308 nm Photolysis of Nitric Acid in the Gas Phase, on Aluminum Surfaces, and on Ice Films

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Received: October 14, 2009; Revised Manuscript Received: January 16, 2010

We have studied the photolysis of nitric acid (HNO₃) in the gas phase at 253 and 295 K, on aluminum surfaces at 253 and 295 K, and on ice films at 253 K, by using 308 nm excimer laser photolysis combined with cavity ring-down spectroscopy. We monitored both the ground-state NO₂ and the electronically excited NO₂, NO₂*, produced from the HNO₃ photolysis. NO₂* + OH is a predominant photolysis pathway (if not the only photolysis of HNO₃ at 308 nm. The NO₂* quantum yields from the HNO₃ photolysis on aluminum surfaces are 0.80 ± 0.15 at 295 K and 0.92 ± 0.26 at 253 K, where errors quoted represent 2σ measurement uncertainty. The corresponding NO₂* quantum yield from the HNO₃ photolysis on ice films is 0.60 ± 0.34 at 253 K. The 308 nm absorption cross sections of HNO₃ on Al surfaces and on ice films have been directly measured. Absorption cross sections of HNO₃ on Al surface at 308 nm are (4.19 ± 0.17) × 10⁻¹⁸ and (4.23 ± 0.45) × 10⁻¹⁸ cm²/molecule at 253 and at 295 K, whereas the corresponding absorption cross section of HNO₃ on ice films is (1.21 ± 0.31) × 10⁻¹⁸ cm²/molecule at 253 K (errors quoted represent 2σ measurement uncertainty). Atmospheric implications of the results are discussed.

1. Introduction

Nitric acid (HNO₃) is a major atmospheric oxidation product of NO_x (NO_x = NO + NO₂).^{1,2} Although its gas-phase photolysis in the troposphere is slow,^{3,4} the photolysis rate for HNO₃ deposited on ground and vegetation surfaces to form HONO and NO_x has been reported⁵ to be 1-2 orders of magnitude faster than that in the gas phase. The photolysis of HNO3 adsorbed on ground surfaces has been proposed as a major daytime source of HONO in low- NO_x environments.^{5–7} To understand the difference between the nitric acid photolysis rate in the gas phase and the rate of photolysis on surfaces, the Zhu group has recently determined the UV absorption cross sections of surface-adsorbed HNO₃ in the 290-330 nm region⁸ through the use of Brewster angle cavity ring-down spectroscopy. The study⁸ showed that the surface absorption cross sections of HNO₃ are at least 2 orders of magnitude higher than the cross section values of the nitric acid vapor, in the wavelength region studied. Since the product channels and quantum yields associated with the HNO3 photolysis on the surface have not been directly measured, further investigations are necessary to characterize the photolysis quantum yields of surface-adsorbed HNO₃.

The gas-phase photolysis of nitric acid in the actinic UV region ($\lambda \ge 290$ nm) can occur through the following pathways:

$HNO_3 + hv \rightarrow OH + NO_2$	$(\lambda \le 604 \text{ nm})$	(1g)
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 \rightarrow OH + NO₂* ($\lambda \le 381 \text{ nm}$) (2g)

$$\rightarrow$$
 HONO + O(³P) ($\lambda \le 393$ nm) (3g)

where photochemical thresholds were calculated from the corresponding enthalpy changes.⁹ NO₂ and NO₂* represents the ground state and the electronically excited state of NO₂, respectively. Riffault et al.¹⁰ used laser-induced fluorescence (LIF) to determine the OH quantum yield from the photolysis of HNO3 vapor; they obtained an OH quantum yield of 1.05 ± 0.29 at 308 nm photolysis wavelength. However, OH quantum yield determination alone would not tell whether OH is a coproduct of the NO₂ channel or a coproduct of the NO2* channel. An earlier HNO3 photodissociation dynamics study at 193 nm by Jacobs et al.¹¹ found that the OH radicals formed are vibrationally and rotationally cold but translationally hot, suggesting HNO₃ photolysis occurring on a repulsive potential energy surface. On the basis of the results of this HNO₃ photodissociation dynamics study, we infer that the majority of the nitrogen dioxide molecules formed from the HNO₃ photolysis at 308 nm are vibrationally cold but electronically hot in order to account for the energy release beyond products translational energy following the 308 nm photolysis of HNO₃. Our postulate is supported by the work of MacLeod et al.¹² who monitored the NO₂* fluorescence emission (the onset of emission occurs near 400 nm and has a maximum around 558 nm) from the 248 nm photolysis of HNO₃ vapor and assumed a quantum yield of unity for the NO_2^* + OH channel from the HNO₃ photolysis and used that to calibrate the NO₂* quantum yield from the pernitric acid (HO₂NO₂) photolysis at 248 nm. Assuming that the photolysis of HNO3 adsorbed on Al surfaces or on ice films breaks the same bonds in HNO₃ as does gas-phase photolysis, we would like to determine whether the 308 nm photolysis of adsorbed HNO₃ on Al or ice surfaces proceeds through the following photolysis pathways:

$$HNO_2(ad) + hv \rightarrow OH(g/ad) + NO_2(g/ad)$$
 (1s)

 \rightarrow OH(g/ad) + NO₂*(g/ad) (2s)

The products formed from the 308 nm photolysis of adsorbed HNO_3 are expected to carry excess energy. This excess energy

10.1021/jp909867a © 2010 American Chemical Society Published on Web 02/02/2010

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may break weak bonds between the photolysis products and the surface, resulting in the release of the photolysis products, such as NO_2^* and NO_2 , into the gas phase.

