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Article

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Photolysis of Nitric Acid at 308 nm in the Absence and Presence of Water Vapor

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Abstract

We have re-examined the NO_x channels from the 308 nm gas phase photolysis of nitric acid (HNO_3), by using excimer laser photolysis combined with cavity ring-down spectroscopy. The photolysis products were monitored in the 552-560 nm and 640-648 nm regions. Direct comparison of the photolysis product spectrum in the 640-648 nm region with literature vibronic band origins and line intensities in electronically-excited NO_2 (NO_2*) suggests NO_2* is not formed from the HNO_3 photolysis at 308 nm. A comparison of the photolysis product spectrum in the 552-560 nm region with standard NO_2 spectrum indicates that ground state NO_2 is a photolysis product. We have determined the NO_2 quantum yield from the 308 nm HNO_3 photolysis. We also investigated the HNO_3 photolysis in the presence of water vapor. For equilibrated HNO_3/H_2O mixtures, we did not observe significant variation of product absorption around 552 nm with delay times, between the firing of the photolysis and the probe lasers. Transient product absorption measurements at 342.0 nm and 343.5 nm (respective wavelengths where peak and valley of HONO absorptions are located) are consistent with ground state NO_2 being the predominant NO_x product from the 308 nm photolysis of HNO_3/H_2O mixture. Atmospheric implication has been discussed.

1. Introduction

Field studies[1,2] have shown that atmospheric daytime HONO levels greatly exceed those calculated based upon photochemical stationary state involving OH, NO, and HONO. Various photochemical HONO formation mechanisms have been proposed to explain such a discrepancy. One proposed HONO source is the sunlight photolysis of nitric acid (HNO_3) adsorbed on ground surfaces.[3-5] Observation of HONO formation after exposing glass manifold surfaces coated with HNO_3 and H_2O with sunlight[5] appears to support such a hypothesis. Reaction of H_2O with NO_2*, generated by sunlight photolysis of adsorbed HNO_3, has been postulated[3] to be the cause of HONO formation ($NO_2^* + H_2O = HONO + OH$). Field experiments only monitor the end-products; a complex mixture of reactants in addition to HNO_3 and water vapor, and complex matrices of surface could play the role of photosensitizers in HONO formation. To experimentally verify whether HONO can be formed from the proposed photolysis of HNO_3 and H_2O only system by sunlight, as well as whether NO_2* is a HNO_3 photolysis product, we have investigated the 308 nm gas phase photolysis of HNO_3 in the absence and presence of water vapor. Studying gas phase photolysis of HNO_3 and HNO_3/H_2O mixture is necessary in order to determine whether HONO formation is energetically feasible following sunlight photolysis of HNO_3 in the presence of water vapor.

Gas phase photolysis of nitric acid in the actinic UV region ($\lambda \geq 290$ nm) can occur through the following pathways:

$$HNO_3 + h\nu \rightarrow OH + NO_2 \qquad (\lambda \leq 604\text{ nm}) \qquad (1)$$

$$\rightarrow OH + NO_2^* \qquad (\lambda \leq 381\text{ nm}) \qquad (2)$$

$$\rightarrow HONO + O(^3P) \qquad (\lambda \leq 393\text{ nm}) \qquad (3)$$

where photochemical thresholds were calculated from the corresponding enthalpy changes[6]. While the gas phase photolysis of HNO_3 in the 190-250 nm region has been studied extensively,[7-26] only a few studies[27-29] were conducted at around 300 nm. These few photolysis studies mostly monitored the OH product. The OH quantum yield from the photolysis of HNO_3 vapor at 308 nm was determined[28] using laser-induced fluorescence technique (LIF). An OH quantum yield of 1.05±0.29 was obtained. August and coworkers[27] used Doppler-resolved LIF to probe the scalar and vector properties of the OH(X) fragments generated from HNO_3 photodissociation at 280 nm. Photodissociation at 280 nm was postulated to occur through a vibronically-mediated transition to an electronic state of A" character. 70% of the excess energy was found in the internal modes of NO_2, and 30% was in the OH and NO_2 translational mode. Thermodynamically, the excess energy following 308 nm photolysis of HNO_3 (Eqn. 1) is estimated[29] about 43.8 kcal/mol. Assuming the excess energy is partitioned in a similar fashion for both 308 nm and 280 nm HNO_3 photolysis, the internal energy of the NO_2 chromophore from 308 nm photolysis can be up to 30.7 kcal/mol. In the visible spectral region, the lowest energy vibronic transition for NO_2 is between the electronically-excited 1^2B_2 state and the ground X^2A_1 state. The energy level between these two states is strongly dependent on the geometry of NO_2, in particular the bending angle. The calculated excess internal energy (30.7 kcal/mol) is only slightly higher (about 3 kcal/mol) than the lowest energy between X^2A_1 and 1^2B_2. Thus, in principle, NO_2 chromophore formed from the HNO_3 photolysis at 308 nm could be either NO_2, NO_2^* or both. We previously conducted the only time-resolved study of the NO_x channel[29] following the HNO_3 photolysis at 308 nm; we suggested that $OH+NO_2^*$ is a dominant HNO_3 photolysis channel. The nature of the NO_x product(s) formed from the HNO_3 photolysis is important because if NO_2^* is formed from the HNO_3 photolysis at 308 nm, it may react with

