\Phi_{\text{HNO}_3}(\text{H})$ at 248 and 222 nm [$\Phi_{\text{HNO}_3}(\text{H}) \leq 0.01$ and < 0.002 at 222 nm and 248 nm, respectively].

At 193 nm, however, a measurable H atom signal was obtained in the photolysis of HNO₃. An initial jump in the H atom signal was followed by a slow rise and eventually a decay of the H atom signal. The appearance and decay rate were found to be dependent on the laser fluence (both increasing with laser power), indicating that it was most likely due to the reactions of photoproducts. Based on the appearance rate, and the expected concentrations of O, NO₂, and OH radicals from the photolysis, we identify the reaction



$$k_{298} = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{Ref. 17})$$

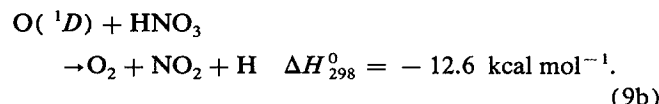
to be the source of the increase in H atom signal and the reaction



$$k_{298} = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{Ref. 22})$$

to be the major reaction influencing its loss rate. The obtained data was fit to a double exponential equation by a nonlinear least squares fitting routine¹⁵ and extrapolated to *t* = 0 to obtain $S_{\text{HNO}_3}^0$. This initial signal varied linearly with laser fluence (0.3–5.5 mJ pulse⁻¹ cm⁻²), which suggests that the observed H atoms are unlikely to be produced by a two photon process. From this we calculate a small yield of H atoms, $\Phi_{\text{HNO}_3}(\text{H}) = 0.011 \pm 0.008$ [2σ, precision and error from $\Phi_5(\text{O}^1\text{D})$] at 193 nm.

When using short time scales (2 μs/channel), the earliest measurable point in our system is at 12 μs in the present experiments. The earlier five channels are obscured by counts picked up by the PMT due to the laser flash. Therefore, the initial H atom signal observed must be generated in this 12 μs period. Other than photolytic production of H(²S) from HNO₃, the only possible secondary reaction which could account for this signal is



From the observed $\Phi_{\text{HNO}_3}(\text{O}^1\text{D})$, a branching ratio of $k_9/k_7 \approx 0.04$ is needed to explain the observed H atom yield. It is also necessary that $k_9 \geq 3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ so that reaction (9) goes to ≈ 90% completion with 12 μs ([HNO₃] = 6 × 10¹⁴ molecule cm⁻³). Otherwise, a noticeable rise in the H(²S) signal would be observable at short reaction times. This reaction could not be ruled out under the experimental conditions employed; therefore, the yield

of H atoms is best considered to be an upper limit, $\Phi_{\text{HNO}_3}(\text{H}) < 0.012$. Gerlach-Meyer *et al.*²³ have previously reported that no H atoms were detected from photolysis of HNO₃ at 193 nm; however, no experimental details were given in order to adequately analyze and compare their results to the present study.

DISCUSSION

A summary of our results and those from other previous studies are shown in Tables II and III. In our experiments, nitric acid concentrations were measured directly by uv absorbance. The measured quantum yields were the same whether HNO₃ concentration was measured before entering or after exiting the reaction cell, indicating no significant loss of HNO₃ within the system. The rate coefficients for reactions (3) and (4) agree with previous measurements so that it is unlikely that any undesirable chemistry is affecting our [OH] measurements at any of the three wavelengths. In the determination of O atom yields from photolysis of HNO₃ using short reaction times (2 μs /channel), the decay of the O(³P) signal was exponential, suggesting that no secondary process was generating the measured O atoms. From the O(³P) decays, the rate coefficient for the reaction of O(³P) with HNO₃ can be estimated to be $< 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is in agreement with the recommended value.¹⁷ The initial O atom signals (f^0/B) were found to vary linearly with [HNO₃] and [O₃] at all wavelengths; therefore, all our measurements were made within a region where the resonance fluorescence signal varied linearly with O atom concentration. It was also observed that the initial O atom signal from HNO₃ photolysis varied linearly with laser fluence (over a factor of 5) at all wavelengths. This strongly suggests that the O atoms observed are primary photoproducts and not produced by multiphoton processes.

TABLE III. Summary of results and comparison with previous study.

