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Evidence for New Sources of NO_x in the Lower Atmosphere

Edward C. Zipf* and Sheo S. Prasad

Laboratory studies show that the reaction of short-lived $\text{O}_2(\text{B}^3\Sigma_u^-)$ molecules (lifetime ~ 10 picoseconds) with N_2 and the photodissociation of the $\text{N}_2:\text{O}_2$ dimer produce NO_x in the stratosphere at a rate comparable to the oxidation of N_2O by $\text{O}(^1\text{D})$. This finding implies the existence of unidentified NO_x sinks in the stratosphere. The NO_2 observed in this experiment is isotopically heavy with a large $^{15}\text{N}/^{14}\text{N}$ enhancement. However, photodissociation of this NO_2 unexpectedly produced NO molecules with a low $^{15}\text{N}/^{14}\text{N}$ ratio. The diurnal odd-nitrogen cycle in the stratosphere will be marked by a complex isotope signature that will be imprinted on the halogen and HO_x catalytic cycles.

Recent atmospheric measurements suggest that the total O_3 removal rate in the stratosphere is determined chiefly by the HO_x and halogen catalytic cycles whose relative roles are controlled by the NO_x abundance (1). A key conclusion of this work is that the loss rate of ozone decreases with increasing NO_x loading in the lower stratosphere. It is therefore important to identify the sources and sinks of odd-nitrogen in the stratosphere and troposphere whose interplay determines the local NO_x abundance. Here, we report laboratory experiments showing that the photoexcitation of $\text{O}_2(\text{B}^3\Sigma_u^-)$ molecules and short-lived collision complexes or weakly bound $\text{N}_2:\text{O}_2$ dimers by the absorption of solar Schumann-Runge (SR) and Herzberg band and continuum radiation is an efficient source of NO/NO_2 in the stratosphere and possibly in the troposphere.

Figure 1 shows a diagram of the ultrahigh vacuum (UHV) system used in the photolysis experiment (2). Substantial amounts of

N_2O and NO_x can be produced in the photolysis cell by a variety of processes that occur when synthetic air or O_2/N_2 mixtures (3) are irradiated with ultraviolet (UV) and vacuum ultraviolet (VUV) continuum radiation from a deuterium arc lamp (wavelength $\lambda = 175$ to 400 nm), an argon flash lamp ($\lambda_{\text{cutoff}} \sim 115$ nm), or by Hg resonance line radiation ($\lambda = 184.95$ nm) (4). The photolysis experiment included a Zeeman-scanned, oxygen absorption filter (5). This device could be used to modify the incident continuum radiation by selectively absorbing individual rotational lines of the SR bands ($\text{B}^3\Sigma_u^- \leftarrow \text{X}^3\Sigma_g^-$) from the input continuum flux while observing the effects of this subtractive process on the N_2O , NO_x , and O_3 production and loss rates.

Although the N_2O and NO_x production rates observed in this experiment were large ($\sim 1 \times 10^{11}$ to 10×10^{11} molecules per second), the equilibrium mixing ratio of these species in the photolysis cell was small (< 10 parts per billion by volume) because we used short irradiation times (< 120 min) and a large photolysis cell to minimize wall effects. To increase the sensitivity of the apparatus, we cryogenically concentrated the N_2O and

NO_x in a liquid N_2 trap (-195.8°C). The trapped NO and NO_x were subsequently separated by distillation at -100°C . We determined the efficiency of this transfer technique by introducing a 10-cm^3 sample of a standard mixture into the absorption cell directly from a calibration loop. The amount of nitrogen oxide (or oxides) in this sample was typically 1×10^{14} molecules. These tests showed that the retrieval efficiency was generally $> 95\%$; no significant wall losses were observed on the short time-scale of the irradiation experiment.

We measured the isotope composition of the NO_x in these small samples (< 2 nmol) with an Extrel quadrupole mass spectrometer (QMS) (1.59-cm diameter poles). The QMS was fitted with a high-efficiency electron-impact ionizer that had been developed specifically to measure the ionization cross sections of radicals and reactive atomic gases present in a source gas with a very small mixing ratio (6–8). QMS measurements of the NO/NO_2 mixing ratios showed that efficient production of NO_x occurred in the photolysis cell when air was irradiated by Hg (185 nm) radiation or by a filtered D_2 lamp (210 to 400 nm). The NO_2 yield varied linearly with the irradiation time (at fixed pressure and light intensity) (Fig. 2). These data represent a lower limit on the total NO_x production because some of the primary NO_x is converted into unmeasured higher nitrogen oxides (for example, N_2O_5) as by-products of secondary reactions and cryogenic cooling.