H_2O to form HONO+OH; the proposed mechanism for atmospheric HONO formation from adsorbed HNO_3 photolysis may hold. On the other hand, if the ground state NO_2 is formed from the 308 nm HNO_3 photolysis, the proposed mechanism for the HONO formation from sunlight photolysis of nitric acid in the presence of H_2O may not hold. Given that there is only one published[29] time-resolved study for the NO_x production channel from the HNO_3 photolysis in the actinic UV region and in light of some of our recent laboratory works, there is uncertainty in the nature of the electronic states of NO_2 in the NO_x production channel from the 308 nm HNO_3 photolysis. This motivated us to revisit the nature of the NO_x production channel from the 308 nm HNO_3 photolysis due to its importance in understanding HONO formation in the troposphere.

In this paper, we directly measured absorption spectra of the NO_x product(s) in the 552-560 nm and 640-648 nm region following 308 nm gas phase photolysis of HNO_3 by using cavity ring-down spectroscopy[32,33]. Photolysis study was conducted in the absence and presence of water vapor. Temporal absorption profile around 552 nm following HNO_3 photolysis was obtained. A survey study was also conducted in the near UV region where both HONO and NO_2 exhibit absorption. Discussions have been made concerning whether HONO formation is energetically feasible following actinic UV photolysis of HNO_3/H_2O only system.

2. Experimental

The experimental setup is briefly described here. Details can be found elsewhere.[34-36] The output from a 308 nm excimer laser (Coherent; LPX 110i) is introduced into a stainless-steel reaction cell, at a 15° angle with the main cell axis through a side arm. The probe beam from a dye laser (Continuum, ND6000) pumped by a Nd:YAG laser (Continuum, Surelite II) is directed along the main optical axis of the cell, which is vacuum-sealed with a pair of high reflectance cavity mirrors. Laser dyes used include Rhodamin 590, 4-Dicyanmethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM), and Pyridine 1 (LDS-698). The probe beam overlaps geometrically with the photolysis beam at the center of the cavity. The photolysis/probe laser overlap region can be conceptualized as a rectangular prism in which the prism's center coincides with that of the cell; its width and height defined by those of the photolysis beam and its length defined by (beam width)×(tan 15°)$^{-1}$, where 15° is the crossing angle between the pump and the probe laser beams. The length of the photolysis/probe laser 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 prior to the beam's entrance to the cell. For a 12 mm wide photolysis beam, the length of the photolysis/probe laser overlap region is about 4.6 cm. After the probe beam enters the cell through the front cavity mirror, its intensity decay inside the cavity is monitored with a photomultiplier tube (PMT) placed behind the back cavity mirror. The PMT output is amplified, digitized, and transferred to a computer. The decay curve is fitted to a single-exponential decay function, from which the ring-down time constant (τ) and the total loss (Γ) per round-trip pass are calculated. Nitric acid and its photolysis product spectra were recorded by scanning the wavelength of the probe beam in the 552-560 nm and 640-648 nm regions in the absence and presence of the photolysis beam. Potential HONO product following 308 nm photolysis of HNO_3 in the presence of H_2O was examined by probing absorptions at 342.0 nm and 343.5 nm (corresponding to the peak and valley of HONO absorption), both with and without photolysis pulses. A pulse/delay generator was used to vary the delay time between the firings of the photolysis and the probe lasers.

High-purity HNO_3 was prepared by vacuum distillation of 3:2 mixture of sulfuric acid (98%; Mallinckrodt Baker) and nitric acid (70%; Mallinckrodt Baker) at 273 K; the distilled

HNO_3 was collected into a trap cooled at ethanol/dry ice temperature (195 K).[37] At least four successive distillations were conducted to purify the HNO_3 sample. Extra distillation of the HNO_3 sample was made on the day of the experiment to further reduce NO_2 impurity. After the purification, we subsequently transferred HNO_3 into a clean bubbler and continued purge NO_2 by flowing N_2 carrier gas through the bubbler (held in ice-water bath) for about 20-25 min, followed by pumping the bubbler (held in ice-water bath) in the absence of N_2 flow for about 10-15 min. The NO_2 impurity in the purified HNO_3 vapor was determined to be about 0.02%, obtained by measuring NO_2 absorption *in situ* in the 552-560 nm region using cavity ring-down spectroscopy. Distilled water was drawn from a Barnstead nanopure ultrapure water system (Thermo Scientific, USA); the distilled water was evacuated at room temperature for 30 min to remove dissolved air.

