Supporting Online Material for

Atmospheric Hydroxyl Radical Production from Electronically Excited NO₂ and H₂O

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Materials and Methods:

The experimental apparatus has been described previously (SI). Briefly, the reaction chamber consists of a glass cell equipped with a viewing window for monitoring laser-induced fluorescence (LIF), two sets of mutually orthogonal side arms for introducing laser light, and several inlet ports for adding reagents and monitoring pressure. The inside of the cell is coated with halocarbon wax to minimize radical wall loss. Water, NO₂ and N₂ gases are introduced through separate ports and slowly flow through the reaction cell. The reaction cell is evacuated using a mechanical vacuum pump that is connected to the cell through a liquid nitrogen cold trap and a bellows valve. For the kinetic measurements the total pressure in the cell is typically kept at 2 Torr and consists primarily of N₂ (1.7 Torr), 60 mTorr of NO₂ and water vapor. The water vapor pressure is varied in the kinetics measurement between 30-300 mTorr. Visible light for electronically exciting NO₂ is generated by an optical parametric oscillator (Spectra Physics: MOPO-730), which is pumped by the third-harmonic of an injection seeded Nd:YAG laser (Spectra Physics: GCR-270). The signal beam from the MOPO laser provides the required tunable radiation between 560-640 nm with a bandwidth of ~0.4 cm⁻¹ and pulse energies ranging from 12-15 mJ over this spectral region. The OH products resulting from the reaction are probed via the diagonal A-X transitions at ~308 nm using laser induced fluorescence (LIF). The 308 nm laser radiation, which has a bandwidth of 0.13 cm⁻¹, is generated by frequency doubling the output of a second Nd:YAG laser (Continuum: NY81-20) pumped dye laser (Continuum: ND60). The NO₂ electronic excitation laser propagates counter to the probe laser beam and is focused into the center
of the cell, to a diameter between 1-2 mm, using a 355 mm focal length lens. For most of our kinetics measurements, the probe laser pulse fires 500 ns after the MOPO. In certain “low” pressure experiments we have also probed the near nascent OH product state distributions. In this case the N2 buffer gas is absent and the experiments are conducted at ~180 mTorr total pressure (~120 mTorr H2O and 60 mTorr NO2) with the time delay between the excitation and probe lasers reduced to 70 ns. For all measurements the probe laser intensity is greatly attenuated in order to avoid photodissociation of the NO2 sample. Typically the 308 nm probe laser pulse energy is 0.2 µJ and it is focused down to a beam diameter of ~1-2 mm. The OH fluorescence excited by the probe laser is collected using an f/1 lens system and imaged onto an end-on photomultiplier (EMI: 9813QB). A color glass filter (Schott UG-11) located in front of the photomultiplier provides discrimination against scattered laser light as well as a significant portion of the NO2* fluorescence. Signal from the PMT is sent to a gated charge integrator (LeCroy: 2249SG ADC) and subsequently digitized and passed on to a laboratory computer for storage and analysis. The NO2 gas sample used in the experiment is synthesized by adding excess O2 to NO and storing the mixture for 24 hours and then removing high vapor pressure components from the mixture using several freeze-pump-thaw cycles at -78 °C using a liquid nitrogen-ethanol cooling bath.