Surface reactions are unlikely to be the primary source of the observed NO_x because (i) no NO_x formation was observed under dark conditions; (ii) the irradiated surfaces were limited to the MgF_2 windows, which are too small in area to synthesize the observed NO_x even if we assumed that irradiated surfaces were able to do so; and (iii) although atomic oxygen is present in the system in nonnegligible amounts (at least in

E. C. Zipf, Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260, USA.
S. S. Prasad, Creative Research Enterprises, Post Office Box 174, Pleasanton, CA 94566, USA.

*To whom correspondence should be addressed.

Fig. 1. Block diagram of the UHV vacuum system used in the photolysis experiment. V, S, and P represent a UHV valve, servo-controlled leak valve, and an MKS Baratron pressure gauge, respectively.

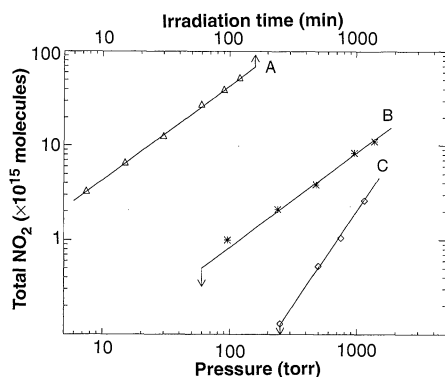
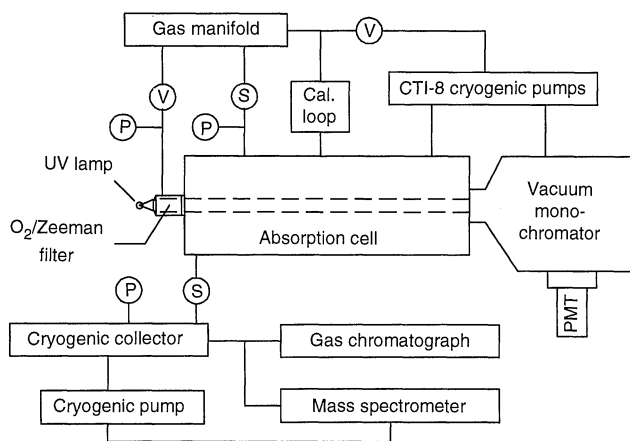


Fig. 2. Plot showing the linear growth of ($\text{NO}_2 \times 100$) with time (A) when synthetic air (500 torr) was irradiated with continuum radiation from a D_2 arc lamp (210 to 400 nm) and its linear (B) and quadratic (C) pressure dependence when air was irradiated for 120 min with Hg (185 nm) and D_2 (210 to 400 nm) radiation, respectively.

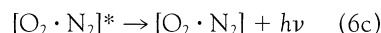
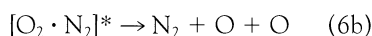
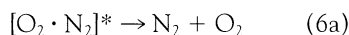
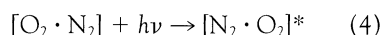
the lower pressure regime) and is capable of producing N_2O by surface reactions, it probably does not produce NO heterogeneously because it is difficult to break the triple $\text{N} \equiv \text{N}$ bond of N_2 under our experimental conditions (9). Furthermore, the change in the pressure dependence of the NO_x production with the change of the wavelength of the irradiating photons (Fig. 2) also makes surface reactions unlikely as the primary source. Secondary reactions involving the oxidation of N_2O by $\text{O}(^1\text{D})$ can also be ruled out in the long-wavelength experiments because there was no N_2O present when the filtered D_2 lamp was used. For the 185-nm source, N_2O was produced in our experiment and in other similar photolysis studies [for example, (10)]. However, in our experiment, there was no evidence on the basis of growth-curve data that any N_2O was destroyed. Thus, the NO_x production is most likely linked to gas phase photochemistry of O_2/N_2 mixtures irradiated by SR and Herzberg band photons.