The HNO_3 pressure inside the cell was monitored by an MKS Baratron capacitance manometer (10 Torr full scale, measurement accuracy is about 10^{-4} Torr). The inner surfaces of the cell and the stainless steel joints on the gas transport lines were treated with halocarbon wax or grease (series 1500 or 25-5S; Halocarbon Products Corp.) to minimize decomposition of HNO_3 on surfaces. Although coating of the cell surfaces with halocarbon wax decreased the rate of decomposition of HNO_3, the NO_2 impurity in HNO_3 was found to increase with residence time in the cell on the time scale of several minutes. For quantitative HNO_3 photolysis product study, an equivalent method of fast flow was used. In other words, HNO_3 was first evacuated in the bubbler; then it was introduced into the cell. The photolysis and background measurements were carried out immediately after filling the fresh HNO_3 sample (the background and the photolysis measurements were done at time scale of less than 25 seconds in order to beat the background NO_2 increase), and afterward the HNO_3 sample was pumped out. We repeated this procedure for every experiment. Detailed methodology used in studying the photolysis of

HNO_3/H_2O mixture is described in the Results and Discussion Section. All experiments were carried out at an ambient temperature of 295 K.

Results and Discussion

3.1. Gas Phase Photolysis of HNO_3 in the Absence of Water Vapor

3.1a. Nitric Acid and Photolysis Product Spectra in the 640-648 nm Region.

Shown in Figure 1 are nitric acid absorption spectra in the 640-648 nm region recorded by cavity ring-down spectroscopy, in the absence and presence of 308 nm photolysis pulses, and the difference spectrum. Also illustrated in Fig. 1 is literature vibronic band origins and line intensities[38] in electronically-excited $NO_2(^2B_2)$.

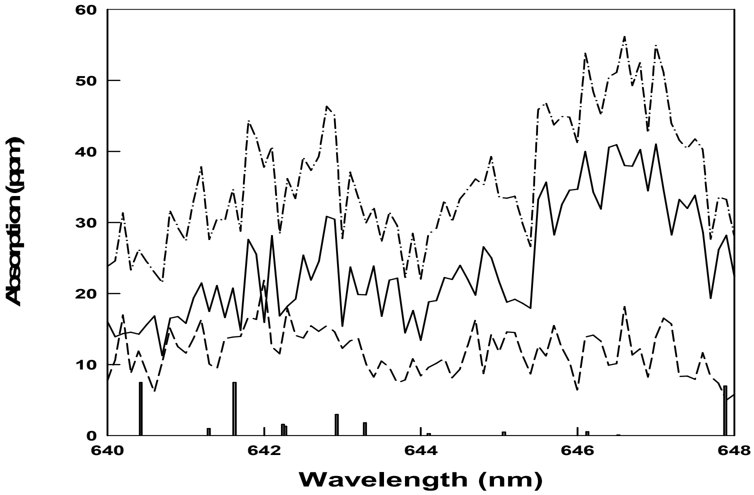

Figure 1. Cavity ring-down absorption spectra of 1.2 Torr HNO_3 in the 640-648 nm region, in the absence (solid line) and presence (dash-dot line) of 308 nm photolysis. The spectra were recorded at a wavelength interval of 0.1 nm. The difference spectrum is shown as medium dash line. The bar graph shows literature[38] vibronic band origins and line intensities in electronically-exited NO_2 ($^2B_2$).

A comparison of the difference spectrum with literature NO_2* vibronic band origins and line intensities in the same wavelength region shows that NO_2* has different spectral pattern compared with that of HNO_3 photolysis product, suggesting NO_2* is not formed from the HNO_3 photolysis at 308 nm.

3.1b. Nitric Acid and Photolysis Product Spectra in the 552-560 nm Region.