λ , (nm)	Species, X	$\Phi_{\text{HNO}_3}(\text{X})$	Reference
200–300	OH, NO ₂	~ 1	2
266	O*	0.03	8
	H	< 0.002	8
248	OH	0.75 ± 0.10	11
		0.95 ± 0.09	This work ^b
	O	0.031 ± 0.009	This work
	O(³ P)	0.031 ± 0.009	This work
	H	< 0.002	This work
222	OH	0.89 ± 0.08	3 ^c
		0.90 ± 0.11	This work
	O	0.20 ± 0.03	This work
	O(³ P)	0.126 ± 0.022	This work
	H	< 0.01	This work
193	OH	0.47 ± 0.06	11
		0.33 ± 0.06	This work
	O	0.81 ± 0.13	This work
	O(³ P)	0.53 ± 0.13	This work
	H	< 0.012	This work

^a Defined as $\text{O} = \text{O}(\text{}^3\text{P}) + \text{O}(\text{}^1\text{D})$.

^b Errors are reported in the present work as 2σ and are described in the text.

^c Error reported as the 95% confidence limit of the experimental precision.

From the shape of the absorption spectrum of HNO₃, Johnston and Graham²⁴ suggested that two or more different continuum states are excited, depending on the wavelength, upon light absorption by HNO₃. CNDO/s-CI calculations by Harris²⁵ have assigned the two bands to an $n\text{--}\pi^*$ transition (1 ¹A₂ state between 230 and 320 nm) and a $\pi\text{--}\pi^*$ transition (1 ²B₂ state centered about 185 nm), with both bands originating from the nitro chromophore. It is likely that these two or more different states dissociate differently, i.e., give different products. Our present work is consistent with this idea.

The first major absorption is centered about 260 nm, and it is shown to produce mostly OH + NO₂ as photoproducts. We measure the OH yield at 248 nm to be $\Phi_{\text{HNO}_3}(\text{OH}) = 0.95 \pm 0.09$. This is consistent with earlier work by Johnston *et al.*,² who photolyzed HNO₃ in excess CO and O₂ and, using end-product analysis, deduced the OH yield to be essentially unity. However, Schiffman and Nesbitt¹¹ recently measured the quantum yield for OH at 248 nm to be significantly less than unity [$\Phi_{\text{HNO}_3}(\text{OH}) = 0.75 \pm 0.10$]. They used laser photolysis of HNO₃ followed by time-resolved high resolution infrared absorption spectroscopy to detect the OH photofragment. They also measured the quantum yield of OH from H₂O₂ photolysis (the reference compound used in the present study) to be $\Phi_{\text{H}_2\text{O}_2}(\text{OH}) = 1.58 \pm 0.23$ which is lower than the value of 2.0 adopted here from a prior study in our laboratory.¹² It can be seen that when the relative quantum yields [$\Phi_{\text{HNO}_3}(\text{OH})/\Phi_{\text{H}_2\text{O}_2}(\text{OH})$] are compared, the agreement is excellent (see Table IV). This suggests a possible systematic error in one of the two studies, the nature of which is unknown at present. However, the H₂O₂ photolysis study of Vaghjani and Ravishankara¹² at 248 nm also included upper limits for the quantum yields for both H atoms [$\Phi_{\text{H}_2\text{O}_2}(\text{H}) < 0.0002$] and the sum O(¹D) + O(³P) [$\Phi_{\text{H}_2\text{O}_2}(\text{O}) < 0.002$]. The possibility of the channel



is discussed by Vaghjani *et al.*¹³ and determined to be unimportant at 248 nm. Therefore, we believe that photolysis of H₂O₂ at 248 yields only OH as a photolysis product with a quantum yield of 2.00 ± 0.05 .

HNO₃, like H₂O₂, exhibits a continuous uv spectrum and is expected to dissociate upon absorption of a photon. We have measured the quantum yield for one photoproduct from each thermochemically possible dissociative channel at 248 nm [O atoms—channel (2b), OH—channel (2a), and H atoms—(2c) + (2d)]. The observation of $\Phi_{\text{HNO}_3}(\text{OH})$

TABLE IV. Comparison of the ratio of the OH quantum yield to the OH quantum yield for H₂O₂ at 248 nm.