Although both radiation sources produced NO_x , the results imply that the for-

mation mechanisms and kinetics were different. For example, at $\lambda = 185$ nm, radiation is absorbed by O_2 on the shoulder of the $J = 11$ rotational line of the $(0 \rightarrow 8)$ SR band (R branch). The magnitude of the SR absorption cross section for the O_2 monomer at 185 nm is known (11). Our data imply that, under these conditions, chemical reactions involving N_2 and short-lived (10 to 100 ps) $\text{O}_2(\text{B}^3\Sigma_u^-)$ molecules with 5 to 6 eV of electronic energy produce N_2O efficiently, confirming the earlier observations of Maric and Burrow (10). Using the Zeeman-scanned oxygen filter, we found that discrete absorption of SR-band radiation was also involved in the NO_2 synthesis when short-wavelength sources (< 200 nm) were used, but it was not clear from these experiments whether the initial NO formation was from $\text{O}_2(\text{B}^3\Sigma_u^-)$ reactions with N_2 as in the case for N_2O synthesis,



or due to absorption by O_2 molecules in the weakly bound N_2O_2 dimer (16) or in a short-lived collision complex,



where $h\nu$ is a photon of light.

From the measured activation energy of the reverse reaction $\text{NO} + \text{NO} \rightarrow \text{N}_2 + \text{O}_2$ (12), it can be shown that reaction 3 can occur only at the short wavelengths used in the present photolysis experiment. Reactions 4 to 6 are possible at longer wavelengths where the complexation process can affect the chemistry by altering the energetics of the reaction (13) and by al-

lowing new bonds to form that would not be likely in a conventional bimolecular reaction (14, 15). The reactions $\text{O}_{\text{fast}} + \text{N}_2 \rightarrow \text{NO} + \text{N}$ and $\text{N}_2(\text{A}^3\Sigma_u^-) + \text{O} \rightarrow \text{NO} + \text{N}$ can be shown to be negligible because the oxygen atoms formed in the present experiment lack the required center of mass kinetic energy and $\text{N}_2(\text{A}^3\Sigma_u^-)$ molecules are not formed by 185-nm absorption. The possible reaction $\text{O}_2(\text{B}^3\Sigma_u^-) + \text{N}_2 \rightarrow \text{N} + \text{NO}_2$ is practically indistinguishable from reaction 3, in the present context of net NO_x yield, because of the ultimate conversion of N to NO by way of $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$.

The NO formation rate, $\eta(\text{NO})$, from the O_2^* and $[\text{N}_2 \cdot \text{O}_2]^*$ mechanisms, can be written as

$$\eta(\text{NO}) = 2\Phi_0 \int_0^z e^{-\sigma_{\text{O}_2} n(\text{O}_2)z} \sigma_{\text{O}_2} n(\text{O}_2) \frac{k_3 n(\text{N}_2)}{A_8} dz \quad (7)$$

and

$$\eta(\text{NO}) = 2\Phi_0 \int_0^z e^{-\sigma_{\text{O}_2} n(\text{O}_2)z} \sigma_d K_{\text{eq}} n(\text{O}_2) n(\text{N}_2) \varpi dz \quad (8)$$

where Φ_0 is the incident flux from the lamp, σ_{O_2} and σ_d are the O_2 and $\text{N}_2 \cdot \text{O}_2$ dimer absorption cross sections, K_{eq} is the dimer equilibrium constant (16), $n(X)$ is the number density of species X, k_n is the rate coefficient for reaction n, and ϖ is the branching ratio, $(A_5/\Sigma A_i)$. A_8 is the total transition probability of the $\text{O}_2[\text{B}^3\Sigma_u^-(v' = 8)]$ state. Radiative decay, predissociation, and collisional line-broadening effects (17, 18) contribute to the transition probability: $A_8 = [(5 \times 10^7) + (1.55 \times 10^{11}) + (9.2 \times 10^{-10})n(\text{N}_2)] \text{ s}^{-1}$. Both Eqs. 7 and 8 yield nearly linear pressure dependences after integration over z under optically thick experimental conditions where all of the incident photons are absorbed in the reaction chamber. Process 3 ultimately saturates at very high pressures when collisional quenching finally dominates predissociation. The predicted linear behavior is observed for the 185-nm source (Fig. 2, line B). If process 3 is assumed to dominate the NO production, then our data show that $k_3 \sim 1 \times 10^{-11}$ to $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. However, if it is assumed that dimer absorption of the 185-nm radiation is the dominant NO source, then our data are consistent with $\varpi \cdot (\sigma_d/\sigma_{\text{O}_2})_{185 \text{ nm}} \sim 0.3$, assuming the theoretical value for K_{eq} (16).

