AIP | The Journal of Chemical Physics

Surface mediated radical recombination luminescence: O+NO+Ni

Graham S. Arnold and Dianne J. Coleman

Citation: The Journal of Chemical Physics **88**, 7147 (1988); doi: 10.1063/1.454365
View online: http://dx.doi.org/10.1063/1.454365
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/88/11?ver=pdfcov
Published by the AIP Publishing

Surface mediated radical recombination luminescence: O+NO+Ni

Graham S. Arnold and Dianne J. Coleman
Chemistry and Physics Laboratory, The Aerospace Corporation, El Segundo, California

(Received 21 December 1987; accepted 25 February 1988)

Results of an experimental investigation of the chemiluminescence produced by the interaction of atomic oxygen and nitric oxide on a nickel foil surface are reported. Visible luminescence which depends linearly on the atomic oxygen and nitric oxide fluxes, on the substrate temperature, and on the substrate temperature history has been observed under conditions for which the three-body gas-phase reaction of O and NO is negligible. The intensity of the luminescence is greater than can be accounted for by the gas-phase two-body radiative recombination reaction of O and NO. The time, flux, and temperature dependences, along with the intensity of the emission support strongly the notion that the observed luminescence stems from excited species, most probably electronically excited NO_2, formed in a surface mediated reaction.

INTRODUCTION

The evolution of nonequilibrium product state distributions in surface-catalyzed reactions has been a subject of considerable interest for some time.[1–4] In addition to the fact that such processes are fundamentally intriguing, relatively recent observations of atmospheric effects on spacecraft surfaces in low Earth orbit have provided a new impetus for gaining a better understanding of the kinetics and dynamics of gas–solid reactions, particularly those involving atomic oxygen.

A spacecraft in the altitude range of 200–700 km experiences bombardment by an atmosphere whose primary constituent is neutral atomic oxygen.[5] In the 250–300 km range in which the space shuttle orbits, the atomic oxygen density is on the order of 10^9 cm^{-3}, which the 8 $km\,s^{-1}$ vehicle velocity converts to a flux of about 10^{15} $cm^{-2}\,s^{-1}$. These conditions present a regime of gas–surface chemistry which has been the subject of very little experimental investigation because of the difficulties inherent in reproducing them in the laboratory.[6] A variety of effects observed on spacecraft have been ascribed to the action of the ambient atmosphere. These include macroscopic material erosion,[7,8] degradation of optical materials,[9] and visible luminescence.[10,11]

This atmosphere-induced visible luminescence, which has become known colloquially as "shuttle glow" or "vehicle glow," appears on the space shuttle, while it is in orbit, as a tenuous red-orange layer[12] several centimeters thick[13] on windward surfaces of the vehicle. In sufficiently low orbits, it is visible to the unaided eye. Several suggestions have been put forward for the origin of this glow, including chemiluminescence from the products of surface erosion reactions,[14] direct, or sequential processes which (in the net) convert the translational energy of impact of atmospheric gases into internal excitation,[15,16] vehicle–plasma interactions,[17] and surface-catalyzed radical recombination reactions.[18–20] The implications of these various mechanisms have been discussed,[21–25] but experimental evidence remains sparse.

In the earliest published reference to an atmosphere-induced vehicle glow[18] it was hypothesized that recombination of adsorbed atmospheric O and NO to produce excited NO_2 in the gas phase was responsible for the observed visible emission. This explanation has subsequently been proposed repeatedly.[19,20] In particular, Swenson and Mende have argued for this reaction's being the origin of shuttle glow on account of an inferred negative Arrhenius behavior (in surface temperature) of the glow, which agrees with the temperature dependence of NO_2 production in mass spectrometers flow in the thermosphere.[25]

The evolution of excited products by surface-catalyzed radical recombination is a well documented phenomenon.[1] However, both Swenson and Mende[20] and Torr *et al.*[18] have suggested that for the O + NO recombination luminescence to account for the majority of the observed glows, the spectrum of the NO_2 product must be shifted compared to the spectrum obtained from three-body gas-phase recombination.[26]

The history of flow-tube investigations of surface-catalyzed reactions of O and NO is a long one, and the conclusions of various experimenters are not always in agreement. Harteck and Reeves attributed a red emission observed when O and NO were flowed over a nickel catalyst to gas-phase reaction of NO with electronically excited O_2 produced by Ni-catalyzed recombination of O atoms.[27] Thrush and co-workers[28] later suggested that a surface-catalyzed reaction of O and NO was responsible. Kenner and Ogryzlo subsequently reported[29] experiments which they believed to show that neither of these explanations was correct. They concluded that the red-orange emission in the O + NO + Ni system arose from the reaction of NO with vibrationally excited ozone formed in a sequence of steps beginning with catalytic recombination atomic oxygen.