The ground state and the electronically excited states of NO₂ can be monitored by their vibronic absorption and/or emission in the visible region. Since there are four electronic states of NO₂ in the visible region $({}^{2}A_{1}, {}^{2}B_{2}, {}^{2}B_{1}, \text{ and } {}^{2}A_{2})$ and each one can interact with the other three electronic states, the visible spectra of NO₂ are very complex. Detailed description about the visible spectra of NO₂ can be found in the "Spectral Atlas of Nitrogen Dioxide, 5530 to 6480 Å" by Hsu et al.¹³ and the references within. The ground-state NO₂ can be monitored by its near UV-vis absorption¹⁴⁻¹⁹ in the 255-600 nm region with peak absorption occurring at about 400 nm. Most of the oscillator strength of the visible spectrum for the ground state of NO₂ comes from the X ²A₁-²B₂ transition.¹³ The excited NO2 exhibits structured UV-vis absorption bands in the 350-650 nm region.¹⁴ In the study of Davidson et al.,¹⁴ the excited NO₂ was formed by heating the NO₂ sample to 124 °C, and the excited NO₂ absorption spectrum was attributed to that of the vibrationally excited ground-state NO₂. As the wave functions of the electronically excited NO₂ and the high vibrational levels of the ground-state NO₂ are strongly mixed, the excited NO₂ spectrum in the 350-650 nm region can be that of the electronically excited NO₂ or that of the vibrationally excited ground-state NO₂, depending upon how the excited NO₂ was generated. The electronically excited NO2 has "anomalously" long radiative lifetime possibly caused by the interelectronic level mixing with the ground state.²⁰ Although there is a strong transition moment between the vibrational levels of the electronically excited NO2 and the high vibrational levels of the ground-state NO₂, the high vibrational levels of the ground state have essentially no transition strength to the lowest vibrational levels of the ground state. The lifetimes of the electronically excited NO₂ vary²¹ in the range of 55–90 μ s as the excitation wavelength is varied in the 3980-6000 Å range.

In this paper, we report results obtained from the 308 nm excimer laser photolysis of HNO₃ in the gas phase at 295 and 253 K, on Al surfaces at 295 and 253 K, and on ice films at 253 K, using cavity ring-down spectroscopy.^{22,23} The NO₂* quantum yields from the HNO₃ photolysis on Al surfaces and on ice films have been measured. In addition, the adsorbed HNO₃ absorption cross sections on Al surfaces and on ice films at 308 nm have been directly determined. Atmospheric implications of the results are discussed.

2. Experimental Technique

An excimer laser operating at 308 nm was used to photolyze HNO₃ in the gas phase, on Al surfaces, and on ice films; the photolysis products formed from the HNO₃ photolysis were then probed by cavity ring-down spectroscopy. A stainless steel reaction cell for gas-phase study (the gas cell) has been described in detail elsewhere.²⁴⁻²⁶ It is shown in Figure 1 to enable comparison with a cell used for the surface studies. Only the essential features of the gas cell are summarized here. The gas cell has a double-walled configuration to facilitate variation of the cell temperature; it was vacuum-sealed by a pair of highreflectance cavity mirrors at both ends. The output from the photolysis laser was propagated into the reaction cell at a 15° angle to the main cell axis, through a side arm. The probe laser pulse, delayed relative to the photolysis laser pulse and used to detect NO_2* (at 552.57 nm) and NO_2 (at 352 nm), $^{\rm 14-16}$ was introduced into the cell along the main optical axis. The probe laser beam overlapped the photolysis beam at the center of the



Figure 1. Schematics of the stainless steel cells used for the gas-phase study (above) and for the surface study (below).

cavity. The inner diameter of the jacketed gas cell is 4 in., and the cell has an inner volume of 2.4 L. For this gas cell configuration, the photolysis products detected by cavity ringdown spectroscopy were those formed from the gas-phase photolysis.

The stainless steel flow cell used for studying HNO₃ photolysis on Al surfaces and on ice films (the surface-study cell) has been described in detail elsewhere.²⁷ It has the form of a hollow rectangular prism (see Figure 1). The length of the cell is 55 cm, and the cell's cross section is 2.54 cm \times 2.54 cm. A pair of high-reflectance cavity mirrors vacuum-sealed the two ends of the cell. Fused-silica windows were mounted to the front and back of the cell, for transmission of the photolysis beam. A pair of rectangular Al reflectors ($\sim 47\%$ measured reflectivity inside the cell at 308 nm) were mounted inside the cell, along its length. The photolysis beam entered the cell through the window on the front side. The photolysis beam was subsequently bounced back and forth by the Al reflectors, a number of times, before it exited the cell through a window. The probe laser beam entered the cell along the main optical axis. A fraction of the probe laser pulse was injected into the cavity through the front mirror, and the intensity decay of this fraction inside the cavity was measured by monitoring the weak transmission of light through the rear mirror, with a photomultiplier tube (PMT). The amplified PMT signal was fitted to a single-exponential decay function, from which the ring-down time constant and the total loss per optical pass were calculated.

The surface-study cell is equipped with various reagent ports, a pumping port, and pressure- and temperature-measurement ports, all located on top of the cell. A rectangular viewport, made of transparent plastic (acrylic) and installed on the top, along the main optical path, allowed us to view the ice film growth conditions and the photolysis beam. The bottom of the cell had a cooling block, which was connected to a lowtemperature bath/circulator (Neslab ULT-80; ethanol was used as the coolant). Temperature at the Al reflector surface was measured with a thermocouple intact. Helium was bubbled through a distilled water bubbler at 295 K, and water-vapor/ He mixture was admitted to the cell via four feedthroughs placed at the bottom of the cell (Figure 1). At the other end of each feedthrough was a length of stainless steel tubing, 13-14 cm long, $\frac{3}{16}$ in. o.d. diameter. On each length of tubing, a row of precision holes was drilled, with 1 cm spacing. Four lengths of stainless steel tubing were used to form two sets of internally

mounted water vapor outlets directed toward two Al surfaces. Lengths of stainless steel tubing were placed in the bottom of the cell, and the water vapor was sprayed at 45° to the normal, so as to optimize the condensation of water vapor on the Al surfaces. Ice films were formed by vapor deposition on the Al surfaces at 253 K. This cell configuration allowed us to study not only HNO₃ photolysis on ice films but also HNO₃ photolysis on Al surfaces in the absence of ice films. The typical ice film thickness was estimated about 10 μ m calculated from the mass flow rate of water vapor (measured by a Teledyne–Hastings mass flowmeter), the ice deposition time, the bulk density^{28,29} (0.63 g/cm³) of vapor-deposited ice, and the geometric area of the ice films deposited.