In the filtered D_2 lamp experiments, small concentrations of O atoms and metastable $\text{O}_2(\text{A}^3\Sigma_u^-, \text{A}^3\Delta_u, \text{c}^1\Sigma_u^-)$ molecules were formed from optical pumping of O_2 by the

Herzberg continuum and the forbidden triplet bands, respectively. The excitation rates for these processes can be calculated from known oscillator strength values (19, 20) and a knowledge of the D_2 lamp's spectral intensity. The experiment shows that neither monomer process was a factor in producing the observed NO_x because (i) the continuum excitation rate for O_2 is too small by at least two orders of magnitude, (ii) it creates O atoms with insufficient kinetic energy, and (iii) the NO yield from O_2 metastable chemistry is pressure independent at very high pressure and is linear at moderate to low pressures. A quadratic pressure dependence is actually observed (Fig. 2, line C). These developments suggest that the NO_x production in the D_2 lamp experiments was chiefly a result of $N_2 \cdot O_2$ dimer photochemistry, which does have a NO_x quantum yield that varies as p^2 under optically thin conditions. It is likely that the NO_x quantum yield for the dimer process was strongly wavelength-dependent with both discrete and continuum components.

The dimer photochemistry results in an unusual isotope signature. Because ozone is produced efficiently in the photolysis chamber [$n(O_3) \sim 1 \times 10^{13}$ to $10 \times 10^{13} \text{ cm}^{-3}$], we could not observe the primary NO as it is formed because it reacts rapidly with O_3 to form NO_2 . This NO_2 is isotopically heavy with $\delta^{15}N \sim +150\%$ and $\delta^{18}O \sim +30\%$. We could not determine whether the initial NO is formed heavy or if the NO_2 enrichment occurs in the NO reaction with O_3 . When the heavy NO_2 photodissociated, the newly formed NO molecules had a $\delta^{15}N \sim -100\%$, a shift, $\Delta(\delta^{15}N)$, of -250% . Similar shifts were observed when commercially prepared NO_2 was photodissociated; the industrial NO_2 is not significantly enriched in ^{15}N relative to air. These results imply that as NO and NO_2 are cycled by the sun during the normal diurnal cycle, their photochemistry will be accompanied by large changes

in the $^{15}N/^{14}N$ ratio. The isotope fingerprint of the dominant odd-nitrogen catalytic cycle will be imprinted on other species (for example, $ClONO_2$, HNO_3).

The estimated NO formation rates in the lower stratosphere due to $O_2(B^3\Sigma_u^-)$ /dimer photochemistry are comparable to that of NO production from N_2O oxidation by $O(^1D)$ (21) (Fig. 3) if the rate coefficient, k_3 , measured at 185 nm is representative of the entire SRB band system. Continuum UV ($\lambda = 175$ to 200 nm) measurements support this view. The model calculation also includes a contribution from the photodissociation of the dimer in the Herzberg continuum in the 175- to 200-nm range, assuming a quantum yield of 2×10^{-4} and using the cross-section data of Shardanand (22). The NO_x production associated with long-wavelength sources (210 to 400 nm) may extend this source to much lower altitudes depending on the as yet unknown spectral characteristics of this NO_x source mechanism (or mechanisms). These findings imply that there are additional, unidentified NO_x sinks because atmospheric models (23) already overestimate the NO_y in the stratosphere even without the new source (or sources). The isotope signature of this new process may aid in the identification of the missing NO_x sink (or sinks).