Flow tube experiments at about 20–40 mTorr performed by Halstead *et al.* have revealed a red-orange luminescence, discernible from the three-body gas-phase emission spectrum, which they ascribe to gas-phase NO_2 produced by the nickel-catalyzed reaction of O and NO.[4] The substrate temperature dependence of the red-orange luminescence in their experiment is small and positive. Chu, Reeves, and Halstead report further work[30] which again revealed that in flow of O and NO over a nickel catalyst at 20 mTorr total pressure there is visible luminescence with ki-

J. Chem. Phys. 88 (11), 1 June 1988 0021-9606/88/117147-10$02.10 © 1988 American Institute of Physics

netic behavior consistent with both gas-phase and surface-catalyzed reactions of NO. They again concluded that the red-orange emission arose from the surface-catalyzed process.

This paper reports the first results of an investigation undertaken to search for and characterize luminescence from surface-catalyzed NO_2 production under "single collision" conditions. The second section of this paper provides a brief description of the experimental apparatus and procedures. The third section presents the observations of luminescence in the $O + NO + Ni$ system. The final two sections present a discussion and conclusions in which it is argued that the intensity and behavior of the observed luminescence are consistent with the formation of excited products from a surface mediated reaction under conditions in which preceding or subsequent gas-phase collisions are unimportant.

EXPERIMENTAL

In the experiments reported in this paper, a collimated supersonic beam containing atomic oxygen and an uncollimated effusive beam of nitric oxide were directed at a nickel surface. Luminescence resulting from the interaction of these species was detected by a photomultiplier tube viewing perpendicular to the oxygen beam, parallel to the nickel surface.

The molecular beam facility used in these experiments has been described in detail elsewhere.[6] The vacuum system, as currently configured, is comprised of three differentially pumped stainless steel chambers. The first two chambers, which are evacuated by oil diffusion pumps, provide differential pumping for the atomic oxygen source. The two pumps on the second chamber are equipped with gate valves and liquid nitrogen-cooled baffles.

The third, or experimental, uses crushed metal seals and is equipped with a high vacuum gate valve and a 570 ℓs^{-1} turbomolecular pump. The base pressure of this chamber is in the low-to-mid 10^{-9} Torr range. A quadrupole mass spectrometer mounted in the experimental chamber is used for beam source characterization and residual gas analysis.

The nickel target is mounted on a three-axis-plus-rotation precision manipulator. The target mount is equipped with a cartridge heater and target temperature is actively controlled by a proportional temperature controller using an iron–constantan thermocouple attached directly to the nickel surface. The nickel sample was a foil which was cleaned by etching in a solution of $HNO_3/CH_3COOH/H_2SO_4/H_2O$ prior to mounting in the vacuum system.

The atomic oxygen source has been described in detail elsewhere.[9,31] The source uses an extended 2450 MHz microwave cavity similar to the design of Murphy and Brophy.[32] A mixture of $He/O_2/H_2O$ (90:10:1) is discharged at 8–10 Torr to produce a beam with a velocity of about 1.4 km/s. Gas flow is regulated by a conventional rotameter. Because the source plasma produces light as well as atomic oxygen, the source nozzle is separated from the discharge region by two right angles. A "Wood's horn" at the first bend served to reduce background light further. The oxygen beam is directed normal to the target surface and delivers an atomic oxygen flux of approximately $3\times10^{15}\ cm^{-2}\ s^{-1}$. An electromechanical shutter is mounted in the second chamber to act as a "beam flag."

The apparent fractional dissociation of oxygen in the beam was calculated from mass spectrometer signals at mass 16 and 32 (using the formula of Miller and Patch[33]) to be approximately 25%. Doering has used a similar source for measuring inelastic electron scattering cross sections of O and O_2.[34,35] His energy loss spectra reveal that the great preponderance of O produced by this sort of source is in the ground state. Molecular oxygen in the metastable "a" state is observed, but higher excited states are not.[35] The metastable a state of O_2 is not sufficiently energetic to react with NO.[36–38]

An uncollimated effusive (or nearly so) beam of NO is formed from a stainless steel tube terminated in a 30 μm diameter platinum aperture. The aperture is located about 4 cm from the target, 30° off-normal. The ratio of direct to background NO flux delivered to the target is about 5.