Our previous study[29] shows that 308 nm HNO_3 photolysis product displays absorption in the 552-560 nm region. Both NO_2 and NO_2* have broad visible absorption;[39,40] 552-560 nm is at the longer-wavelength tail of the ground state NO_2 absorption spectrum.[41-43] It is also a wavelength range that NO_2* starts to exhibit absorption.[38,44-46] In our previous study, we monitored the decay of product absorption at 552.57 nm, and obtained a decay time constant of 55 μs. The measured decay time constant, which was within the range of the literature decay lifetime of NO_2* of 55-90 μs, led us to suggest NO_2*+OH is a predominant channel from the 308 nm photolysis of HNO_3 (The ground-state NO_2 was monitored at 352 nm. The total absorption of HNO_3 and the NO_2 impurity was on the order of thousand of ppm; transient ground-state NO_2 formation was not observed after the HNO_3 photolysis). Yet, a direct comparison of the 308 nm HNO_3 photolysis product spectrum to that of literature NO_2* in the 640-648 nm region in the current study (Fig. 1) suggests that NO_2* is not formed. So could the product spectrum in the 552-560 nm region come from the ground state NO_2 generated by the HNO_3 photolysis at 308 nm? Could NO_2 impurity in the HNO_3 sample interfere with the decay profile measurement at 552.57 nm in the previous study? Could the NO_2 impurity in the sample be too high such that NO_2 formed from the 308 nm HNO_3 photolysis was too small in comparison, which led to the conclusion that the ground state NO_2 was not formed in the previous study? To address these questions, we prepared a high purity HNO_3 sample and have an independent method to measure the NO_2 impurity concentration *in situ* at the time of the experiment.

To ensure the high purity of the HNO_3 sample for the photolysis study, we always performed a redistillation of the HNO_3 sample on the day of the experiment in the current study. In the previous study,[29] we did not perform additional distillation on the day of the experiment. We later found[47] that additional distillation on the day of the experiment significantly reduces the NO_2 impurity in the HNO_3 sample. Also, our previous reported NO_2 impurity[29] (< 0.05%) was determined at the sample preparation and made at 448-452 nm. Knowing that NO_2 impurity in the sample varies with time and using absorption cross section data of NO_2 in the 552-560 nm region obtained in this study, we directly determined the NO_2 impurity in the HNO_3 sample immediately before the photolysis experiment.

Shown in Figure 2 are cavity ring-down absorption spectra of 1.0 Torr HNO_3 vapor in the 552-560 nm region in the absence (solid line) and presence (dashed line) of the 308 nm photolysis. The plots showed that the absorbance was increased after HNO_3 was photolyzed at 308 nm. The spectra were scanned from shorter wavelength to longer wavelength, and during the spectral recording process (it took about 10 min to complete a spectral scan), the decomposition of HNO_3 contributed to the upward sloping of the recorded spectra. A close examination shows that the peaks and valleys of both spectra are matched on each other, suggesting that no new species were formed and the ground state NO_2 is likely a product from the HNO_3 gas phase photolysis. Also plotted in Figure 2 is an absorption spectrum of a 1:98.3 mixture of NO_2:N_2 with NO_2 partial pressure of 0.33 mTorr in the cell. A comparison of the NO_2 spectrum and that of the HNO_3 photolysis product provides clear experimental evidence that ground state NO_2 is indeed a product from the HNO_3 photolysis. To understand the cause of

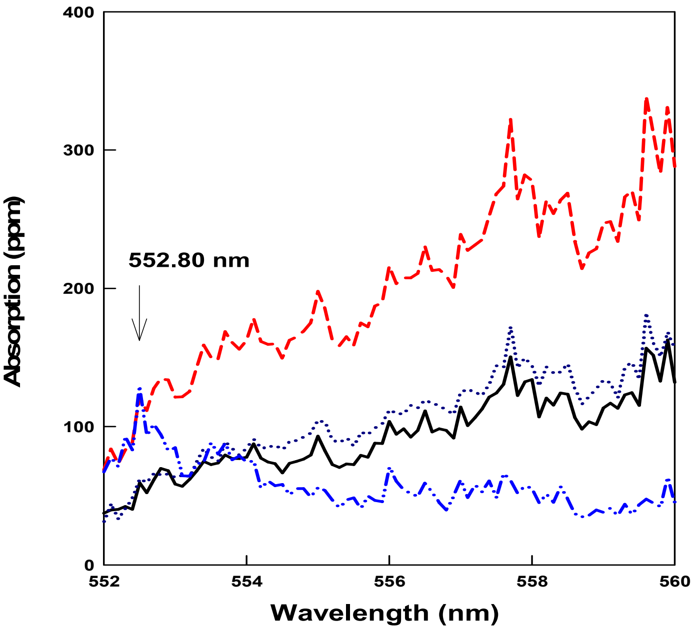

Figure 2. Cavity ring-down absorption spectra of 1.0 Torr HNO_3 vapor in the 552-560 nm region in the absence (solid line) and presence (dashed line) of photolysis at 308 nm. Both spectra were taken under closed cell conditions, and at a wavelength interval of 0.1 nm. The difference spectrum (dotted line) for HNO_3 with and without photolysis is also included. Also shown for comparison is a cavity ring-down absorption spectrum (dash-dot-dot line) of 1:98.3 NO_2:N_2 mixture at an NO_2 partial pressure of 0.33 mTorr.