The inner surfaces of both gas and surface-study cells, and the stainless steel joints on the gas transport line, were coated with halocarbon wax (series 1500; Halocarbon Products Corp.) or treated with halocarbon grease (Halocarbon 25-5S grease; Halocarbon Products Corp.), to minimize decomposition of HNO3 on cell surfaces and on stainless steel joints. The vapordeposited ice is polycrystalline at 253 K.³⁰ The ice film deposited on the Al surface was uniform to the naked eye and was freshly prepared in every experiment. Following the generation of ice films, HNO₃ was introduced into the cell under slow-flow conditions. The vapor pressure of ice at 253 K is about 0.75 Torr.³¹ The total pressure in the cell for the ice film experiments was the vapor pressure of ice at 253 K, plus the added HNO₃ pressure. In the absence of ice films, the total pressure in the surface-study cell was equal to the admitted HNO₃ vapor pressure.

Once the 308 nm excimer laser radiation was introduced into the surface-study cell, the photolysis of HNO₃ in the gas phase and the photolysis of adsorbed HNO₃ on the surface occurred simultaneously. The absorption of the probe beam at 552.57 nm by electronically excited NO₂, obtained through measurement of the cavity losses with and without a photolysis pulse, was the sum of the contributions both from the photolysis of HNO₃ in the gas phase and on surface. The NO₂* absorption produced from the HNO₃ photolysis on surface was obtained by subtracting the NO₂* absorption from the gas-phase HNO₃ photolysis from the total NO2* absorption. A pulse/delay generator was used to vary the delay time between the firing of the photolysis laser and the firing of the probe laser. Quantum yield measurements in the gas phase and on Al surfaces were made at a laser repetition rate of 0.1 Hz, whereas measurements on ice film surfaces were made at 1 Hz. The spectrum scan was performed at a laser repetition rate of 1 Hz.

High-purity HNO₃ was prepared by vacuum distillation of a 3:2 mixture of sulfuric acid (98%; Mallinckrodt Baker) and nitric acid (70%; Mallinckrodt Baker) at 273 K into a trap cooled at ethanol/dry ice temperature (195 K).³² Five successive distillations were conducted, to purify the sample. To further reduce NO₂ impurity before each experiment, we purged NO₂ from the liquid HNO₃ bubbler, by flowing N₂ carrier gas through the bubbler for about 30 min;³³ we then pumped the liquid HNO₃ bubbler for 10 min in the absence of N₂ flow. The NO₂ impurity in the purified nitric acid vapor was determined by monitoring the NO₂ absorption¹⁸ in the 448–452 nm region, using cavity ring-down spectroscopy. The NO₂ impurity was determined to be less than 0.051%.

3. Results and Discussion

3.1. General Features. We investigated the 308 nm photolysis of HNO_3 in the gas phase at 295 and 253 K, on Al surfaces at 295 and 253 K, and on ice films at 253 K; we then



Figure 2. Cavity ring-down absorption spectrum of the product in the 550-560 nm region, after the gas-phase photolysis of 1.50 Torr of HNO₃ at 308 nm and at 295 K. The spectrum was recorded at a wavelength interval of 0.05 nm.

probed for possible HNO₃ photolysis products using cavity ringdown spectroscopy under each condition. The ground-state NO₂ was monitored¹⁴⁻¹⁶ at 352 nm. The electronically excited NO₂ was probed¹⁴ at 552.57 nm. As stated in the Experimental Technique section, there is a very small amount of (unavoidable) NO₂ impurity ($\leq 0.05\%$) in the HNO₃ sample, but we did not observe transient ground-state NO2 formation immediately after the HNO₃ photolysis. Upon the basis of the magnitude of the NO₂* absorption generated from the HNO₃ photolysis, the lack of observation of the transient ground-state NO₂ signal from the HNO₃ photolysis, and the OH quantum yield of 1 from the HNO₃ photolysis at 308 nm,¹⁰ we conclude that $NO_2^* + OH$ is the predominant photolysis pathway (if not the only photolysis pathway) from the HNO₃ photolysis in the gas phase at 308 nm. Results from the HNO₃ photolysis in the gas phase, on Al surfaces, and on ice films are described in individual sections below.

3.2. Photolysis of HNO₃ in the Gas Phase at 295 and 253 K. Figure 2 is a cavity ring-down absorption spectrum of the product in the 550–560 nm region after the 308 nm gas-phase photolysis of HNO₃ at 295 K. This is a spectral region with high NO₂* absorption¹⁴ and low absorption from the ground-state NO₂ (the previous literature NO₂* spectroscopic study¹⁴ was done at 1.5 nm resolution). The observation of transient product from the HNO₃ photolysis at 308 nm, in a spectral region that NO₂* exhibits strong absorption, suggests that NO₂* is a 308 nm photolysis product of HNO₃. A similar product absorption spectrum was also obtained following the gas-phase HNO₃ photolysis at 253 K. The cavity ring-down spectrometer was tuned to the NO₂* absorption maximum at 552.57 nm, and the total absorption resulting from the gas-phase HNO₃ photolysis was measured as a function of time.