A photomultiplier tube views the region near the surface at right angles to the oxygen beam, parallel to the surface through a glass window. The tube (Hamamatsu 932-1), which has a gallium arsenide photocathode,[39] is mounted in a thermoelectrically cooled housing maintained at 253–260 K. The dark current of the tube is 30–60 pA. The photocathode is located 35 cm from the target surface, resulting in an approximately 8×10^{-4} sr field of view for the immediate vicinity of the surface.

Two methods of recording luminescence signals were employed. For broad (wavelength) band measurements, the anode current of the photomultiplier tube was measured with a picoammeter and recorded on a strip-chart recorder. In this case, the wavelength range was limited only by the glass window on the vacuum chamber and the cathode sensitivity of the photomultiplier tube. For spectrally filtered measurements, anode pulses were amplified, filtered by a lower-level discriminator, and counted on a conventional timer–scaler.

RESULTS

A photocurrent was detected when the oxygen and nitric oxide beams were directed at the nickel foil. Figure 1 shows plots of the broad band photocurrent measured under various NO fluxes and substrate treatments. The ordinate is the phototube anode current, with the background current (NO source pressure = 0, discharge source on and impinging on the sample, and phototube shutter open) subtracted. The abscissa is NO source pressure. NO flux on the Ni substrate is proportional to NO source pressure. The O atom flux is held constant. The NO source pressure dependence of the signal was obtained by valving off the NO flow and recording the photocurrent as the source evacuated into the experimental chamber.

The chamber base pressure was about 4×10^{-9} Torr. The oxygen atom beam (a mixture of helium, O_2, O, H_2O, OH, and H) causes the background chamber pressure to rise to about 5×10^{-7} Torr. Even at the highest NO source pressures the background pressure was less than 1×10^{-5} Torr (uncorrected for gas composition) in all cases.

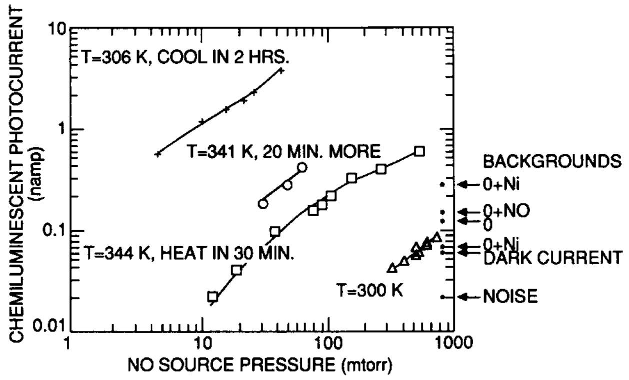

FIG. 1. Luminescence from the interaction of O and NO on a nickel foil for various surface treatments, at nominally constant O atom flux. The background current ($P_{NO} = 0$) is subtracted. The substrate condition is indicated with each curve. Various background levels are indicated on the right. (The level labeled "noise" is the noise on the dark current; noise on the photocurrent itself is somewhat higher, owing to rapid fluctions in the atomic oxygen source.)

Four sets of data are shown. The triangles are for the sample at 300 K, exposed to chamber residual gas for several days. The squares are the signal obtained after heating the sample at 344 K over a period of 30 min. The circles result with the sample at 341 K, after an additional 20 min at elevated temperature. The plusses were obtained at 304 K, after heating the substrate to 353 K and allowing it to cool over about a 2 h period. Various noise and background levels are indicated on the figure. In each of these measurements a monotonic dependence of signal on NO flux (at constant surface temperature and O atom flux) was observed. However, it was clear that the dependence was not purely linear during this period of sample heating.

There is some signal detected (above dark current and chamber background) when the O atom source discharge is on and the beam is striking the sample but no NO is present. It is not possible to ascribe this signal to luminescence from surface-catalyzed oxygen recombination luminescence[1] since the source itself produces light within the bandpass of the detector.[9] Although several steps were taken to reduce this source of background, deep red light (most probably hydrogen Balmer beta emission[9]) from the source is just detectable by the dark adapted eye when one looks directly along the source axis (through the mass spectrometer ionizer, the collimating aperture, and the skimmer).