time-resolved absorption at 552.57 nm from the HNO_3 photolysis in our previous study,[29] we tuned the cavity ring-down spectrometer to product absorption maximum at 552.80 nm (the probe laser system used in previous study was replaced with a more accurate current probe laser system; there is slight difference in wavelength reading, but it is within the uncertainty of the instrument); transient round-trip absorptions from the HNO_3 photolysis at 0.5, 1.0, and 2.0 Torr pressures were measured as a function of delay time between the firing of the photolysis and the probe laser. We cannot decrease the HNO_3 pressure to that much lower than 0.5 Torr as the product absorption in the 552-560 nm region decreases with decreasing HNO_3 pressure; we need to have sufficient signal-to-noise ratio to prove the point. Illustrated in Figure 3 is a temporal absorption profile from the photolysis of 1.0 Torr HNO_3.

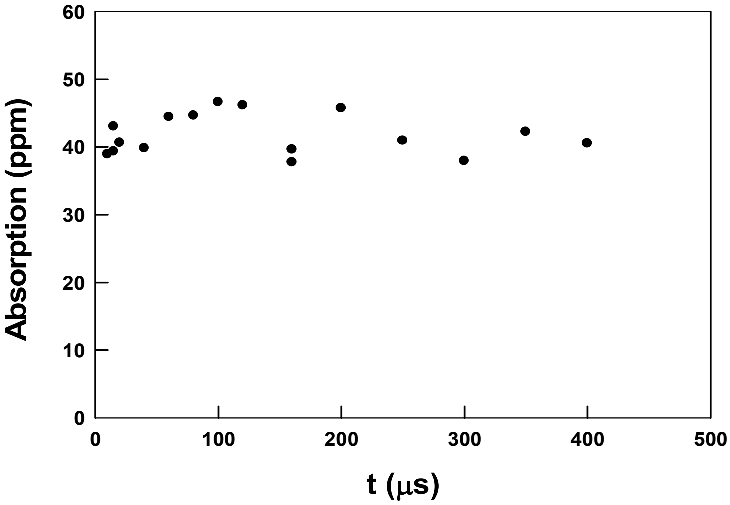

Figure 3. Round-trip absorption at 552.80 nm as a function of pump-probe laser delay time after 308 nm photolysis of 1.0 Torr HNO_3. Each absorption value is that from an accumulation of 10 photolysis pulses.

Consistency check at 15 μs was performed at the beginning, in the middle, and at the end of the time dependence experiments. Absorptions at 552.80 nm from photolyzing 0.5, 1.0, or 2.0 Torr HNO_3 are found to be independent of the photolysis/probe laser delay time over the 10-400 μs range, within the experimental error. The lack of temporal dependence of the product absorption from the 308 nm photolysis of HNO_3 in the 0.5-2.0 Torr range and the larger product absorption in the 552-560 nm region compared to that in the 640-648 nm region are consistent with the ground state NO_2 (not the electronically-excited NO_2) being a product from the 308 nm photolysis of HNO_3.

Reported decay lifetimes[48-54] of NO_2* with NO_2 as a quencher are in the range of 30-100 μs as the NO_2 excitation wavelength is varied in the 398 to 600 nm range. The long lifetime of NO_2* is postulated[55] to arise from the vibrational energy mismatch between the vibronically-excited NO_2 (i.e., NO_2*) and the ground state NO_2; thus, the vibrational-to-vibrational ($V \rightarrow V$) energy transfer between NO_2* and NO_2 bath molecules is not that efficient. The quenching rate constant of NO_2* by NO_2 was found[48] to decrease with decreasing photon energy used to excite NO_2 into NO_2*. The quenching rate constant of NO_2* by HNO_3 has not been previously reported. In the presence of a quencher such as 0.5-2.0 Torr HNO_3, the lifetime of the presumed NO_2* is expected to be shorter than the literature NO_2* decay lifetime of 30-100 μs. If NO_2* were indeed a predominant NO_x product formed from the 308 nm HNO_3 photolysis, we expect to see absorption at 552.80 nm to show prompt increase immediately after photolysis, and then decrease quickly with delay time at a short time scale in Fig. 3. But that is not the case in the current study. So why did our previous study[29] show time-resolved absorption in the 552-560 nm region? Was such time-dependence real or was it a spurious effect likely caused by the NO_2 impurity in the previous HNO_3 sample? In our earlier study,[29] the temporal absorption profile was determined by performing measurements at short photolysis/probe laser delay time first, then intermediate delay time, and subsequently longer delay time. The NO_2 impurity in the HNO_3 bubbler decreased with increasing pumping-flow time, and the experiment was done from shorter delay time to longer delay time. This is equivalent to sampling more NO_2 absorption at shorter delay time and less at longer delay time. The interference from the NO_2 impurity could give this coincidental agreement between the HNO_3 photolysis product decay rate constant and the literature reported decay rate constant of NO_2*. As mentioned earlier in this section, our previous study had a higher NO_2 impurity in the HNO_3 sample. In addition, no *in situ* measurement of the NO_2 impurity level was made during the photolysis experiments in the previous study. A constant NO_2 impurity level in HNO_3 was assumed in the slow-flow system in the previous study, our current *in situ* measurement shows that the NO_2 impurity level in HNO_3 is not a constant; it decreases with time in the slow-flow system. We also concluded that it is best to prepare the high purity HNO_3 rather than to use this flow system to remove the NO_2 impurity in HNO_3. The later depends on the delicate balance between the impurity NO_2 formation and removal rate. Given that the previous study had more NO_2 impurity in the HNO_3 sample, the impurity level could be variable and was not monitored in the experiment, the results of the current study should supersede those from our previous study[29].