	Present study	Schiffman and Nesbitt (Ref. 11)
$\Phi_{\text{HNO}_3}^{248}/\Phi_{\text{H}_2\text{O}_2}^{248}$	0.48 ± 0.05	0.47 ± 0.09
$\Phi_{\text{HNO}_3}^{193}/\Phi_{\text{H}_2\text{O}_2}^{248}$	0.17 ± 0.03	0.30 ± 0.04
$\Phi_{\text{H}_2\text{O}_2}^{193}/\Phi_{\text{H}_2\text{O}_2}^{248}$	0.76 ± 0.09^a	0.77 ± 0.14

^a Data taken from Refs. 12 and 13.

$= 0.95 \pm 0.09$ and $\Phi_{\text{HNO}_3}(\text{O}) = 0.031 \pm 0.010$ and $\Phi_{\text{HNO}_3}(\text{H}) \leq 0.002$ successfully accounts for all of the photolysis products. The small yield for O atoms of $\Phi_{\text{HNO}_3}(\text{O}) = 0.031 \pm 0.010$ observed here is in excellent agreement with the work of Margitan and Watson⁸ who reported that $\Phi_{\text{HNO}_3}(\text{O}) = 0.03$ at 266 nm. Also, the H atom yield of ≤ 0.002 at 248 nm we measured is in agreement with the upper limit reported by Margitan and Watson⁸ at 266 nm [$\Phi_{\text{HNO}_3}(\text{H}) \leq 0.002$]. Therefore, we believe that $\Phi_{\text{HNO}_3}(\text{OH}) \approx 1$ at 248 nm.

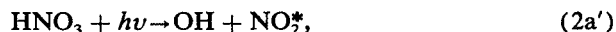
At shorter wavelengths, absorption into a second state centered about 182 nm predominates and the yield of OH was observed to decrease to $\Phi_{\text{HNO}_3}(\text{OH}) = 0.33 \pm 0.06$ at 193 nm. The use of N₂ as a buffer gas eliminates the possibility of excess OH being produced by the reaction



since O(¹D) will be rapidly quenched by N₂ to O(³P) ($t < 100$ ns), and the reaction of O(³P) with HNO₃ is too slow to produce OH on the time scale of our experiments. Schiffman and Nesbitt¹¹ report an OH yield at 193 nm of $\Phi_{\text{HNO}_3}(\text{OH}) = 0.47 \pm 0.06$ which is somewhat higher than the yield reported here. The ratio of the yield of OH from HNO₃ photolysis (at 193 nm) relative to the OH yield from H₂O₂ at 248 nm from the work of Schiffman and Nesbitt is nearly a factor of 2 larger the corresponding ratio measured in the present work (Table IV). There is no clear reason for this discrepancy at present. Both results do indicate that photodissociation pathways other than channel (2a) are important at 193 nm.

At 193 nm, production of atomic oxygen becomes a major channel, with $\Phi_{\text{HNO}_3}(\text{O}) = 0.81 \pm 0.13$. Previous laser photolysis studies by Kenner *et al.*⁹ provided indirect evidence for the production of a long-lived intermediate from HNO₃ photolysis at 193 nm, which could subsequently absorb a second photon to give OH ($A^2\Sigma^+$). Energy and spin conservation arguments suggested that this intermediate was HONO (a coproduct with O atoms). Studies by Curl and co-workers¹⁰ have since observed HONO from HNO₃ photolysis at 193 nm in a jet expansion using infrared laser absorption indicating the presence of channels (2b) and/or 2(e). Our study is the first to measure a quantum yield or limits for its quantum yield by directly detecting and quantifying the total O atoms produced in 193 nm photolysis of HNO₃.

However, it should be noted that production of OH and O atoms are not necessarily mutually exclusive channels. Channel (2f) is thermochemically possible at $\lambda \leq 239$ nm. This channel most likely proceeds through a two step process, and can occur by two different mechanisms. The first can proceed through an excited NO₂ intermediate, and the second through an excited HONO molecule



The above processes require that a large fraction of the ex-

cess energy be deposited in the NO₂^{*} or HONO^{*} fragment upon absorption of the photon. Although there is no direct evidence for the production of HONO^{*}, there is evidence for the production of NO₂^{*}. Fluorescence from electronically excited NO₂ (emission over the 400–900 nm range) has been observed from HNO₃ photolysis over the wavelength range of 105–220 nm.²⁶ Although the fluorescence quantum yield is rather small ($\Phi_f = 0.3\%$, \approx constant over 103–220 nm,²⁶ this does indicate that a fraction of the NO₂ produced in the photolysis is formed with a large degree of internal energy. This is similar to the case of N₂O₅ photodissociation, where NO₂ is formed hot and dissociates to NO + O.^{27,28}