Shown in Figure 3 is a transient round-trip absorption profile measured at 552.57 nm following the 308 nm photolysis of 0.75 Torr of HNO₃ at 295 K. Figure 3 shows that the probe laser absorption at 552.57 nm decreases rapidly with delay time, between the firing of a photolysis and a probe laser, at less than 60 μ s, and then the probe laser absorption is nearly independent of time. Since both NO₂* and NO₂ absorb probe laser beam at 552.57 nm with respective absorption cross sections of 9.4 × 10⁻¹⁹ and 8.9 × 10⁻²⁰ cm²/molecule at 295 K (cross section measurement for NO₂* at 552.57 nm is described later in this section), the following kinetic scheme was used to fit the



Figure 3. Time profile of the total round-trip absorption measured at 552.57 nm following the 308 nm gas-phase photolysis of 0.75 Torr of HNO₃ at 295 K. Symbols (\bullet) denote experimental data. Curves shown are the kinetic simulations using the ACUCHEM software. See text for details.

experimental temporal round-trip absorption profile at 552.57 nm:

$$NO_2^* = NO_2 \tag{4}$$

$$NO_2^* + HNO_3 = NO_2 \cdot HNO_3$$
(5)

$$absorption(t) = 2l\sigma_{NO2^*}[NO_2^*] + 2l\sigma_{NO2}[NO_2] + 2l\sigma_{NO2\cdot HNO3}[NO_2 \cdot HNO_3]$$
(6)

where NO₂ • HNO₃ represents the adduct formed from the NO₂* + HNO₃ reaction; l is the length of the photolysis/probe laser overlap region (more detailed description of the photolysis/probe laser overlap region is given later in this section); σ_{NO2^*} , σ_{NO2^*} , $\sigma_{\rm NO2 \cdot HNO3}$ denote the respective absorption cross sections of NO₂*, NO₂, and NO₂•HNO₃ at 552.57 nm; [NO₂*], [NO₂], and $[NO_2 \cdot HNO_3]$ represent the respective concentrations of NO_2^* , NO₂, and NO₂•HNO₃. The formation of an NO₂•HNO₃ adduct has been invoked from the reaction of $NO_2^* + HNO_3$ rather than the direct quenching of NO_2^* by HNO_3 ($NO_2^* + HNO_3$) = NO₂ + HNO₃) in order to explain the absorption value at 552.57 nm as a function of time (the derivation of the cross section value for the NO₂·HNO₃ adduct will follow; it is $1.8 \times$ 10^{-18} cm²/molecule at 552.57 nm, which is 20-fold the cross section value for the ground-state NO₂ (8.9 \times 10⁻²⁰ cm²/ molecule) at the same wavelength). Also, the NO2 • HNO3 adduct was previously observed in the IR region.34 Transient absorption profiles at 552.57 nm from the photolysis of 0.5, 0.75, and 1.5 Torr of HNO₃ were compared with the values calculated by

the ACUCHEM simulation program.³⁵ The radiative decay rate constant of NO₂* (k_{NO2} *), the NO₂* + HNO₃ reaction rate constant ($k_{\text{NO2}*+\text{HNO3}}$), $\sigma_{\text{NO2}\cdot\text{HNO3}}$, and the initial NO₂* concentration ($[NO_2^*]_0$) were used as input parameters. Initial values of $k_{\rm NO2^*}$, $k_{\rm NO2^*+HNO3}$, and $\sigma_{\rm NO2\cdot HNO3}$ were given to the program, and the simulated absorption profiles were compared with the experimental results. Numerical values of k_{NO2^*} , k_{NO2^*+HNO3} , and $\sigma_{\rm NO2 \cdot HNO3}$ were subsequently adjusted so as to optimize the fit. The following extracted values are obtained: $k_{\text{NO2}*}$ of 1.8×10^4 s⁻¹ at 295 K, $k_{\text{NO2}*+\text{HNO3}}$ of $1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K, and $\sigma_{\rm NO2 \cdot HNO3}$ of 1.8 \times 10⁻¹⁸ cm²/molecule at 552.57 nm. The extracted value of k_{NO2*} corresponds to a radiative lifetime of 56 μ s, which agrees well with the reported lifetimes²¹ for electronically excited NO₂ of 55–90 μ s. Temporal absorption profiles at 552.57 nm from the photolysis of HNO₃ at three pressures are well-fitted by the extracted k_{NO2^*} , k_{NO2^*+HNO3} , and $\sigma_{\text{NO2}-\text{HNO3}}$ values at 295 K. The quality of the fit is shown in Figure 3 for temporal absorption profile generated from the photolysis of 0.75 Torr of HNO₃ at 295 K.

The NO₂* quantum yields from the nitric acid photolysis at 308 nm, at 295 and 253 K, were determined from the ratio of the NO₂* concentration produced in the photolysis/probe laser overlap region to the absorbed photon density in that region. The overlap region in the cell for the gas-phase study can be thought of as a rectangular prism: the prism's center coincides with that of the cell, its width and height are defined by the dimensions of the photolysis beam, and its length is defined by the length over the overlap region. The length over the overlap region was calculated using (beam width)(tan 15°)⁻¹, where 15° is the crossing angle between the pump and probe laser beams. The length of the overlap region is defined by (beam width)(sin 15°)⁻¹. A 12 mm wide × 6 mm tall rectangular aperture was placed in the photolysis beam path before the beam's entrance to the cell.

The photolysis beam is absorbed by HNO₃ over the entire level arm through which it travels. The absorbed photolysis photon density in the overlap region can be derived from (i) the difference between the transmitted photolysis beam energies entering (E_{in}) and leaving (E_{out}) that region, (ii) the individual photon energy (hc/λ) at the photolysis wavelength (λ), and (iii) the volume (V) of the overlap region, via the following equations:

absorbed photon density =
$$(E_{\rm in} - E_{\rm out})/((hc/\lambda)V)$$
 (7)

V =

(beam width)(beam height)(length of the rectangular prism)