The ground state NO_2 quantum yield from the HNO_3 photolysis at 308 nm was obtained from the ratio of the NO_2 concentration generated in the photolysis/probe laser overlap region per photolysis pulse to the absorbed photon density in the same region. Absorbed photolysis photon density in the pump/probe laser overlap region was derived from the difference between the transmitted photolysis beam energies entering (E_{in}) and leaving (E_{out}) that region, the individual photon energy (hc/λ) at the photolysis wavelength (λ), and the volume (v) of the overlap region. The photolysis beam energy entering or leaving the overlap region was calculated from the incident photolysis beam energy entering the cell (E_0), the HNO_3 absorption cross section (σ_{HNO_3}) at 308 nm, the HNO_3 concentration (n_{HNO_3}) in the cell, and the absorbing path length, by applying Beer's law:

$$E_{\mathrm{in}} = E_0 \bullet \exp(-\sigma_{HNO_3} \bullet n_{HNO_3} \bullet l_1) \qquad (4)$$

$$E_{\mathrm{out}} = E_0 \bullet \exp(-\sigma_{HNO_3} \bullet n_{HNO_3} \bullet l_2) \qquad (5)$$

where l_1 represents the distance between the incident beam at the cell entrance and the initial position of the overlap region, and l_2 denotes the distance between the photolysis beam entrance and the end of the overlap region. E_0 was determined by a Joulemeter placed in front of the cell. The photolysis 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 incident photolysis fluence inside the cell was determined to be 0.04-0.05 J/cm^2. In light of low photolysis fluence, multiphoton excitation process is unlikely. We previously obtained[29] an HNO_3 absorption cross section of $(1.24\pm0.19)\times10^{-21}$ cm^2/molecule at 308 nm using cavity ring-down spectroscopy.

The NO_2 concentration generated from 308 nm photolysis of HNO_3 per photolysis pulse was acquired from measurements of the round-trip NO_2 absorption at 552.80 nm averaged over the number of photolysis pulses used. The NO_2 concentration resulting from the HNO_3 photolysis at a given HNO_3 pressure can be obtained from the corresponding round-trip NO_2 absorption per photolysis pulse, the length of the photolysis/probe laser overlap region (l), and the absorption cross section of NO_2, σ_{NO2}, using the equation $[NO_2]$ = Absorption/$(2\sigma_{NO2}l)$. We directly measured NO_2 absorption cross section at 552.80 nm, which is $(1.34\pm0.05)\times10^{-19}$ cm^2/molecule. Using the HNO_3 absorbed photon density and NO_2 absorption determined in this study, we obtain an NO_2 quantum yield of 1.1±0.2 from the HNO_3 photolysis at 308 nm, independent of HNO_3 pressure (~ Torr range).

3.2. 308 nm Gas Phase Photolysis of HNO_3 in the Presence of Water Vapor

To understand the photolysis of the HNO_3/H_2O mixture at 308 nm, we first examined what happened to the cavity loss at 552.80 nm when H_2O was introduced into the cell. Cavity loss increased significantly after the water vapor was introduced into an evacuated reaction cell, previously exposed to HNO_3. This phenomenon suggested that the water vapor likely dispersed HNO_3 or NO_2 that was adsorbed on the cell wall. The back-filled water vapor was then pumped away along with HNO_3 that was adsorbed on the chamber wall. This process was repeated a number of times to condition the cell wall.

