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# Surface-Catalyzed Production of NO from Recombination of N and O Atoms

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**An experimental method has been developed that uses laser-induced fluorescence detection of N atoms to monitor NO formation from a surface-catalyzed reaction on quartz. Well-characterized mixtures of N and O atoms were generated through NO titration of N atoms produced in a microwave discharge. Experiments were carried out in a diffusion reactor designed for measurement of atom recombination coefficients on surfaces exhibiting low catalytic activity. The results have shown that a significant concentration of NO is generated in the room temperature reaction of N and O atoms on quartz surfaces. This work has demonstrated that N- and O-atom recombination on surfaces cannot be treated independently.**

## Nomenclature

$C_0$ = initial atom concentration
$C(x)$ = atom concentration at distance $x$
$k$ = concentration decay constant
$x$ = distance down the reactor sidearm

## Introduction

ATOM recombination on surfaces contributes to the heating of thermal protection materials during high-speed vehicle re-entry. Because the Earth's atmosphere is made up of O- and N-atom-containing species, recombination of these atoms is dominant in terrestrial re-entry. Experimental data on temperature-dependent surface-catalytic reactions are essential to the development of lighter-weight thermal protection materials and future vehicle designs for entry spacecraft. Current computational models for surface heating rates on entry spacecraft assume that the thermal protection material is fully catalytic, this may add a significant unjustified heat load to the vehicle. Because many thermal protection systems (TPS) exhibit low catalytic activity, TPS sizing requirements are overestimated in current designs.[1-3] If reliable atom recombination coefficients and kinetic data were readily available for input into the computational models, more reasonable sizing estimates could be made with minor modifications to the existing computer codes.

Up to this point, most of the catalysis research in the laboratory focuses on Earth entry vehicles and surface reactions encountered in a one-component system containing only O or N atoms. In computer codes developed to account for reduced-surface-catalytic activity, only recombination resulting in formation of $O_2$ or $N_2$ is considered. Although this reduces the number of specified parameters, it ignores the potential importance of the surface-catalyzed $N + O \rightarrow NO$ reaction. Under conditions where $N_2$ is highly dissociated, NO is expected to be a major product of catalysis. It is important to understand the reaction dynamics for the formation of all three products $O_2$, $N_2$, and NO, because the maximum energy that can be released to the surface is different for each reaction $E(O_2) \sim 5$ eV, $E(N_2) \sim 9$ eV, and $E(NO) \sim 7$ eV. In this work, a system containing a mixture of both N and O atoms is examined to study the interaction between these two important species. Titrations of nitrogen atoms produced in a microwave discharge in $N_2$ with NO will generate well-characterized mixtures of O and N atoms. The interaction of this mixed system with a quartz surface at room temperature is investigated.

The authors are unaware of any experimental data in the literature that addresses this interaction under gas-phase pressure and compositional conditions similar to those present during Earth re-entry. However, mass spectrometry experiments carried out in low Earth orbit (LEO) have detected small amounts of NO formed from the reaction of N and O atoms on the metal surfaces of a spectrometer inlet.[4] If a large number of N atoms are present in the gas phase then NO disappears in the fast reaction $NO + N \rightarrow N_2 + O$.[5] In the LEO experiments, the ability to detect any NO in the gas phase is attributed to the fact that the ratio of N to O atoms is extremely small. For high N to O atom concentration ratios, it is not possible to directly detect NO produced from surface catalysis and this is the primary reason why no kinetic data is available for high-speed Earth entry conditions.

Crucial to this study is a detection technique that is species selective and can distinguish between O and N atoms along with possible recombination products like NO. Previous diffusion reactor studies have used a thermocouple to monitor atom concentrations by the heat generated in the recombination. In a two-component system this procedure is no longer sufficient because of its inability to distinguish between the two atom reactants and reaction products.[6] Two-photon laser-induced fluorescence (LIF) has been applied as a detection method for both N and O atoms, and one-photon LIF as an NO monitor. LIF is species selective, extremely sensitive, and has good spatial resolution. Applying these methods to a prototypical diffusion reactor is a significant component of this work.