= (beam width)²(beam height)(tan15°)⁻¹

The energy of the photolysis beam entering or leaving the overlap region can be calculated from the energy of the incident photolysis beam entering the cell (E_0), the nitric acid absorption cross section (σ) at 308 nm and the density (n) of nitric acid in the cell, and the absorbing path length, through application of Beer's law:

$$E_{\rm in} = E_0 \exp(-\sigma n l_1) \tag{8}$$

$$E_{\rm out} = E_0 \exp(-\sigma n l_2) \tag{9}$$

where l_1 is the distance between the photolysis beam entrance and the beginning of the overlap region and l_2 is the distance between the photolysis beam entrance and the end of the overlap region. The incident photolysis beam energy was measured by a calibrated joulemeter placed in front of the cell. This energy inside the cell was corrected for transmission loss at the front cell window and for reflection of the photolysis beam from the rear cell window. The 308 nm absorption cross sections of the nitric acid vapor at 295 K were measured by cavity ring-down spectroscopy. By measuring the round-trip cavity loss as a function of HNO₃ pressure in the cavity and plotting the round-trip cavity loss against HNO₃ pressure in the cell, we obtained a gas-phase HNO3 absorption cross section value of $(1.24 \pm 0.19) \times 10^{-21}$ cm²/molecule at 308 nm and at 295 K, where error quoted represents 1σ measurement uncertainty. Our HNO3 vapor absorption cross section at 308 nm and at 295 K agrees within 15% with the values of 1.06×10^{-21} and 1.08×10^{-21} cm²/molecule that were previously obtained by Rattigan et al.³² and by Burkholder et al.³⁶ The 308 nm absorption cross section of HNO₃ at 253 K was obtained by monitoring the transmitted photolysis fluence as a function of HNO₃ pressure in the cell and by application of Beer's law to the experimental data (the transmitted photolysis fluence was measured using a photodiode. The transmitted photolysis fluence measured by the photodiode was found to vary linearly with the transmitted photolysis fluence measured by the joulemeter in the calibration experiments over a range of photolysis fluences). The corresponding cross section value is $(8.50 \pm 0.24) \times 10^{-22}$ cm²/molecule at 253 K, where the error quoted represents 1σ standard deviation from three repeated cross section measurements. Our 308 nm HNO₃ absorption cross section value at 253 K agrees within 10% with the recommended HNO₃ cross section of 9.0×10^{-22} cm²/molecule at 253 K.37

The NO₂* concentrations after 308 nm photolysis of HNO₃ at 295 K and at 253 K were obtained from measurements of the round-trip NO₂* absorptions at 552.57 nm at a photolysis laser-probe laser delay of 15 μ s. The NO₂* concentration resulting from the HNO₃ photolysis at a given HNO₃ pressure can be obtained from the corresponding round-trip NO2* absorption, the length of the photolysis/probe laser overlap region (l), and the absorption cross section of NO₂*, σ_{NO2*} , via $[NO_2^*]$ = absorption/($2\sigma_{NO2^*}l$). A literature absorption cross section value of $\sim 5.3 \times 10^{-19}$ cm²/molecule was reported for excited NO2 around 552 nm.14 That study14 assumed the excited NO₂ to come from vibrationally excited ground-state NO₂ and also assumed equilibrium between different vibrational modes of NO₂. If we use that reported literature excited NO₂ absorption cross section to convert NO2* absorption into absolute NO2* concentration, and if we use HNO3 absorbed photon density as well as NO2* absorption determined in our study, we would obtain an NO₂* quantum yield of $\sim 1.7 \pm 0.1$ from the HNO₃ photolysis at 308 nm and 295 K, independent of HNO3 pressure in the 0.5-3.0 Torr pressure range. With the use of the literature excited NO₂ cross section data, we would obtain an NO₂* quantum yield of $\sim 1.8 \pm 0.2$ from the HNO₃ photolysis at 308 nm and at 253 K. As stated in the Introduction, the NO2* formed from the 308 nm photolysis of HNO₃ is that of the electronically excited NO₂. Thus, we cannot rely on literature excited NO₂ cross section data,14 based upon equilibration of different vibrational modes of NO₂, to calculate the electronically excited NO₂ concentration, generated from the HNO₃ photolysis. Since we did not observe the transient ground-state NO₂ formation from the HNO₃ photolysis at 308 nm, and a previous LIF study¹⁰ reported an OH quantum yield of 1 from the gas-phase HNO₃ photolysis at 308 nm, we conclude that $OH + NO_2^*$ is a predominant (if not the only) photolysis pathway from the HNO3 photolysis in the gas phase at 308 nm. A plausible explanation for the predominance of the $OH + NO_2^*$ channel from the HNO₃ photolysis at 308 nm is that this pathway has lower energy gap between the energy carried by the photolysis products and the excess energy released following the photodissociation of HO–NO₂ bond in nitric acid. Assuming an NO₂* quantum yield of 1 from the gas-phase photolysis of HNO₃ at 308 nm, we obtain an NO₂* absorption cross section of (9.4 ± 1.0) × 10⁻¹⁹ cm²/molecule at 552.57 nm and at 295 K. Assuming the absorption cross section of NO₂* at 253 K to be the same as that at 295 K, and using the HNO₃ absorbed photon density and NO₂* absorption values determined in the current study, we obtain an NO₂* quantum yield of 0.99 ± 0.17 from the 308 nm HNO₃ photolysis in the gas phase at 253 K, where error quoted represents 1 σ measurement uncertainty.

The near-invariance with temperature of the NO₂* quantum yield from the 308 nm photolysis of gas-phase HNO₃ can be rationalized on the basis that the 308 nm photon energy is much higher than the HO–NO₂ bond dissociation energy in HNO₃. Thus, temperature is not expected to affect the HO + NO₂* quantum yield from the nitric acid photolysis.

3.3. Photolysis of HNO₃ on Aluminum Surfaces and on Ice Films. Following the introduction of HNO₃ into the surfacestudy cell, gaseous HNO₃ and adsorbed HNO₃ on Al or ice film surfaces were photolyzed by 308 nm excimer laser radiation at 295 and 253 K. By subtracting NO₂* absorption resulting from the HNO₃ photolysis in the gas phase at 295 and 253 K, we obtained values for the NO₂* absorption resulting from the HNO₃ photolysis on Al surfaces (295 and 253 K) or on ice films (253 K). The 308 nm absorption cross sections of HNO₃ on Al surfaces and on ice films have been directly measured in this study. Results obtained from HNO₃ surface absorption cross section and surface photolysis quantum yield measurements are described below.