When the source discharge is extinguished, the photocurrent drops to the chamber background level (essentially the dark current of the phototube), regardless of the level of NO flow. When the source feed gas is changed from $He/O_2/H_2O$ to He/H_2O, the signal dropped rapidly by about a factor of 30, and continued to drop slowly by another factor of 2 over the next few minutes, presumably as residual O_2 was removed from the gas manifold and the bubbler used to add water to the source feed gas.[9]

To examine further the processes occurring when the substrate is heated over the temperature range used in these experiments, the sample was allowed to sit in the vacuum chamber for a week and was then heated to 363 K, in the absence of the O and NO beams, while the chamber pressure and residual gas mass spectrum were recorded. The sample was rotated 180° from its usual position so that its surface faced directly the entrance aperture of the mass spectrometer ionizer. Upon being heated, the sample evolved water and carbon dioxide.

The substrate temperature dependence of the photocurrent exhibited complicated behavior. This dependence was measured by heating the substrate to 350 K at constant NO source pressure and O atom beam conditions, waiting for the photocurrent to reach some steady-state value, and then allowing the sample to cool to 303 K. For a new nickel foil, the photocurrent exhibited a fairly good fit to negative Arrhenius behavior over the temperature range examined, although some negative curvature was evident, as is shown in Fig. 2(a). However, after the substrate had been subjected to repeated heating and cooling cycles under O and NO flow, the temperature dependence of the photocurrent developed the shape shown in Fig. 2(b). (The smooth curves are simply third order polynomials drawn through the data to aid the eye.) The development of the temperature dependence shown in Fig. 2(b) was accompanied by a decrease in signal intensity. When the results of Fig. 2(b) are normalized to the maximum measured photocurrent for each set, it becomes clear that the shape of the temperature dependence is independent of the NO flow rate.

In an attempt to ascertain whether any of the background photocurrent arose from surface reactions of the

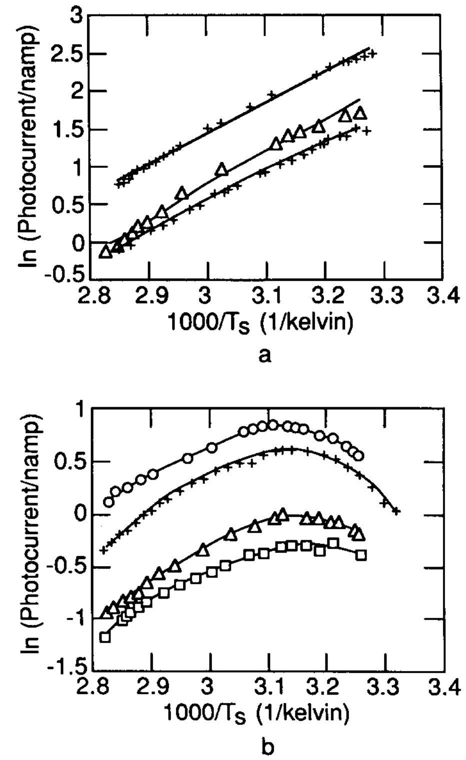

FIG. 2. Temperature dependence of O + NO + Ni chemiluminescence. (a) Nickel substrates freshly loaded into vacuum system. Curves differ by the nitric oxide flux. Different symbols are for two different substrates. (b) Nickel substrate subjected to multiple heating and cooling cycles *in vacuo*, under O and NO flow. Curves differ by the nitric oxide flux. (Smooth curves are third order polynomials drawn through the data to aid the eye.)

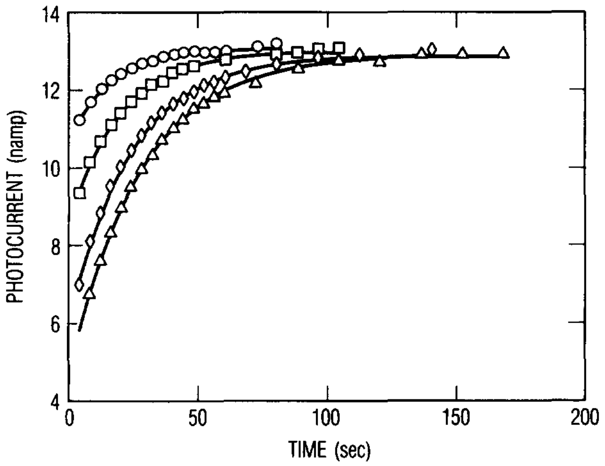

FIG. 3. Return of the O + NO + Ni chemiluminescence signal to steady state after blocking the O atom beam. Solid curves are best least-squares fits of the data to the form $A - B\exp(t/\tau)$. Conditions are substrate temperature of 304 K and NO source pressure of 117 mTorr. Circles: beam flagged for 28 s; squares: beam flagged for 64 s; diamonds: beam flagged for 132 s; triangles: beam flagged for 188 s.

atomic oxygen beam, a measurement of the background as a function of target temperature was made. No temperature dependent background was detected, indicating that the preponderance of the background signal is scattered light from the discharge beam source.