## Experimental

### Apparatus and Technique

The diffusion/flow reactor used for this work is shown in Fig. 1 and is described in detail elsewhere.[7,8] A microwave

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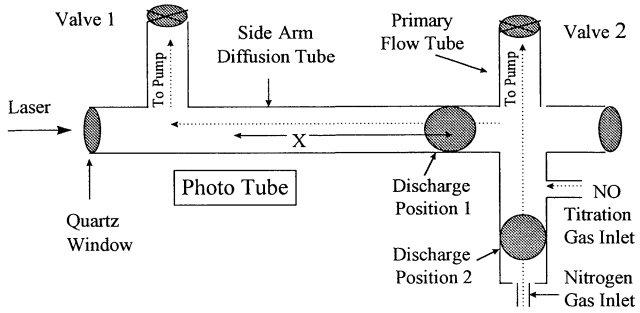

**Fig. 1 Schematic diagram of quartz reactor designed in a tee-shaped configuration. Dashed arrows refer to gas flow direction and X represents the distance between the discharge or the tee and the detector.**

discharge dissociates a fraction of the $N_2$ molecules to create N atoms. The microwave cavity can be mounted in the tee-shaped system at several positions as shown in Fig. 1. Experiments are performed with the cavity attached on the diffusion sidearm (30 cm from the tee) and also on the upstream end of the primary flow tube (25 cm below the tee). The atoms diffuse down a 22-mm (i.d.), 80-cm-long, dead-end sidearm tube where they recombine on the walls that are fabricated from the material of interest (quartz walls in this case). At steady state, a decaying atom concentration profile is established down the length of the sidearm tube. Under proper experimental conditions, uniform temperatures, surfaces with low catalytic activity, negligible gas-phase recombination, and first-order surface recombination, this concentration profile is well represented as an exponential decay in the atom concentration

$$C(x) = C_0 \exp(-kx) \tag{1}$$

Here, $x$ is the distance from the discharge when the discharge is on the sidearm or the distance from the tee when the discharge is on the primary flow tube. $C$ and $C_0$ represent the concentration at any position in the reactor and the initial concentration, respectively. The concentration decay constant is represented by $k$ and the atom recombination coefficients can be extracted from this decay constant as described in Refs. 7 and 8.

When the discharge is placed on the main flow tube, other gases can be added to the discharge products to reactively generate atomic species or to titrate the atoms to obtain absolute concentrations. By dissociating $N_2$ in the discharge and adding NO downstream in the flow tube, known mixtures of O and N atoms can be generated. The reaction of N + NO is rapid ($\sim 3 \times 10^{-11}$ $cm^3$ $s^{-1}$) and generates one O atom for each NO added.[5] At the concentrations and flow rates used for this work, the reaction is essentially complete within a few centimeters. The reaction O + NO is not energetically favorable and therefore does not occur in this system. By injecting increasing amounts of NO, the ratio of O atoms to N atoms can be monotonically increased until all of the N atoms are consumed and only O atoms remain. This condition is defined as the titration endpoint. By accurately measuring the amount of NO added at the tiration endpoint, the absolute concentration of N atoms generated in the discharge can be determined. Further addition of NO will result in excess NO appearing in the gas stream. Thus, the titration endpoint can be determined by either detecting the complete disappearance of N atoms or the appearance of NO in the gas stream. The latter is the most direct, obvious, and sensitive indication of the endpoint.

Three-body reactions in the gas phase are sufficiently slow that they are negligible in the pressure range of these experiments (0.1–0.5 torr).[7,8] Thus, downstream of the NO injection point, surface reactions are the only processes that can change the N- and O-atom concentrations. If the reactor is switched into flow-tube mode, i.e., valve 1 opened and valve 2 closed (Fig. 1), and if the pumping speed is sufficiently high, even surface reactions will be too slow to change the gas-phase composition. Measurements of N- or O-atom concentrations in the sidearm should then give values identical to the concentrations established at the NO injection point. If the reactor is configured in the diffusion mode (valve 1 closed and valve 2 opened) and the only surface reactions are O + O and N + N that proceed independently and according to Eq. (1), then concentration measurements at a fixed location in the sidearm should give values smaller than, but still directly proportional to, the composition established at the injection point, i.e., $\exp(-kx)$ is a constant. Deviation from direct proportionality is an indication that either the O + O and N + N recombination rates are not independent or that additional surface reactions are present. If the $N + O \rightarrow NO$ surface recombination reaction occurs, deviation from direct proportionality could be expected by the following mechanism. NO produced on the surface desorbs and then undergoes the same rapid gas-phase reaction, $NO + N \rightarrow N_2 + O$, exploited in the titration. This process consumes another gas-phase N atom and regenerates the gas-phase O atom that is consumed at the surface to produce NO. Thus, a greater concentration of O atom and a reduced concentration of N atom is created, and atom concentration measurements made in the sidearm would not have a constant proportionality to the concentrations established at the NO injection point. The experiments reported here have been designed to test for NO surface production by monitoring the N-atom concentration in the gas phase as a function of the O-atom concentration created at the injection point (or, equivalently, as a function of the NO added at the injection point).