The formation of OH radicals from reaction-7, the NO2* + H2O reaction, was confirmed by its characteristic LIF spectrum (S2) as mentioned in the main text and shown there in Fig.1(a). In order to confirm that the OH was indeed from this reaction, several diagnostics were carried out. These diagnostics, taken together, confirmed our hypothesis. First, the time dependence of the OH product appearance, relative to the
excitation laser pulse, was measured and found to exhibit a build-up time of a few microseconds consistent with that expected for a bimolecular reaction requiring collision times appropriate for the pressure used and not “prompt” photodissociation, which typically takes place in less than a fraction of a nanosecond; much faster than the temporal resolution of our lasers. This ruled out the possibility that the detected OH radicals were from photolysis of impurities such as HONO or nitric acid that can form in NO2-water mixtures through heterogeneous chemistry taking place on glass surface (S3, S4). In separate experiments we also confirmed the absence of these species in our starting reaction mixture. Using $5\nu_{\text{OH}}$ vibrational overtone initiated unimolecular dissociation (S5, S6), we probed the H2O/NO2 reaction mixture for the presence of HONO and HNO3. Figures S1(a) and S1(b) respectively show the $5\nu_{\text{OH}}$ action spectra of HONO and HNO3, when these species are deliberately introduced into the reaction cell at a pressure of ~20mTorr in order to demonstrate our ability to detect them using the $5\nu_{\text{OH}}$ vibrational overtone initiated unimolecular dissociation technique. We estimate our detection sensitivity for these species to be $\sim 1 \times 10^{12}$ molecules/cm$^3$ using this method. Figure S1(c) shows a scan over the same spectral regions when the $5\nu_{\text{OH}}$ excitation is used to investigate for the presence of HONO and HNO3 in our H2O/NO2 reaction mixture. During this scan the time delay between the excitation and probe lasers is kept short at ~20 ns in order to minimize OH signal contribution from the NO2* + H2O bimolecular reaction, the reaction under study, which also occurs for this sample mixture over this spectral region. The absence of any HONO or HNO3 features in the spectrum of Fig. S1(c) demonstrates that these species are not present at any significant levels. We also eliminated the possibility that our measurements on the NO2* + H2O reaction was
being influenced substantially by heterogeneous chemistry by conducting the reaction in a separate cell having a different surface/volume ratio and made of different material, stainless steel. The results in the metal cell were identical to those found using the glass cell. Another diagnostic for the $\text{NO}_2^* + \text{H}_2\text{O}$ reaction that we investigated involved measuring the excitation laser power dependence of the OH signal. This was carried out at three separate wavelengths corresponding to 565, 590 and 612.5 nm. The power dependence was found to be linear at all three wavelengths. Fig. S2 shows data for the 565 and 590 nm wavelengths. As the figure shows, the OH product yield varies linearly with excitation laser power over the range from 4.5 to 50 mJ. This finding is consistent with a single-photon excitation process involving the absorption of a visible photon by NO$_2$ to form NO$_2^*$, followed by the collision of NO$_2^*$ with H$_2$O to form OH radicals. It also suggests that contribution to the OH signal from side reactions involving vibrationally excited water molecules, formed through collisional energy transfer, and NO$_2^*$ are small as this would require the OH signal to vary as the square of the laser power.