3.3.a. Absorption Cross Sections for HNO₃ on Al Surfaces and on Ice Films. Nitric acid was introduced into the surfacestudy cell, to be photolyzed by the 308 nm photolysis beam. Once the photolysis beam entered the surface study cell (Figure 1) through a fused-silica window at 45° incident angle, it was bounced back and forth nine times by the Al reflector or by ice film surfaces, before it exited the cell through another fusedsilica window. The photolysis beam inside the surface-study cell experienced transmission loss on Al or ice film surfaces, loss associated with HNO3 absorption in the gas phase, and loss due to absorption by adsorbed HNO₃ on Al or ice film surfaces. A calibrated photodiode was placed at the photolysis beam exit, and the transmitted 308 nm photolysis beam energy ($E_{s,out}$) was determined as a function of HNO_3 pressure in the cell, $P(HNO_3)$. Figure 4 is a plot of $ln(E_{s,out})$ versus $P(HNO_3)$, for HNO_3 pressures in the range of 0.0023-0.105 Torr at 253 K and with Al surfaces. Figure 4 shows that the $ln(E_{s,out})$ versus $P(HNO_3)$ plot is linear for the HNO₃ pressure up to about 20 mTorr, and then the slope of the plot changes at higher HNO₃ pressures. For our current surface-study cell geometry (Figure 1), the photolysis beam was absorbed by HNO3 adsorbed on Al or ice film surfaces at nine locations inside the cell and was absorbed by gas-phase HNO₃ in 10 regions inside the cell. The relationship between the transmitted photolysis beam energy, measured immediately after it exited the cell, and the HNO₃ pressure inside the cell can be described by the following equation:

$$E_{\rm s,out} = (E_{\rm s,in})(T_{\rm w}^{2})(e^{-\alpha(g)/(g)P(\rm HNO_{3})})^{10}(e^{-\sigma(s)n(s)})^{9}R^{9}$$
(10)

where T_w represents the transmission coefficient of the fusedsilica window, $E_{s,in}$ denotes the photolysis beam energy measured prior to the beam's entry into the cell, *R* represents the



Figure 4. Plot of the logarithm of transmitted photolysis beam energy $(E_{s,out})$ vs the HNO₃ pressure over the Al surfaces in the surface-study cell, at 253 K.

reflectivity of Al or ice film surfaces toward the photolysis beam, $e^{-\alpha(g)/(g)P(HNO3)}$ denotes the percentage of transmitted photolysis light following its absorption by HNO₃ vapor at each of the 10 regions inside the cell ($\alpha(g)$ is gas-phase absorption coefficient of HNO₃ at 308 nm, l(g) is path length traveled at each of the 10 regions), $e^{-\sigma(g)n(g)}$ represents the percentage of transmitted photolysis beam following its absorption by adsorbed HNO₃ on Al or on ice film surface at each of the nine cell surfaces struck by the photolysis beam ($\sigma(g)$ for HNO₃ represents "apparent surface absorption cross section" defined by eq 10 and obtained with an incident angle of 45° in the current experiments, n(g) represents the HNO₃ surface density). By taking the natural logarithm of eq 10, we obtain the following equation:

$$\ln(E_{s,out}) = \ln(E_{s,in}) + 2 \ln T_w - 10\alpha(g)l(g)P(HNO_3) - 9\sigma(s)n(s) + 9 \ln R$$
$$= C - 10\alpha(g)l(g)P(HNO_3) - 9\sigma(s)n(s)$$
(11)

where C is a constant, which can be determined from the measurement of the transmitted photolysis energy in the absence of HNO_3 in the surface-study cell. As seen from eq 11, a plot of $ln(E_{s,out})$ versus $P(HNO_3)$ would be linear at all HNO_3 pressures, if the photolysis beam experienced only gas-phase HNO3 absorption. The sudden change in the slope of the plot of $\ln(E_{s,out})$ versus $P(HNO_3)$ at an HNO₃ pressure of about 0.020 Torr (Figure 4) suggests a change in the nature of adsorption of HNO₃ on Al surfaces, from monolayer to multilayer. This conjecture is supported by results from the previous study⁸ of the Zhu group for the HNO3 adsorption on fused-silica surfaces, in which saturation of monolayer adsorption sites of HNO3 on fused-silica surfaces was observed at an HNO₃ pressure of about 0.015 Torr in the cell. If we substitute $E_{s,out}$ and $\alpha(g)l(g)P(HNO_3)$ values into eq 11 with $E_{s,out}$ and $P(HNO_3)$ values corresponding to the change of slope in Figure 4, and if we also use the Cvalue determined from this study, we obtain a value for $\sigma(s)n(s)$ that corresponds to the monolayer coverage of HNO₃ on Al surfaces. The monolayer HNO₃ surface concentration on Al surfaces is estimated to be 1.1×10^{14} molecules/cm², using a van der Waals radius of 5.5 Å for HNO₃.³⁸ Thus, the "apparent absorption cross section" for HNO3 on Al surface at 308 nm and 253 K is $(4.19 \pm 0.17) \times 10^{-18}$ cm²/molecule, where error quoted (2σ) represents measurement uncertainty. Similarly, we obtained a 308 nm "apparent absorption cross section" of HNO₃ on ice films of $(1.21 \pm 0.31) \times 10^{-18}$ cm²/molecule at 253 K. The "apparent absorption cross section" of HNO3 on Al surfaces at 295 K is $(4.23 \pm 0.45) \times 10^{-18}$ cm²/molecule, where error quoted (2σ) represents measurement uncertainty. Previously, we reported⁸ a 308 nm absorption cross section of HNO₃ on fusedsilica surfaces of 1.22×10^{-18} cm²/molecule. The absorption cross section of HNO3 on Al surfaces at 308 nm and 295 K agrees within a factor of 3.5 with the 308 nm absorption cross section of HNO₃ on fused-silica surfaces at 295 K. The 308 nm surface cross section values of HNO3 on Al, ice, and fusedsilica surfaces were obtained using a calculated HNO3 monolayer coverage of 1.1×10^{14} molecules/cm². Our results can be scaled accordingly if the measured saturation HNO₃ surface coverage on Al, on ice, or on fused-silica surface becomes available in the future. The 308 nm absorption cross sections of HNO₃ on Al and ice surfaces are about 3 orders of magnitude larger than the 308 nm HNO₃ gas-phase cross section value of $\sim 1.2 \times 10^{-21}$ cm²/molecule. When HNO₃ adsorbs on Al surfaces, an imaging dipole near the gas-metal interface is produced due to the polarizability of the adsorbed HNO₃, which enhances the observed dipole transition probability. This results in a higher cross section value for HNO3 adsorbed on Al surfaces than that in the gas phase. It is very likely that the HNO₃ molecules are much more aligned and with preferred orientation on ice surfaces as a result of the interaction between the adsorbed HNO_3 molecules and the $H_2O(s)$ molecules on ice to cause the much enhanced absorption cross sections of HNO₃ on ice surfaces compared to cross section value in the gas phase. The adsorbed HNO3 molecules on surfaces are not isolated HNO3 molecules like those in the gas-phase at low pressures. The absorption cross section of HNO₃ adsorbed on surface is in fact the absorption cross section of HNO₃ under the influence of the field strength imposed by surfaces. Since the possible interference of the incident 308 nm beam and the 308 nm beam reflected off an aluminum or an ice film surface is not expected to be significant for a 45° incident angle, and since such interference can only be observed³⁹ at the contact point the incident and the reflected beam overlapped, we did not observe such an interference pattern with our current experimental configuration in which we monitored the reflected beam outside of the overlap region.