When the oxygen beam was interrupted by the beam flag, the luminescence signal went to zero, instantaneously (within the time constant of the picoammeter). However, when the flag was opened, the signal did not immediately return to the steady-state value obtained before flagging. Indeed, several seconds were required for the signal to return to its previous level. The ratio of the prompt signal to the steady state value (the attenuation) depended on how long the oxygen beam had been blocked. A plot of the natural logarithm of the attenuation vs the time the flag was closed is very nearly a straight line passing through zero, indicating that the process responsible for the observed attenuation is more-or-less first order, with a time constant of about 200 s. This sort of first-order kinetic plot was insensitive to substrate temperature (from 305–350 K) and NO source pressure (over a factor of 3).

The return of the photocurrent to steady state after the O beam was blocked could be well described by a single exponential. Figure 3 shows four fits of the transient signal to the form

$$I(t) = A - B\exp[-t/\tau], \tag{1}$$

where time is measured from the opening of the O atom flag. However, the time constant for return to steady state (tau) was monotonically dependent on the time the beam had been blocked. Figure 4 shows a plot of τ vs the time of beam blocking, for a substrate temperature of 304 K. Unlike the time constant for attenuation, τ exhibited a strong dependence on substrate temperature. It was about a factor of 3 smaller at the 350 K than at 305 K. At the higher temperature was much less sensitive to the time of beam blocking. The time constant was about 10 s for blocking times of 150 and 350 s, at 350 K.

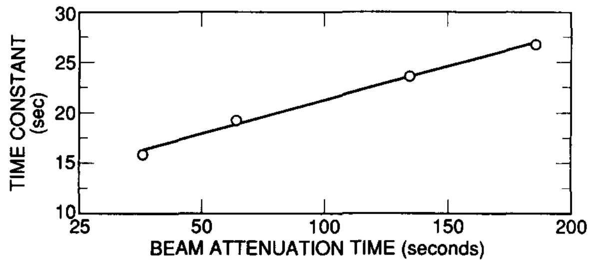

FIG. 4. Time constant for the return of the O + NO + Ni chemiluminescence signal to steady state as a function of O atom beam flagging time (from data in Fig. 3).

The dependence of the photocurrent on the NO flow was measured by establishing the beam flows, heating the sample to 353 K, allowing it to cool to a chosen temperature, and then varying the NO source pressure, at nominally constant O atom flux, taking care to wait until a steady state was reached at each NO pressure. Figure 5 shows the results of one such measurement. Within the scatter in the data, the photocurrent was linearly dependent on the NO pressure.

The dependence of the photocurrent on the O atom flux was measured by establishing the beam flows, heating the sample to 353 K, allowing it to cool to 303 K, and then varying the oxygen source pressure at nominally constant NO flux. Figure 6 shows the photocurrent for four different oxygen flow rates at four different NO source pressures. The photocurrent was linearly dependent on the O atom flux for a surface which demonstrates a monotonic dependence of signal on temperature.

A measurement of the spectral distribution of the luminescence was obtained by placing a series of bandpass filters in front of the photomultiplier tube. The count rate was measured with and without the oxygen beam blocked for each filter, at constant NO flow. (Separate measurements re-

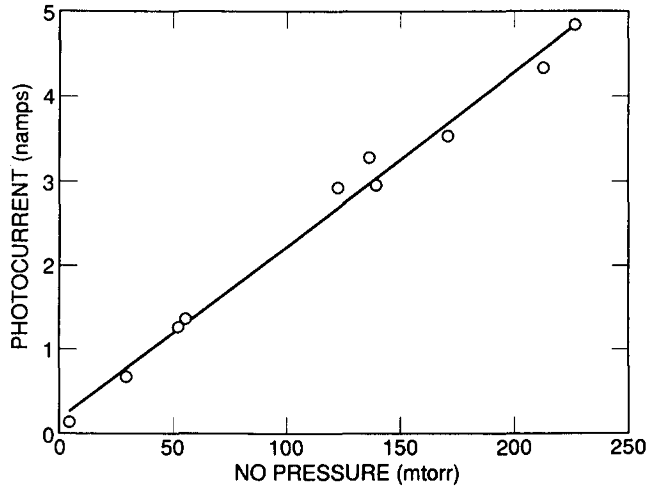

FIG. 5. Dependence of the O + NO + Ni chemiluminescence signal on NO source pressure (for a surface exhibiting a monotonic dependence of intensity upon temperature).