### Species Detection

Two-photon LIF is used to monitor the concentration of N atoms in the diffusion reactor. In this experimental method, laser radiation near 211 nm excites N atoms from the $2p^3\ {}^4S^0$ ground state to one of the four fine-structure components of the $2p^2 3p\ {}^4D^0$ state. After excitation, the N atoms will fluoresce near 870 nm to the $2p^2 3s\ {}^4P$ state. This method was developed earlier[9,10] and the details of the collisional energy transfer in the excited electronic states have been studied extensively over the past 14 years.[11,12] The radiative lifetime of the ${}^4D^0$ state is 43 ± 3 ns as measured by Copeland et al.[11] The collisional removal and transfer between the fine structure states is rapid in collisions with $N_2$. The $N_2$ removal-rate constant is $(4.6 \pm 0.6) \times 10^{-10}$ $cm^3$ $s^{-1}$, and at 0.3 torr this process accounts for a decrease of 15% because of quenching of the fluorescence. Collisional processes involving atoms are insignificant because the atom concentrations are very low when compared to the rapid collider $N_2$. From NO titration measurements the approximate N-atom concentration is determined via titration to the NO endpoint. The concentration varies between 0.4 and 0.7 mtorr out of the total concentration of $N_2$ of 300 mtorr. This lack of dependence of the rates of gas-phase collisional processes on atom concentration is important in converting the signal profiles directly into relative concentration profiles.

For these experiments, a 40-cm focal length lens focuses the frequency-doubled output of an excimer-pumped dye laser into the cell. The visible radiation near 422 nm is separated from the doubled light using a series of dichroic mirrors. Because no wavelength dispersive elements are used in the optical train, the wavelength of the excitation light can be scanned without movement of the excitation beam. During the experiments the laser energy is monitored. The N-atom fluorescence from the focal region is detected at right angles to the input beam through the side wall of the tube with a filtered (combination of an 800-nm-long pass filter and an 850 ± 35-nm interference filter) photomultiplier tube (PMT). The output of the PMT is amplified by a factor of 25 and sent to a gated integrator. The resolution down the tube axis is about 1 cm determined by a mask on the PMT. The spatial resolution across the tube is less than 0.5 mm.

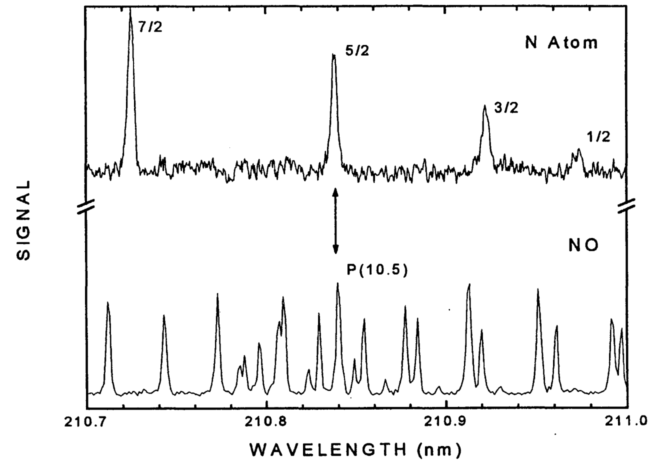

**Fig. 2 LIF excitation scan for N atoms (top) and NO (bottom).**

The upper trace in Fig. 2 shows an excitation scan over the N-atom resonance. The upper state is composed of four sublevels, 7/2, 5/2, 3/2, and 1/2 levels, where the labels refer to the total angular momentum of the state. The spacing between the lowest-lying 1/2 level and the highest-lying 7/2 level is 110.94 $cm^{-1}$. The strongest transition, which is to the 7/2 level, lies at 47,440.90 $cm^{-1}$, which is one-half the energy of the 7/2 state. The relative intensities should be 4:3:2:1 for the 7/2:5/2:3/2:1/2 levels, respectively.

A coincidental overlap is observed between the two-photon transition to the 5/2 level of the N atom and the one-photon P(10.5) rotational transition in the (2,0) vibrational band of the NO ($B^2\Pi - X^2\Pi$) system (see Fig. 2). Although the intensity of the signal from the 7/2 level of the N atom is the largest, most of this work is performed by exciting the 5/2 level because of the coincidental overlap with the NO transition. This allows excitation of both N atoms and NO simultaneously, without changing the wavelength of the excitation laser. To detect NO, fluorescence is observed with a second PMT that is filtered (255 ± 10 nm) to be sensitive in the ultraviolet for detection in the B−X system.