As an additional diagnostic, we recorded an NO$_2$ action spectrum. This is shown in Fig.1(c) of the main text as well as Fig. S3. In Fig. S3 each spectrum appearing in Fig. 1c is shown separately in order to more clearly display their respective baseline. The action spectrum, Fig S3(c), was generated by scanning the excitation laser over the region from 560 to 640 nm while monitoring the yield of OH products in the indicated quantum state. The time delay between the excitation and probe lasers were set at ~1 µs. The baseline in the action spectra rise a bit towards the blue end of the scan due to an increase in NO$_2^*$ fluorescence that makes it through our optical filtering system. Simultaneously,
during the recording of the action spectrum, a portion of the excitation laser is sent into a photoacoustic cell containing the gaseous reaction mixture that allows us to record a photoacoustic spectrum shown in Fig. S3(b). As Fig. 1(c) in the main text and Fig. S3 here show, the peaks and valleys in the action spectra obtained by monitoring OH yield match well with those in the photoacoustic as well as the reference NO$_2$ absorption spectrum ($S7$). As the photoacoustic spectrum is equivalent to an absorption spectrum, the above correspondence confirms that the OH signal arises from photoexcited NO$_2$ molecules and not an impurity such as N$_2$O$_4$. As a final diagnostic we also eliminated the possibility that the OH signal was being generated from the reaction of water with either electronically or translationally excited oxygen atoms formed in the reaction mixture through photolysis. Although the linearity of the excitation laser power dependence (discussed earlier) ruled out this possibility, we tested for the production of oxygen atoms using additional complementary diagnostics. We tested for the presence of electronically excited O($^1D$) atoms by replacing the water reagent with H$_2$. It is well known that O($^1D$) reacts rapidly with H$_2$ to produce OH + H ($S8$). The fact that we did not see any OH signal when H$_2$ was added, confirmed that O($^1D$) was not involved in the reaction under consideration. We next tested for the possibility of whether translationally hot ground state oxygen atoms were involved. The reaction of ground state oxygen atoms with water, O($^3P$) + H$_2$O, is known to have a ~16-17 kcal/mole barrier ($S8$) and thus only translationally excited O($^3P$) atoms can initiate the reaction. On energetic grounds, two-photon dissociation of NO$_2$ over the 560-625 nm region can, in principle, produce translationally hot O($^3P$) atoms with sufficient energy to react with water. We tested for this possibility by working near the energetic threshold for the O($^3P$) + H$_2$O reaction.
Assuming that all the available energy from the photolysis of a room temperature NO$_2$ sample goes solely into fragment translation, the energy required to generate O($^3$P) atoms with sufficient translation energy to overcome the ~16-17 kcal/mole reaction barrier requires photolysis of NO$_2$ at wavelength to the blue of around ~300 nm. We tested for the O($^3$P) mechanism by directly introducing ~1.25 mJ of tunable UV light at 312.5 nm (i.e. doubled 625 nm) into our reaction mixture. The UV light generated O($^3$P) atoms whose translational energy were assumed to be similar to that which would be generated from two-photon dissociation of the NO$_2$ at the corresponding fundamental visible wavelength. We found that the UV light did give rise OH signal through the O($^3$P) + H$_2$O reaction. However as the O($^3$P) formed at these wavelengths are energetically near the threshold for reaction, we found a large (factor of ~9) increase in reaction cross-section, as reflected by changes in the OH signal level, when the UV photolysis wavelength was scanned slightly to the blue from 312.5 nm to 298 nm (doubled 596 nm) while the laser power was kept constant. Thus if translationally hot O($^3$P) atoms were the source of the signal in the reaction under study, through two-photon dissociation of NO$_2$, one would expect to see large changes in the relative intensities of the peaks appearing in the action spectrum as one scans over the 625 to 596 nm range. This follows since the intensities appearing in the action spectrum basically reflect contributions from both the reaction cross-section as well and the absorption cross-section. Experimentally, we find that the relative intensities appearing action spectrum closely mimics those in the absorption spectrum over the 625-596 nm wavelength range (see Fig S3). This finding indicates that the reaction cross-section for the system under study is not changing rapidly over this wavelength. Thus, the fact that the intensities of peaks in the action spectrum do not
change as rapidly, as would be expected for OH generated from the O($^3$P) + H$_2$O reaction initiated near its energetic threshold, rules out the O($^3$P) mechanism.

The choice of excitation wavelength for studying the NO$_2^*$ + H$_2$O reaction is worthy of comment. The NO$_2$ absorption spectrum, shown in Fig. S4, extends from about 250 nm to 650 nm. Excitation to the red of roughly ~420 nm results in accessing of the excited bound states of NO$_2$. While it is tempting to excite the molecule in the bluest possible region in order to have the NO$_2$ excitation cross section be as large as possible, we chose to work in region between 560-640 nm in order to avoid several potential complications associated with the bluer wavelengths. First, several groups have reported sequential multi-photon excitation effects in NO$_2$ in the region between 420-540 nm (S9-S11). These excitations can result in the formation of electronically excited oxygen atoms that can interfere with the kinetics measurements. Second, various energy transfer studies on NO$_2$ suggest that the amount of energy transferred from electronically excited NO$_2$ to its collision partner, depends strongly on the wavelength at which the NO$_2$ is excited (S12-S16). These studies reveal that for a given collision partner, the amount of energy transferred per collision increases as the NO$_2$ excitation energy is increased. This in turns implies that the excitation volume region of the reaction zone in our experiment can potentially become enriched with vibrationally excited water molecules through collision energy transfer when working too far into the blue regions of the NO$_2$ absorption curve. We minimized these problems by working in the red-tail region of the NO$_2$ absorption curve. We note that excitation over the 560-640 nm range provides the system with sufficient energy to overcome the 39.8 kcal/mol reaction endothermicity associated with the NO$_2 +$ H$_2$O reaction (S8). The reaction is not expected to have a significant barrier
above this endothermicity as the reverse exothermic reaction involving, OH + HONO, does not exhibit an appreciable barrier (S8).