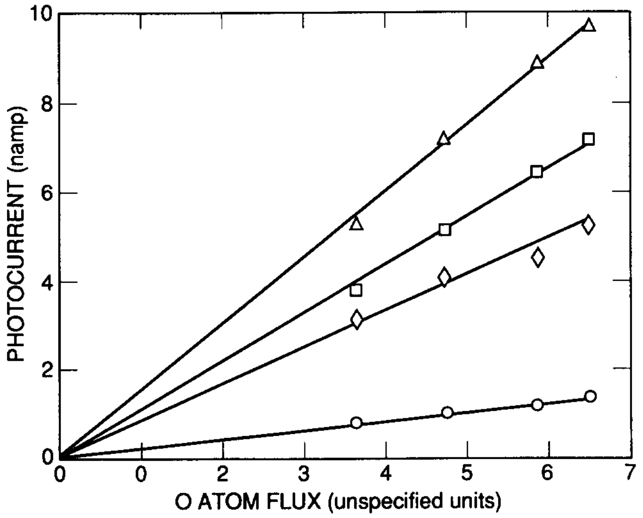

FIG. 6. Dependence of the O + NO + Ni chemiluminescence signal on the atomic oxygen flux (for a surface exhibiting a monotonic dependence of intensity upon temperature).

vealed that the dispersed O atom source background was either sufficiently broad as to be negligible compared to the dark current or lies predominantly outside the pass bands of the various filters.) The spectrum of the emission was obtained from a nominal transformation of the signal count rates:

$$I(\lambda) = C(\lambda)/[Q(\lambda)W(\lambda)T_m(\lambda)]\,, \tag{2}$$

where λ is the center wavelength of the filter, Q is the manufacturer's quoted photocathode quantum yield, W is the full width at half-maximum of the filter, and T_m is the maximum transmission of the filter. This corrected spectrum is shown in Fig. 7.

DISCUSSION

It is always difficult (and not particularly satisfying) to argue convincingly about what is not the mechanism responsible for an observed phenomenon. However, it is incumbent that the question of the possible role of gas-phase interactions in producing the observed luminescence be examined. The chemiluminescent reaction

$$O + NO + M \rightarrow NO_2^* + M \tag{3}$$

has been well studied, and its rate constants with several third bodies have been accurately evaluated.[40] There is also evidence that the two-body radiative recombination reaction

$$O + NO \rightarrow NO_2^* \tag{4}$$

proceeds at a finite rate.[40–43] Order-of-magnitude estimates have been made to examine whether either of these gas-phase reactions could be contributing significantly to the observed signals.

Before presenting these estimates, it is useful to quantify better the level of light represented by the signals observed. The photocurrents were of the order of nanoamps. The manufacturers quoted gain for the photomultiplier tube used is 5×10^5. The average quantum efficiency of the GaAs photocathode is about 0.15. Therefore, 1 nA of photocurrent corresponds to about 8×10^4 photons per second striking the photocathode. The photocathode is 1 cm square, and is located 35 cm from the nickel target. Therefore, the field of view for the volume in the immediate vicinity of the target is 8×10^{-4} sr. Thus, 1 nA of detected photcurrent resulting from luminescence near the solid target corresponds to a production rate in excess of $10^9\ s^{-1}$.

It is unlikely that the direct interaction of the two beams would result in the detection of substantial luminescence from either reaction (2) or (3).[43] However, the presence of the solid target can result in local density enhancement near the target from the scattered beams. The densities of various species on the centerline of the O beam, as a function of distance from the surface, were estimated as

$$n(i,r) = F_b(i,r)/\langle v_b(i)\rangle + F_b(i,0)\, r_b(i)/[(r_b(i)^2 + r^2)\langle v_s(i)\rangle]\,, \tag{5}$$

where i implies the particular species (He, O, O_2, NO), F_b is the incident beam flux, $\langle v_b\rangle$ is the average beam velocity, r is the axial distance from the target, r_b is the radius the beam subtends on the target, and $\langle v_s\rangle$ is the average speed of species i when it is in thermal equilibrium at the temperature of the source. Note that this approximation incorporates the conservative assumption that the atoms and molecules scatter from the surface with complete thermal accommodation and no loss.