We noticed that it took much longer time for the water vapor to reach equilibrium pressure inside the cell than that of HNO_3. In the experiment, H_2O was first introduced into the cell to allow sufficient time to reach pressure equilibrium. During this time, HNO_3 was pumped in the bubbler. When H_2O pressure reached the equilibrium inside the cell, the HNO_3 vapor was then admitted to the cell. The HNO_3/H_2O mixture background absorption was first determined, followed by prompt measurement of absorption of the 308 nm photolyzed mixture. In this way, the photolysis of the equilibrated HNO_3/H_2O mixture was studied. Presented in Figure 4 is a plot of absorption at 552.80 nm as a function of photolysis/probe laser delay time, after 308 nm photolysis of mixtures containing 1.0 Torr HNO_3 and 0.2 Torr H_2O. Figure 4 shows that absorption at 552.80 nm is independent of delay time after the photolysis of the HNO_3/H_2O mixtures, suggesting that the HNO_3 photolysis product does not react with H_2O. If NO_2* were the predominant product formed from the 308 nm photolysis of the HNO_3 vapor, and if NO_2*

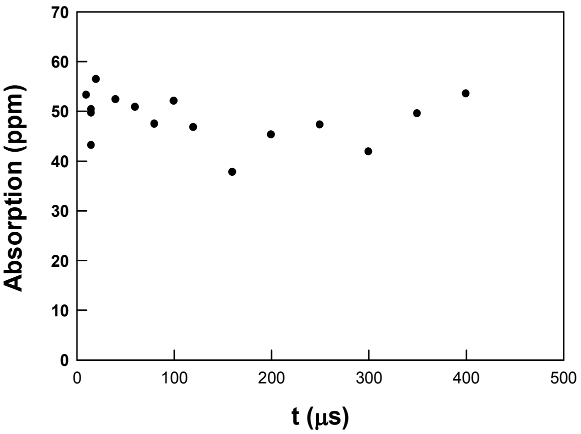

Figure 4. Round-trip absorption at 552.80 nm as a function of time after 308 nm photolysis of mixtures containing 1.0 Torr HNO_3/0.2 Torr H_2O.

underwent physical and/or chemical quenching by H_2O, we should expect absorption at 552.80 nm to decay with time. The lack of time-dependent absorption from the photolysis of mixtures containing 1.0 Torr HNO_3/0.2 Torr H_2O or 1.1 Torr HNO_3/0.5 Torr H_2O is consistent with ground state NO_2 being formed from the 308 nm photolysis of the HNO_3/H_2O mixture.

To investigate whether HONO was formed from the 308 nm photolysis of HNO_3/H_2O mixture, we also tuned the wavelengths of the ring-down probe beam to those at 342.0 nm and 343.5 nm, where literature[56-60] peak and valley of HONO absorption are located. Brief survey study showed that absorptions at 342.0 nm and 343.5 nm are comparable in size, but lack temporal dependence following the 308 nm photolysis of HNO_3/H_2O mixtures. The result suggests that HONO is not formed from the 308 nm photolysis of HNO_3/H_2O mixture. Since the ground state NO_2 is produced from the 308 nm photolysis of HNO_3, it is not surprising we did not observe HONO formation at < 1 ms after the 308 nm photolysis of the HNO_3/H_2O mixture. The reaction of the ground state NO_2 with H_2O ($2NO_2+H_2O+M = HNO_3+HONO+M$) occurs slowly through heterogeneous process, with a rate constant[61] of $\sim 2.4\times10^{-23}$ $cm^3 molecule^{-1} s^{-1}$.

3.3. Comparison with Literature Studies and Atmospheric Implications.

Both the photolysis product absorption spectrum and the lack of dependence of absorption on photolysis/probe laser delay time in the 552-560 nm region indicate that the NO_x product produced from the 308 nm photolysis of HNO_3 is that of NO_2 in the ground electronic state. Our observation is consistent with those[18,27] from the HNO_3 photodissociation dynamics studies. On the basis of thermodynamic analysis and literature report[7], one might argue for the formation of some NO_2* from the 308 nm photolysis of HNO_3. But if we take the symmetry, barrier, and adiabatic state correlation into the consideration, our experimental observation can be fully explained. *Ab initio* calculation[7] shows that the ground state and two lowest energy excited states of HNO_3 are 1 ^{1}A', 1 ^{1}A", and 2 ^{1}A". The energy difference[7,62] between these two electronically-excited states and the ground state are 3.40 and 4.54 eV, respectively. Once HNO_3 molecule absorbs a 308 nm photon, it can be excited into the first electronically-excited 1^1A" state due to the fact that the absorption band is broad and the vertical excitation energy is 3.73 eV. In terms of electronic structure, the transition essentially involves excitation of an electron from non-bonding NO_2 molecular orbital to NO_2 π^* antibonding orbital in HNO_3, with symmetry a' → a" (Cs). This HNO_3 1^1A" quantum state is correlated[7,18] with X $^2A_1$ in NO_2, which is the ground electronic state of the NO_2 molecule. On the other hand, 308 nm light is not energetic enough[7,61] to access 2 ^{1}A" of HNO_3 (4.54 eV); this 2 ^{1}A" state is correlated with 1 $^2B_2$, which is the first electronically-excited state of NO_2. The correlation diagram is shown in Figure 5.