The study of Kenner *et al.*⁹ hypothesized that HONO was produced from HNO₃ photolysis at 193 nm in its first excited triplet state. This triplet state has been calculated to lie approximately 2.5–2.6 eV above the ground singlet state.^{29,30} By spin conservation rules, they suggested that O(³P) would be the coproduct.⁹ We have directly measured the quantum yield for O(³P) at 193 nm [$\Phi_{\text{HNO}_3}(\text{O } ^3P) = 0.53 \pm 0.13$]. Moreover, we have detected the occurrence of channel (2c) which produces O(¹D) atoms [$\Phi_{\text{HNO}_3}(\text{O } ^1D) = 0.28 \pm 0.7$], which is most likely accompanied by ground state HONO. Preliminary measurements by Schiffman and Nesbitt³¹ show that the yield of O(¹D) is ≈ 0.3 in excellent agreement with the value reported here. Measurement of the quantum yield for HONO and NO production would be very useful in separating out the various channels.

Photolysis at 222 nm represents a transition wavelength between the two major absorption features of HNO₃. The primary quantum yield for OH radicals was measured relative to the value of $\Phi_{\text{HNO}_3}(\text{OH})$ at 248 nm obtained in our earlier experiment. At 222 nm, the observed yield of OH was $\Phi_{\text{HNO}_3}(\text{OH}) = 0.90 \pm 0.11$. This is in excellent agreement with the previously reported value of Jolly *et al.*³ [$\Phi_{\text{HNO}_3}(\text{OH}) = 0.89 \pm 0.08$], and is in reasonable agreement of unit quantum yield by Johnston *et al.*² The measured quantum yield of O atoms is $\Phi_{\text{HNO}_3}(\text{O}) = 0.20 \pm 0.03$ at 222 nm, and is not inconsistent with our measured OH yield. As described above, production of both O(³P) and OH is energetically possible at 222 nm. NO₂ fluorescence from HNO₃ photolysis has been observed out to 220 nm,²⁶ suggesting that NO₂ dissociation to form O(³P) atoms is a plausible explanation. Again O(³P) and O(¹D) were observed to appear in approximately the same ratio as was found at 193 nm, O(³P)/O_{tot} ~ 0.6 . This leads to $\Phi_{\text{HNO}_3}(\text{O } ^3P) = 0.126 \pm 0.022$, and $\Phi_{\text{HNO}_3}(\text{O } ^1D) = 0.074 \pm 0.013$ at 222 nm.

Nitric acid has been used numerous times as a photolytic precursor for OH radicals. Most of these studies have assumed that OH is produced with a quantum yield of unity. Our work shows that one must be concerned with photoproducts other than OH and NO₂ upon HNO₃ photolysis. This becomes imperative at short wavelengths such as 193 nm, which is quite often used because of the large cross section of HNO₃ at this wavelength. If unaccounted for, unwanted reactions of O(³P) and O(¹D) could adversely affect the observed chemistry. It is also necessary to account for other photoproducts when one relies on the quantum yield to de-

termine OH concentrations accurately.

In the stratosphere, nitric acid is a temporary reservoir for NO_x and HO_x species. Its photolysis regenerates NO_x and HO_x species which can catalytically destroy ozone. In the lower stratosphere, contributions to HNO₃ photolysis at $\lambda < 290$ nm is relatively small, and hence it can be assumed that OH and NO₂ are the sole photoproducts. However, at higher altitudes, the contribution of photolysis in the 190–220 nm region increases, and the occurrence of the channels noted here could be important. However, the production of OH and NO₂ is, to a zeroth approximation, the same as channels (2b) and (2c) since both NO₂ and HONO are rapidly photolyzed. Also O(¹D) is rapidly quenched to O(³P). The end result is that OH, NO, and O(³P) are produced. On the other hand, if H and NO₃ (or H + NO + O₂) are produced in HNO₃ photolysis, it is possible that HNO₃ photolysis could be a small O₃ loss process in the stratosphere. In this study we have measured an upper limit for this process which suggests a negligible contribution of HNO₃ photolysis to O₃ loss.

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