3.3.b. Time-Resolved Study of the Photolysis of HNO₃ on Al Surfaces at 295 and 253 K and on Ice Films at 253 K. Both the photolysis of gas-phase HNO₃ and the photolysis of HNO₃ adsorbed on Al surfaces or on ice films occurred when HNO₃ was photolyzed in the surface-study cell. NO₂* formed from the HNO₃ photolysis on a surface can have excess energy, if the absorbed 308 nm photon energy exceeds the HO-NO₂ bond energy in HNO₃ (the calculated photochemical threshold for the formation of NO₂* + OH is 381 nm); the result is desorption of NO₂* from the surface. When the surface photolysis-generated NO2* molecules reached the center of the cell, they were detected by cavity ring-down spectroscopy, along with NO₂* molecules generated by gas-phase HNO₃ photolysis. We varied the delay time between the firings of the photolysis laser and the probe laser and obtained the overall temporal absorption profile at 552.57 nm resulting from the HNO₃ photolysis in the surface-study cell. Shown in Figure 5, for



Figure 5. Overall round-trip absorption profile (●) measured at 552.57 nm as a function of time, after the photolysis of 0.5 Torr of HNO3 in the surface-study cell at 253 K. The gas-phase absorption contribution (dotted line) was constructed from the following parameters: the incident photolysis fluence and the number of beam bounces inside the cell; the reflectivity of Al surfaces; the HNO3 pressure in the cell and the 308 nm absorption cross section of HNO₃ in the gas phase; the NO₂* quantum yield from HNO₃ photolysis in the gas phase; the radiative decay rate constant of NO_2^* and the NO_2^*/HNO_3 reaction rate constant. The Al surface temporal absorption profile (O) was obtained by subtraction of the gas-phase absorption profile (dotted line) from the observed overall round-trip absorption profile (\bullet) in the cell with the Al surface. The inset is a product absorption spectrum in the 550-560nm region measured after the 308 nm photolysis of 0.5 Torr of HNO3 in the surface photolysis cell with Al surfaces at 253 K and at a photolysis/probe laser delay of 30 μ s.

example, is an overall transient absorption profile from the photolysis of 0.5 Torr of HNO₃ in the gas phase and on Al surfaces, at 253 K (we could not reliably measure the probe laser absorption at 552.57 nm at photolysis/probe laser delay of shorter than 15 μ s because the PMT sometimes collected reflections of the photolysis beam from the surfaces inside the cell). The overall temporal profile was extrapolated to t = 0, from which the contribution to absorption from NO2* generated from the HNO₃ photolysis in the gas phase was obtained. The temporal absorption profile generated from the gas-phase HNO₃ photolysis decayed as a result of the radiative decay of NO₂* and the NO_2^* + HNO₃ reaction initially, followed by nearly constant absorption at longer time as a result of the formation of the products such as NO2 and NO2·HNO3. After subtracting the gas-phase temporal absorption profile from the overall temporal absorption profile, we obtained the temporal absorption profile that is due to the HNO₃ photolysis on the Al surface (Figure 5). The surface photolysis temporal absorption profile has a major absorption peak at about 30 μ s, suggesting that the surface photolysis-generated NO2* molecules reached the center of the cell at about 30 µs and were detected by cavity ringdown spectroscopy. Shown in the inset of Figure 5 is a product absorption spectrum in the 550-560 nm region measured after the 308 nm photolysis of 0.5 Torr of HNO₃ in the surface photolysis cell with Al surfaces at 253 K and at a photolysis/ probe laser delay of 30 μ s. The major peak positions of the product absorption spectrum from the HNO₃ photolysis on surfaces agree with those of NO2* formed from the HNO3 photolysis in the gas phase (as shown in Figure 2), suggesting that the 308 nm photolysis of adsorbed HNO3 leads directly to the formation of NO_2^* . The distance between the center of the cell and the surface of the cell is about 1.2 cm. Since an earlier HNO₃ photodissociation dynamics study¹¹ indicated that the HNO₃ photolysis occurs on a repulsive potential energy surface, and since the 308 nm photon energy is much higher than the estimated photochemical threshold (381 nm) for the formation of $OH + NO_2^*$ from the HNO₃ photolysis, it is not surprising that NO₂* formed from the HNO₃ photolysis can be translationally very hot. Assuming all the excess energy after the 308 nm photolysis of HNO3 is released as translational energy of the NO₂* and the OH products, assuming energy and momentum conservation following the photolysis process, and using a photochemical threshold of 381 nm for the formation of OH + NO2* from the HNO3 photolysis, we estimated the mean velocity of NO₂* to be about 935 m/s (or a kinetic energy of 20 kJ·mol⁻¹) which is substantially faster than the thermal velocity of 341 m/s at 253 K. This estimation was made under the collision-free condition. The NO2* molecules generated from the HNO₃ photolysis on the surface experienced collisions with neighboring molecules. The realistic velocity is likely close to the thermal velocity, and this results in the temporal absorption profile to peak at about 30 μ s. The detection of NO₂* is possible because the electronically excited NO₂ has "anomalously" long radiative lifetime (\sim 56 μ s) and because the NO₂*/HNO₃ reaction lifetime at 0.5 Torr of HNO₃ pressure is about 0.56 ms. In addition to the temporal absorption maximum at about 30 μ s, the surface temporal absorption profile, shown in Figure 5, exhibits a minor absorption maximum at about 80 μ s, tentatively attributable to absorption by the vibrationally excited groundstate NO₂ molecules formed from quenching of NO₂* (generated from the 308 nm photolysis of HNO₃ on Al surface) by the surface lattice of Al. The Debey temperature for Al surface⁴⁰ is about 428 K, corresponding to a vibrational frequency of about 302 cm^{-1} .