## Results

Preliminary experiments on a pure $N_2$ system are needed before carrying out routine experiments on the NO-titrated discharge. Profiles of the N-atom signal as a function of distance down the tube are collected by moving the PMT parallel to the sidearm while operating the reactor in the diffusion mode. An exponential decay of the N atoms is observed over a large distance in the reactor tube. This observation is confirmation of a first-order surface reaction and the measured recombination coefficient is consistent with those reported previously.[7,8] Similar data are obtained with the discharge located in both positions shown in Fig. 1.

For all titration experiments the discharge is located in position 2, shown in Fig. 1. The first titration experiment is designed to determine the behavior of the NO signal during titration when the reactor is used in the flow-tube configuration (valve 1 open, Fig. 1). This experiment is carried out to confirm that the NO signal behaves as expected in the absence of wall reactions. Figure 3 shows the N-atom LIF signal measured at a fixed location in the sidearm, as a function of added NO. The volumetric flow rate used in this experiment is 1.1 × $10^3$ $cm^3/s$ (28 ± 3 sccm at 0.31 ± 0.02 torr). Note that no NO is observed in the gas phase above the material until the N-atom titration endpoint is reached. Also, the decay of the N-atom LIF signal with increasing NO injection is linear when the reactor is used as a flow tube. As predicted, this measurement indicates that wall reactions have a negligible effect on the gas-phase concentrations over the distance between the tee and the observation region. Similar experiments were carried out over the range of volumetric flow rates from 1 × $10^3$ to 4 × $10^3$ $cm^3/s$, and the same behavior was observed.

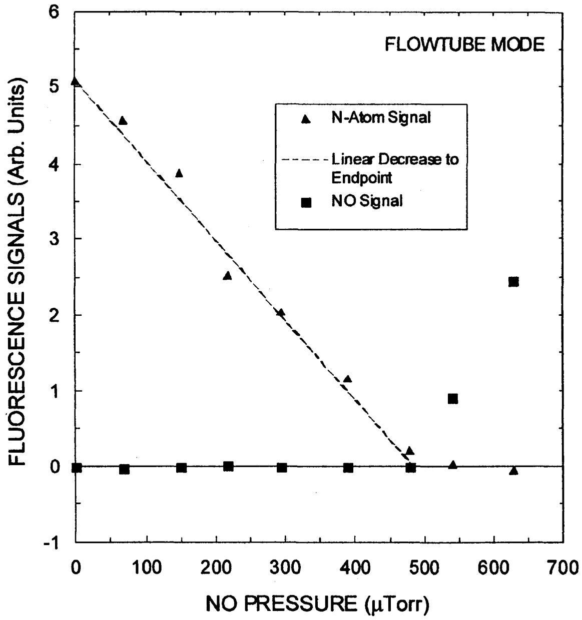

**Fig. 3 N-atom (triangles) and NO (squares) signals in flowtube mode. The dashed line shows the expected N-atom signal, assuming no surface interactions with the generated O atoms.**

The plots in Fig. 4 demonstrate the effect of surface catalysis on the N-atom signal. In these experiments the reactor is configured as a diffusion tube (valve 2 open, Fig. 1) to allow wall reactions to take place. The diffusion coefficient for N atoms in $N_2$ is 630 ± 30 $cm^2/s$ as determined from an empirical model described in Ref. 7. The volumetric flow rate used in the flowing portion of the reactor is 2.7 × $10^3$ $cm^3/s$ (95 ± 3 sccm at 0.44 ± 0.02 torr). Figures 4a and 4b show examples of the room-temperature experimental data with the LIF signal detector located at distances of 41 ± 0.5 cm and 67 ± 0.5 cm, respectively, from the center of the tee in the reactor. The figures also show the differences of the data from the profiles expected if no surface recombination occurs. In this experiment both N and NO signals as functions of added NO are observed at a specified detector position along the sidearm. If the presence of O atoms on the surface does not affect the N atoms, a linear decrease in N atoms with added NO is observed at any given distance from the tee. The dotted lines in Figs. 4a and 4b show this expected dependence. With the sidearm in the diffusion mode this expected linear dependence is not seen. This is particularly apparent in Fig. 4b because there is a significantly larger decrease in N atoms than expected from the pure $N_2$ case. Clearly, the O atoms affect the N-atom destruction on the surface.