Figure 8 shows a plot of the sum of the incident and scattered centerline densities of the various species. The fluxes and velocities of the species in the oxygen containing beam were calculated from the scheme of Lam,[44] assuming a fractional dissociation of 33%. Previous measurements in this laboratory found that the computed flux exceeds the measured flux somewhat.[31] Furthermore, a higher than usually realized fractional dissociation was used to ensure further that the estimate is a conservative one. The NO flux and velocity were calculated assuming the source was purely effusive, for a source pressure of 100 mTorr.

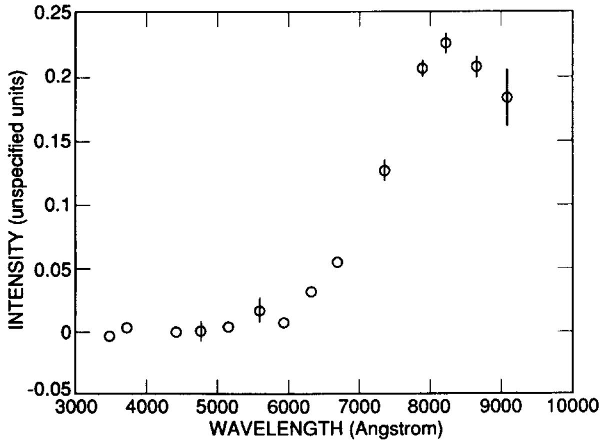

FIG. 7. Spectrum of the O + NO + Ni chemiluminescence signal taken with a series of bandpass filters.

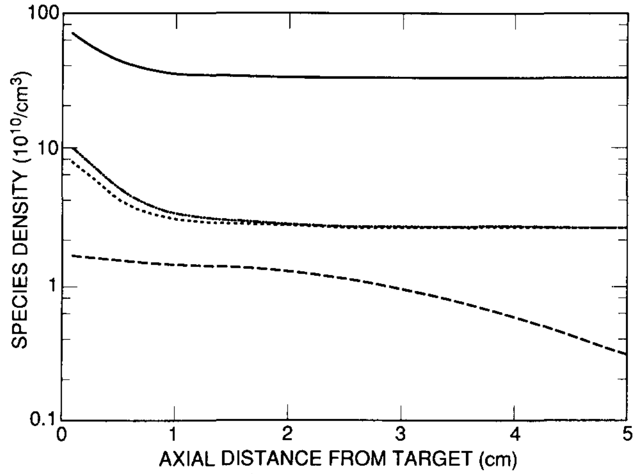

FIG. 8. Modeled centerline densities for various species in the O + NO + Ni experiments. (See the text for details.) Dotted line: O; dot-dashed line: O_2; solid line: He; dashed line: NO.

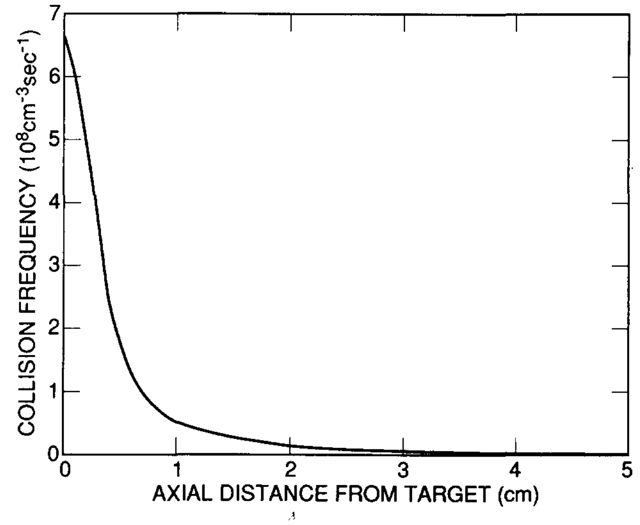

FIG. 9. Estimated upper limit on the rate of production of NO_2 from the gas-phase reaction of NO with the products of surface-catalyzed recombination of atomic oxygen. (See the text for details.)