We next discuss details of the rate measurements. The rate measurements were carried out under “short-time” conditions using a fixed time delay of 500 ns between the NO₂ excitation and OH probe lasers. In addition to the NO₂ and water reagent, N₂ was added to the reaction mixture in order to readily thermalize the rotational distribution of the nascent OH products. We typically used the OH(v=0, 2Π_{3/2}, N=2) rotational level to monitor the kinetics. The kinetics associated with OH radical formation from reaction-7 can be expressed as:

\[
d[\text{OH}]_7/dt = k_7 [\text{NO}_2^*] [\text{H}_2\text{O}] \quad (S1)
\]

Working under conditions where the reaction time, \(\Delta t\), is kept short, the above differential equation becomes:

\[
\Delta[\text{OH}]_7 = k_7 [\text{NO}_2^*] [\text{H}_2\text{O}] \Delta t \quad (S2)
\]

Further, assuming that the starting concentration of H₂O is in excess over that for NO₂*, allows us to write the above equation in terms of a pseudo-first order rate constant \(k_7^I\) = \(k_7 [\text{H}_2\text{O}]\) giving:

\[
\Delta[\text{OH}]_7 = k_7^I [\text{NO}_2^*] \Delta t \quad (S3)
\]

The concentration of electronically excited NO₂, denoted as [NO₂*], is primarily changing with time due to collisional relaxation with N₂, H₂O, and NO₂ as well as through fluorescence emission. The collisional relaxation of NO₂* has been studied by several groups and is rather complicated (S12-S16). The initial levels prepared by laser excitation \(B^2B_1/A^2B_2 \leftarrow X^2A_1\) in the 560-640 nm range are expected to be predominately of \(A^2B_2\) character as this is the “bright” state with the largest cross-section. Subsequent
collisions will transfer population from the initially prepared state to levels that are mostly of $X^2A_1$ character as the energized molecule is high up the $X^2A_1$ potential well and consequently the density-of-states for these levels dominates. Further collisions are expected to transfer energy from the excited NO$_2$ in a step-wise manner with the amount of energy transferred depending on both the energy range and complexity of the collision partner. In the present study we modeled the NO$_2^*$ collisional relaxation very simply by using a first order relaxation rate constant, $k_{rlx}$, given by:

$$k_{rlx} = k_{N_2}[N_2] + k_{H_2O}[H_2O] + k_{NO_2}[NO_2] + \frac{1}{\tau_{flu}}$$  \hspace{1cm} (S4)

where $k_{N_2}$, $k_{H_2O}$, $k_{NO_2}$ are the collisional fluorescence quenching rate constants for NO$_2^*$ by N$_2$, H$_2$O and NO$_2$. These quenching rate constants are respectively $2.7 \times 10^{-11}$, $1.7 \times 10^{-10}$ and $5.7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (S17-S19). The above simple treatment and the values for the rates used also seem reasonable from another perspective. In particular, if one uses the collision energy transfer data available for N$_2$ and NO$_2$, for example, then one finds that taking the excitation energy in excess of the reaction threshold (39.8 kcal) energy and dividing this excess energy by the average energy removed per collision by N$_2$ from NO$_2^*$, gives a rough measure of the number of collisions on average required to remove the available excess energy and terminate the reaction. Taking this value for collision number and scaling the nominal Lennard-Jones collision rate constant for NO$_2$, $\sim 4 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, gives rates that are surprisingly close to the fluorescence quenching rate used above (S20). The fluorescence lifetime for NO$_2^*$ in the absence of any collision is estimated to be $\tau \sim 40$-60 $\mu$sec (S19, S21). As it turns out, the loss of NO$_2^*$ through reaction-7 itself, is negligible compared to these other loss mechanisms.
Thus, we can relate the time dependent $[\text{NO}_2^*]$ concentration in terms of its initial concentration, $[\text{NO}_2^*]_0$ through the equation:

$$[\text{NO}_2^*] \approx e^{-(k_{\text{rx}}) \Delta t} [\text{NO}_2^*]_0 \quad (S5)$$

Substituting equation S5 into equation S3, we get

$$\Delta[\text{OH}] = k_7 e^{-(k_{\text{rx}}) \Delta t} [\text{NO}_2^*]_0 \Delta t \quad (S6)$$

The OH radical concentration is related to the corresponding LIF signal through the empirical factor $\gamma'$ that contains the details of the probe laser related excitation and detection efficiencies. Thus, in terms of detected OH fluorescence signal, $S(\text{OH})_7$, the above equation becomes:

$$S(\text{OH})_7 = \gamma' k_7 e^{-(k_{\text{rx}}) \Delta t} [\text{NO}_2^*]_0 \Delta t \quad (S7)$$

Likewise, the initial concentration of electronically excited NO$_2$ produced by laser excitation can be related to the partial pressure of NO$_2$ in the cell through the relation:

$$[\text{NO}_2^*]_0 = \gamma \sigma_{\text{NO}_2} [\text{NO}_2]_0 \quad (S8)$$

Where in the above equation $\sigma_{\text{NO}_2}$ is the absorption cross section, $\gamma$ is an empirical parameter having to do with the power and focusing characteristics of the excitation laser, and $[\text{NO}_2]_0$ is the initial partial pressure of the sample. Thus we have:

$$S(\text{OH})_7 = \gamma' \gamma \sigma_{\text{NO}_2} k_7 e^{-(k_{\text{rx}}) \Delta t} [\text{NO}_2]_0 \Delta t \quad (S9)$$

We next eliminate the two parameters, $\gamma$ and $\gamma'$, having to do with the detection and excitation lasers, by looking at a reference reaction that also generates OH at roughly the same excitation wavelength, with known quantum yield and absorption cross section. In back-to-back experiments, we use the same lasers powers, focusing conditions, detector setting, and total pressure to carry out the reference reaction and compare its OH fluorescence signal with that from the reaction-7. The reference reaction chosen, involved
looking at the unimolecular dissociation of CH₃OOH excited to the 5νOH vibrational level which is known to dissociate rapidly and with unit quantum yield around ~620 nm (S22).

\[
\text{CH}_3\text{OOH} + \text{hv} \rightarrow \text{CH}_3\text{OOH}(5\nu\text{OH})^* \rightarrow \text{CH}_3\text{O} + \text{OH} \quad (\text{S10})
\]

Analogous to the discussion above, the OH fluorescence signal from this reference reaction is related to the starting CH₃OOH reagent concentration through:

\[
S[\text{OH}]_{\text{ref}} = \gamma' \gamma \sigma^{\text{CH}_3\text{OOH}} \left[\text{CH}_3\text{OOH}\right]_0
\]

(S11)

Where the parameters have same meaning as given earlier. In particular, γ and γ' are the same for the reference reaction and reaction-7 as we use same laser powers, focusing condition, and detection settings. Thus, taking the ratio of equations S9 and S11 we get:

\[
S[\text{OH}]_7/S[\text{OH}]_{\text{ref}} = \sigma^{\text{NO}_2} k_7 I e^{-\left(k_{\text{rx}} \Delta t\right)} \left[\text{NO}_2\right]_0 \Delta t / \sigma^{\text{CH}_3\text{OOH}} \left[\text{CH}_3\text{OOH}\right]_0
\]

(S12)