The average NO₂* quantum yield from the photolysis of adsorbed HNO3 on Al surfaces at 295 and 253 K or on ice films at 253 K at 308 nm for a given HNO₃ pressure can be determined from the ratio of the number of NO2* molecules produced from the HNO₃ photolysis on surfaces to the number of photolysis photons absorbed by adsorbed HNO₃ on surfaces. The total amount of the photolysis beam energy absorbed by HNO₃ adsorbed on surfaces at a given HNO₃ pressure was determined from the difference between (1) the measured energy of the photolysis beam exiting the cell following beam absorption by HNO₃ both in the gas phase and on surfaces and (2) the calculated energy of the photolysis beam exiting the cell with only gas-phase HNO₃ absorption. The energy of the photolysis beam exiting the cell with only gas-phase HNO3 absorption was calculated from the following parameters: the incident photolysis fluence, the number of beam bounces inside the cell, the reflectivity of Al or ice surfaces, the HNO₃ pressure in the cell, and the 308 nm absorption cross section of HNO₃ in the gas phase. The NO₂* absorption resulting from the photolysis of adsorbed HNO₃, at a given HNO₃ pressure, was measured at a photolysis laser-probe laser delay of about 30 μ s, and the contribution of NO₂* absorption from the HNO₃ photolysis in the gas phase was then subtracted from the total NO2* absorption. From the NO₂* absorption resulting from the HNO₃ surface photolysis at a given HNO₃ pressure, the absorption cross section of NO₂* at the probe laser wavelength, the size

of the photolysis beam entering and leaving the cell, and the cell geometry, we can compute the total number of NO_2^* molecules generated from the photolysis of adsorbed HNO₃ at a given HNO₃ pressure in the cell.

The NO₂* quantum yields from the HNO₃ photolysis on Al surfaces and on ice films were determined as a function of HNO₃ pressure and were found to be independent of HNO₃ pressure in the 0.1-0.5 Torr range studied, to within experimental measurement uncertainty. The average NO₂* quantum yields from the HNO₃ photolysis on Al surfaces at 308 nm are 0.92 \pm 0.26 and 0.80 \pm 0.15 at 253 and 295 K, respectively, where errors quoted (2σ) represent measurement precision. The average NO₂* quantum yield from the photolysis of HNO₃ on ice films at 308 nm and 253 K is 0.60 ± 0.34 , where the error quoted (2σ) represents experimental scatter. The lower NO₂* quantum yield from the 308 nm HNO₃ photolysis on ice films is probably due to some degree of solvation of NO_2^* , generated from the HNO₃ photolysis on ice, by ice. However, we did not observe the formation of HONO in the gas phase on the time scale of our measurements.

In this paper, we report determination of the 308 nm photolysis of HNO₃ in the gas phase at 253 and 295 K, on Al surfaces at 253 and 295 K, and on ice films at 253K, acquired through excimer laser photolysis combined with cavity ringdown spectroscopy. We have shown that NO_2^* is a predominant photolysis product (if not the only photolysis product) from the 308 nm photolysis of HNO₃ in the gas phase at 295 K. We obtained NO₂* absorption cross sections, at 552.57 nm, of (9.39 \pm 0.97) \times 10^{-19} cm²/molecule at 295 K and (9.23 \pm 0.69) \times 10^{-19} cm²/molecule at 253 K. We also obtained $k_{\rm NO2^*}$ of 1.8 × 10^4 s^{-1} at 295 K and $k_{\text{NO2}^*+\text{HNO3}}$ of $1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$ s⁻¹ at 295 K. We directly measured the 308 nm "apparent absorption cross sections" of HNO3 on Al surfaces at 295 and 253 K and on ice films at 253 K. We also determined the 308 nm photolysis quantum yields of HNO3 on Al surfaces at 295 and 253 K and on ice films at 253 K. The large near-UV absorption cross sections of HNO3 on surfaces determined in our previous study⁸ and in this work, and the large NO₂* quantum yield from the 308 nm photolysis of adsorbed HNO₃ determined here, provide clear evidence that adsorbed HNO₃ is not a permanent sink for NO_x, as previously assumed.

Acknowledgment. We are grateful for the support provided by the National Science Foundation under Grant ATM0653761. We also thank Dr. Adrian Gilbert from the Halocarbon Corporation for providing us with halocarbon 1.8 oil.

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JP909867A