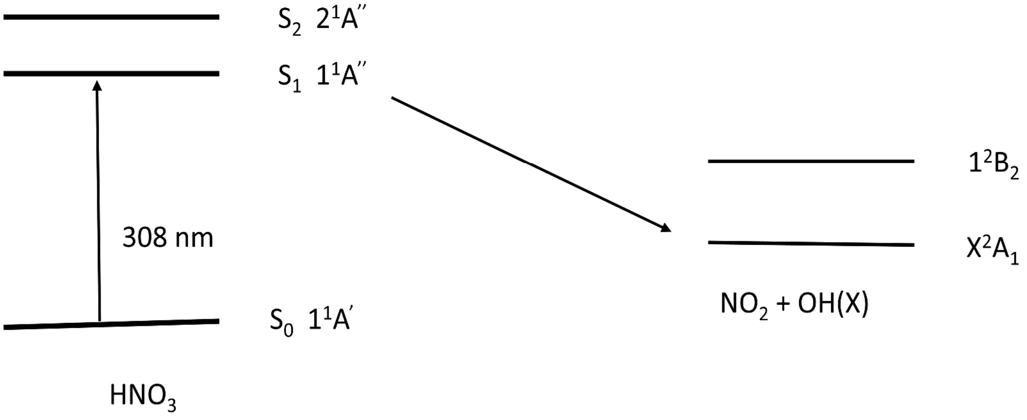

Figure 5. A sketch of the HNO_3 photodissociation energy level diagram based upon reference 18.

Photodissociation of HNO_3 at 2 ^{1}A" is governed by both symmetry and barrier height. Despite the broad HNO_3 absorption, the energy barrier is the limiting step to form NO_2*. This elucidates well our experimental observation that only the ground state NO_2 is observed from the 308 nm photolysis of HNO_3.

Our experimental results are consistent with the ground state NO_2 being the only NO_x product formed from the 308 nm HNO_3 photolysis. Energetically, the electronically-excited NO_2 1 $^2B_2$ is accessible via HNO_3 1 ^{1}A", but it is symmetry-forbidden (Fig. 5). We cannot totally exclude a minor NO_2* channel (e.g., < few percent) formed through a hypothetical, non-adiabatic HNO_3 photodissociation pathway. For example, if there were non-adiabatic interaction between 1 ^{1}A" and higher electronically-excited state(s) of HNO_3, or if the geometry of HNO_3 (NO_2 angle) were changed in a way that the symmetry-forbidden pathway became allowed, the HNO_3 photolysis product might have some characteristics of electronically-excited NO_2 1 $^2B_2$. Nonetheless, we expect this hypothetical non-adiabatic HNO_3 photodissociation channel to be of minor importance.

In this paper, we have reexamined the NO_x product channel from the 308 nm photolysis of HNO_3 in the gas phase; we found ground state NO_2 to be the experimentally-observed NO_x product from this photodissociation process, with a near unit quantum yield. The ground state NO_2 may also be expected to be the NO_x product formed from adsorbed HNO_3 photolysis in the daytime troposphere. As the near UV absorption cross sections of surface-adsorbed HNO_3 are two to three orders of magnitude larger than[47,63] those in the gas phase, photolysis of adsorbed HNO_3 molecules by sunlight is an efficient renoxification process and an important source of OH radicals. However, photolysis of adsorbed HNO_3 only system by actinic UV radiation is not expected to be significant for tropospheric HONO formation, as the solar photon energy in the troposphere is likely not energetic enough to form the HONO product.

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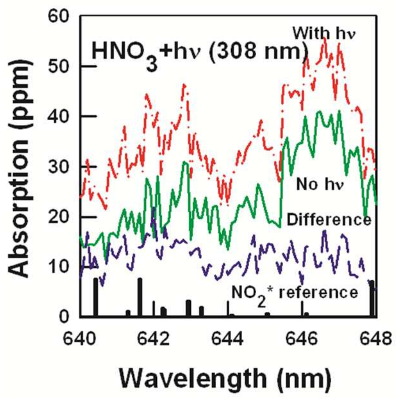
TOC Figure


HNO$_3$+hν (308 nm)
With hν
No hν
Difference
NO$_2$* reference
Absorption (ppm)
0
10
20
30
40
50
60
640
642
644
646
648
Wavelength (nm)