Solving the above equation for \(k_7 I\) gives:

\[
k_7 I = \sigma^{\text{CH}_3\text{OOH}} \left[\text{CH}_3\text{OOH}\right]_0 S[\text{OH}]_7 / \sigma^{\text{NO}_2} e^{-\left(k_{\text{rx}} \Delta t\right)} \left[\text{NO}_2\right]_0 \Delta t S[\text{OH}]_{\text{ref}}
\]

(S13)

Thus, using measured sample pressures, time delays, ratios of OH signals, and literature values for the absorption cross-sections \(\sigma^{\text{NO}_2}\) and \(\sigma^{\text{CH}_3\text{OOH}}\) (S8, S22), allows us to determine \(k_7 I\). Repeating this procedure for several different starting water concentrations then allows us to make a plot of the pseudo-first-order reaction rate constant \(k_7 I\) versus the H₂O concentration, as shown in Fig. 2 of the main text. The slope of this line yields the bimolecular rate constant \(k_7\) to be \(1.7 \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹. The linear dependence of the OH production rate on water concentration as well as the NO₂* concentration, inferred from the power dependence, is again consistent with the OH being formed from the NO₂* + H₂O reaction. The rate constant for reaction-7 was measured at several different wavelengths over the 560 to 640 nm interval and found to be similar.

Our measured value for the rate constant is roughly a factor of ten larger than that
estimated by Crowley and Carl (S11), who based their estimate on their detection sensitivity and their inability to detect OH from the NO$_2^*$ + H$_2$O reaction upon excitation at 532 nm.

There are several potential complications associated with working in the short time limit that is worth commenting. First, the rate may be affected by incomplete relaxation of the OH product internal state distribution. In order to check if this factor was influencing our rate results we also carried out additional rate measurements under near “nascent” conditions where we determined the rate by summing the LIF signal over the entire distribution of OH product internal states in both its ground and first excited vibrational level. This alternate procedure gave rates also in good agreement with those obtained using high-pressure method described above. The second potential complication has to do with formation of vibrationally excited water molecules (H$_2$O$^+$) through rapid collisional energy transfer from NO$_2^*$ to water and the subsequent bimolecular reaction of these vibrationally excited water molecules with the remaining NO$_2^*$. The linear dependence of the OH signal on the NO$_2$ excitation laser power suggests that this channel is minor as production of OH through this mechanism requires in effect two NO$_2^*$ molecules and hence a squared dependence on the excitation laser power. However, we have seen evidence of vibrationally excited OH being formed in the region of 620 nm, which based on energetic grounds, we attribute to reactions involving vibrationally excited water molecules. The formation of OH(v=1) states is not energetically possible from the reaction of ground state water molecules and NO$_2^*$ in the 620 nm wavelength region; they can however form if additional energy associated with vibrationally excited water is present. Based on the measured OH(v=1) population, we estimate the
contribution from this secondary reaction to be ~15-20%. Combining the uncertainty in
the NO$_2^*$ collision quenching rate along with estimated contributions from secondary
chemistry, we approximate the uncertainty in our measured rate for the NO$_2^*$ + H$_2$O
reaction to be about $\pm$ 50 \% resulting in a value for the rate to be $1.7 \pm 0.85 \times 10^{-13}$ cm$^3$
molecule$^{-1}$ s$^{-1}$. The precision of our rate data measurements, however, is substantially
better at $\pm$ 10\%. Indeed in order to test the integrity of our kinetics procedure, we also
measured rates for two other OH forming reactions, O($^3$P) + CH$_3$CH$_2$OH and O($^3$P) +
CH$_3$CHO, whose rates are known (S22, S23) and are of similar magnitude to that of the
NO$_2^*$ + H$_2$O reaction. The oxygen atoms required for these additional studies were
generated by 355 nm photolysis of NO$_2$ and the dissociation of CH$_3$OOH was again used
as our reference reaction. The fact that we were able to get good agreement (within $\pm$
10\%) with the known rate constants for both these calibration reactions using a kinetics
procedure analogous to the one described for NO$_2^*$ + H$_2$O, provides support for the
suitability of the method used.
References:


S20. For example excitation at 560 nm corresponds to an excess energy of \(~3940\) cm\(^{-1}\). The average amount of energy transferred per collision when NO\(_2\) collides with NO\(_2^*\) in this energy range is expected to be \(~700\) cm\(^{-1}\)/collision \((S16)\). Thus, roughly 6 collisions are required to terminate the reaction. Dividing the Lennard-Jones collision rate by this number then gives a rate constant of \(~7 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). This rate constant is similar in magnitude to the fluorescence quenching rate constant used. Similar results are also found for N\(_2\) colliding with NO\(_2^*\) using values of \(~200\) cm\(^{-1}\)/collision \((S16)\).


Supplementary Figure captions:

Figure S1: a) Action spectrum of HONO in the region of its $5v_{OH}$ vibrational band. b) Action spectrum of HONO$_2$ in the region of its $5v_{OH}$ vibrational band. c) Spectrum of the NO$_2$ + H$_2$O reaction mixture over the same spectral range (spectra were taken with the delay between the excitation and probe lasers set at 20 ns).

Figure S2: Dependence of OH signal from the NO$_2^*$ + H$_2$O reaction on the excitation laser pulse energy for two selected wavelengths. The x-intercepts in the graph are likely due to electronics and is found to be higher at the bluer excitation wavelength where a greater amount of NO$_2^*$ fluorescence leaks through the filters. The slopes of the two lines shown do not scale as the ratio of NO$_2$ absorption cross sections for their respective wavelengths since the power dependence measurements were not done under identical sample concentrations.

Fig. S3. Comparison of NO$_2$ spectra: a) absorption, b) photoacoustic and c) action spectrum. The action spectrum is obtained by monitoring the indicated OH product quantum state as a function of the excitation laser wavelength. The reference NO$_2$ absorption spectrum is from the HITRAN database (S7).

Figure S4: The absorption spectrum of NO$_2$. Excitation at $\lambda<420$ nm results in photodissociation while excitation at longer wavelengths produces long-lived
electronically excited NO$_2$ due to vibronic mixing between ground and excited electronic states.
OH LIF signal

Wavelength, $\lambda$ [nm]

(a) HONO (5$\nu_{OH}$)

$0\nu_{OH} \rightarrow 5\nu_{OH} \rightarrow \text{OH}^* \rightarrow \text{OH + NO}$

$\lambda_{Ex}$

(b) HONO$_2$ (5$\nu_{OH}$)

$0\nu_{OH} \rightarrow 5\nu_{OH} \rightarrow \text{OH}^* \rightarrow \text{OH + NO}_2$

$\lambda_{Ex}$

(c) NO$_2^*$ + H$_2$O

Fig. S1 Li et al.
\[ y = m \times + b \]

- \( m_{\lambda=590} = 14.3 \)
- \( b_{\lambda=590} = -35.5 \)
- \( m_{\lambda=565} = 12.7 \)
- \( b_{\lambda=565} = -61.0 \)

Fig. S2 Li et al.
Fig. S3 Li et al.

a) Hitran

b) Photoacoustic

c) OH [v=0, Q_1(2)]
\[
\begin{array}{c}
\text{Wavelength, } \lambda \ [\text{nm}] \\
250 \quad 300 \quad 350 \quad 400 \quad 450 \quad 500 \quad 550 \quad 600 \quad 650
\end{array}
\]

\[
\begin{array}{c}
\text{Cross-section, } \sigma \ [10^{-19} \text{ cm}^2 \text{ molec.}^{-1}] \\
1 \quad 3 \quad 5 \quad 7 \quad 9
\end{array}
\]

\[
\begin{array}{c}
\text{NO + O}^{3\text{P}} \quad \text{NO}_2^{*}\\
\tau_{\text{NO}_2^{*}} \sim 40 - 60\mu\text{sec.}
\end{array}
\]