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2. To minimize hydrocarbon or water vapor contamination (or both), we constructed the photolysis chamber (17.3 liters, 21 cm diameter by 50 cm long) and the supporting gas manifold using stainless steel components that were passivated by a proprietary electropolishing technique (Quantum Mechanics) that reduced the surface outgassing to less than 3.2×10^6 molecule $s^{-1} \text{ cm}^{-2}$ at 298 K. Gold-plated OFC copper gaskets were used in the construction of the apparatus to ensure high-quality seals and to minimize surface reactions with the gasket material. The MgF_2 windows were also sealed to UHV standards and could be baked to 400°C . The entire apparatus was evacuated by three oil-free CTI-8 cryogenic pumps. After a 24-hour bakeout, the system background pressure was $<1 \times 10^{-8}$ Pa. Mass spectrometer measurements with blank tests that lasted as long as 2 years showed that H_2 was the principal gas released by the treated surface.
3. The O_2 and N_2 mixtures used in this investigation were prepared with research-grade oxygen (99.999%) and nitrogen (99.9995%). The N_2 was purified further by passage of the gas through a heated chemical getter and a Supelco OMI-1 purifier containing Nanochem. Both gases were finally passed through a molecular sieve column that had been baked under vacuum at 400°C for 24 hours and then cooled to -160°C by immersion in an isopentane-liquid nitrogen slurry. The residual N_2O/NO_x mixing ratio in the system was generally <10 parts per trillion by volume.
4. The stability of the lamps, their emission spectrum, and the percentage absorption of the continuum radiation were monitored by an Acton 505VB monochromator mounted on the absorption chamber directly opposite the collimated light source. A

Hamamatsu R1259 photomultiplier tube was used as a detector. The monochromator was evacuated and viewed the incoming light beam through a MgF_2 window so that spectral observations down to $\lambda = 115$ nm were possible. The D_2 lamp was calibrated by Optronics with an absolute accuracy traceable to National Institute of Standards and Technology (NIST) of $\pm 10\%$. A NIST-calibrated VUV photodiode was used to calibrate the vacuum monochromator and to measure the absolute VUV flux emitted by the argon flashlamp. This system was also used to monitor the ozone concentration during the photolysis experiment from $\lambda = 250$ nm absorption measurements.

5. The absorption filter consisted of a UHV cell with MgF_2 windows and a path length of 2.5 cm that was evacuated by a CTI-8 cryogenic pump. The filter could be filled with O_2/N_2 mixtures whose composition and pressure could be adjusted, so that the degree of absorption and the extent of pressure broadening could be controlled. A magnetic field with a strength of up to 8800 G could also be applied to the O_2 filter in a direction perpendicular to the optical path in order to modify the transmission of the filter by splitting and shifting the rotational levels of the absorbing gas due to the Zeeman effect.
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7. To maximize the ionization probability, we focused the electron beam onto a small spot, the size of which matched the diameter of the molecular beam effusing from the cryo-trap (~ 1 mm). The energy of the electron beam could be programmed over an energy range (15 to 1000 eV) to facilitate the analysis of fractionation patterns. The ions were focused by an Einzel lens system into the QMS, detected by an off-axis MM-1 charged particle multiplier, counted, and coherently summed. The 300-MHz pulse counting system was overlapped at counting rates $>10^7$ Hz by an electrometer that extended the effective dynamic range of the QMS an additional six orders of magnitude; single-ion detection was feasible.
8. We used NIST SRM standards to calibrate the QMS system in accordance with the same comparative protocol widely adopted in gas chromatography. No detailed knowledge of the molecular, electron, or photon beam was required in this approach. However, careful control of the flow rate, pressure differentials, and other variables was essential to achieve a high precision in the cross-calibration and in the photolysis experiment.
9. Under special conditions some surfaces can catalytically break the $N \equiv N$ bond; for example, an iron-alumina catalyst forms NH_3 in the Haber-Bosch process at very high gas pressures (200 to 600 atm) and temperatures ($\sim 500^\circ\text{C}$). These conditions did not exist in this experiment.
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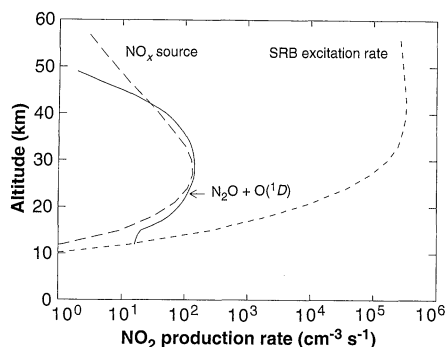


Fig. 3. Plot showing the excitation rates for the SR bands at midlatitude for a solar zenith angle of 0° and the predicted NO formation rate due to $O_2(B^3\Sigma_u^-)$ /dimer photochemistry compared with NO production from N_2O oxidation by $O(^1D)$ (21).