Two scenarios could explain the data in Fig. 4b. The first, and most unlikely, is that the presence of O atoms on the surface enhanced the N + N surface recombination rate increasing the N-atom destruction. No mechanism for this type of enhancement has been previously identified. Reggiani et al.[13] showed that the presence of O atoms adsorbed on the surface blocks the N-atom active sites.[13] Thus, O atoms may actually reduce the number of $N_2$ molecules being formed by the N + N surface reaction. The more likely hypothesis for the observed N-atom decay is that N- and O-atom recombination on the surface generates NO, which then reacts in the gas phase with N atoms. Independent of any model it is concluded that N and O recombination cannot be treated independently. In future work, a two-laser experiment will be set up (one at 226 nm and one at 211 nm) to monitor the concentrations of atomic oxygen and nitrogen simultaneously. It is expected that the measured value of the O-atom concentration

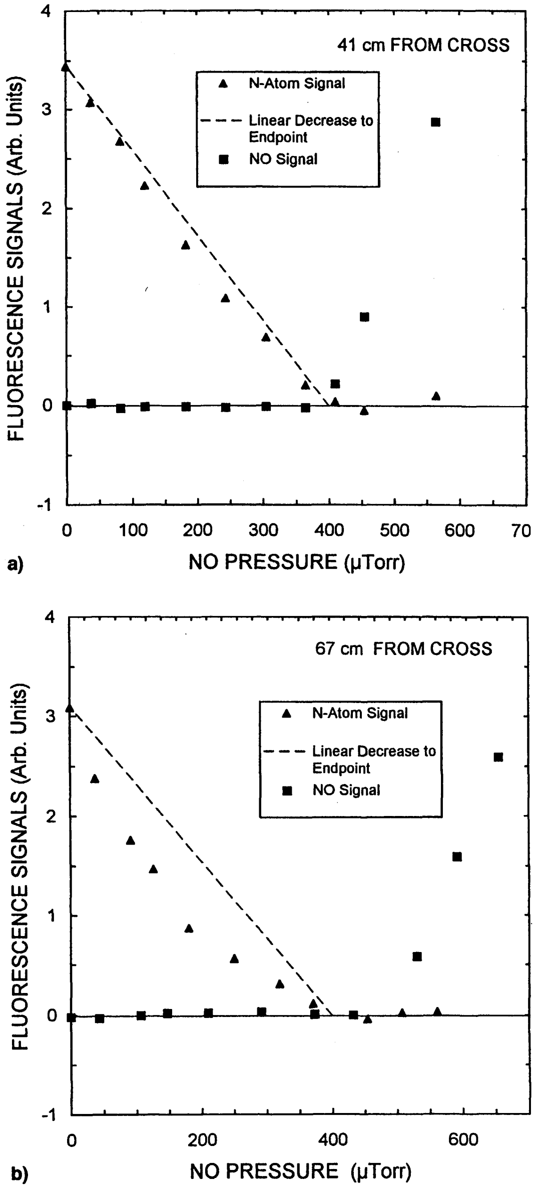

**Fig. 4 N-atom (triangles) and NO (squares) signals as a function of added NO at a position a) 41 ± 0.5 and b) 67 ± 0.5 cm from the tee.**

will increase as the N-atom concentration decreases, which will provide even more compelling evidence for this proposed surface recombination mechanism. Work is currently underway to establish a quantitative model to explain the absolute magnitude of the observed decrease in signal intensity shown in Fig. 4.

## Conclusions

This is the first laboratory evidence that demonstrates that NO formation is important in catalysis on quartz surfaces. The experimental technique developed in this work to measure surface catalytic activity is versatile in that it allows fluorescence detection to be used for monitoring specific species in a multicomponent system. With a titrated $N_2$ discharge, producing known amounts of N and O atoms, the interaction of these two species can be understood using species-specific LIF methods. Using the reactor, the N to O atom partial-pressure ratio is reproducibly controlled. This characteristic is important because the degree of dissociation of the air in the bow shock of a re-entry vehicle will be temperature dependent and data are required over a wide range of heating conditions. These preliminary studies have helped establish that N and O atoms do not act independently and that NO may be a significant reaction product in the surface-catalyzed O atom and N-atom recombination reaction at room temperature. Once the experimental procedures are optimized, numerous thermal protection materials and coatings currently available for new vehicle designs will be tested as a function of temperature and N- to O-atom concentration ratio. Studies of Martian entry conditions will also be carried out by monitoring the CO + O recombination reaction. A database will become available to correlate recombination rates of various materials with vehicle entry conditions.

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