Using the room-temperature rate coefficient[40] for reaction (3) of 6×10^{-32} cm^6 molecule^{-2} s^{-1}, one estimates a three-body chemiluminescence rate on the order of 100 cm^3 s^{-1}. Clearly the observed photocurrent could not arise from this reaction.

The potential contribution of the reported two-body radiative recombination reaction was estimated by means of conventional, crude approximations of gas-phase kinetics. First, the room temperature rate coefficient for reaction (4) reported by Becker *et al.*[40,41] (4.2×10^{-18} cm^3 molecule^{-1} s^{-1}) was converted to an average effective collision cross section by dividing it by the room temperature relative velocity of O and NO. The resulting cross section, 5.4×10^{-23} cm^2 was then used to estimate the two-body chemiluminescence production rate (effective centerline collision frequency for O and NO) in the density model presented above. The relative velocity distribution of the scattered O and NO was assumed to be Boltzmann. In this fashion, the two-body radiative recombination rate was estimated to be less than 10 000 cm^3 s^{-1}, at the maximum density. The volume in which this rate is estimated to obtain is less than 1 cm^3. Therefore, even admitting the crudity of some of the assumptions used in this estimate, it is difficult to credit that the two-body radiative recombination of O and NO could be responsible for the measured photocurrents.

Observations of red luminescence in flow-tube experiments on the reaction of O, NO, and Ni have at times been ascribed to the gas-phase reaction of NO with some energetic product (direct or indirect) of O atom recombination on the nickel surface.[27,29] The mechanism proposed by Kenner and Ogryzlo[29] requires *two* gas-phase collisions, and is therefore extremely unlikely in the conditions of the work reported here. Therefore, only the reaction of NO with excited O_2 produced by surface reaction will be considered here. The maximum rate of this sort of process has been modeled with the same fashion as the two reactions examined above by means of the following assumptions:

(1) The reacting active species is some excited state of O_2, leaving the surface with a velocity characteristic of the surface temperature.

(2) The probability that an O atom striking the target recombines to from this species is 0.017 (the *total* O atom loss coefficient on Ni measured by Mellin and Madix[45]).

(3) The reaction of NO with this active species proceeds with a hard sphere cross section, 1×10^{-15} cm^2.[46]

Figure 9 shows a plot of the centerline collision frequency for the reaction described by these assumptions. Even with the assumptions used to produce a maximum reaction rate, and assuming that every reactive collision results in the emission of a photon within the band of the detector, the estimated luminescence rate is about an order of magnitude too low to account for the observed emission. (The area subtended by the O atom beam on the target is a circle roughly 6 mm in diameter.)

One might suggest that a more severe upper bound on the cross section of this reaction would be a "gas kinetic" cross section of about 10^{-14} cm^{-2}. An examination of the quenching kinetics of excited molecular oxygen suggests that such a value would be unreasonably large. In order for the hypothetical reaction to proceed, the molecular oxygen must either be in the $A\ ^3\Sigma^+$, $c'\ ^1\Sigma_u^-$, or the $c\ ^3\Delta_u$ state, or highly vibrationally excited.

Kenner and Ogryzlo have studied the quenching of $O_2\ A\ ^3\Sigma^+$ and $c'\ ^1\Sigma_u^-$ extensively.[47–49] Although they do not report a rate coefficient for the quenching of either state by NO, the largest quenching coefficient they report is 8.1×10^{11} cm^3 molecule^{-1} s^{-1} for collision with $O_2\ a\ ^1\Delta_g$ with $A\ ^3\Sigma_u^+\ (v=2)$. Under the approximation used in the estimate presented above, this rate is equivalent to an apparent cross section of about 1.2×10^{-15} cm^2. Slanger *et al.* report a rate coefficient for quenching of $O_2\ A\ ^3\Sigma_u^+\ (v=8)$ by ground state molecular oxygen of a similar magnitude.[50] Other reported quenching coefficients for O_2, CO_2, SF_6, N_2O, He, and Ar are substantially smaller.

The possibility of reaction of NO with vibrationally excited O_2 is harder to address. Lipscombe *et al.* have investigated the quenching kinetics of $O_2\,X\,^3\Sigma_g^-\,(v \leqslant 8)$ in flash photolysis, kinetic spectroscopy experiments.[51] Quenching of the exited oxygen by NO_2 was estimated to proceed at a rate of one collision in 500 (or faster). Compared to this rate, quenching by NO was not discernible, even for an NO/NO_2 ratio of 2. The vibrational levels probed in these experiments were not as high as one must invoke to promote the reaction O_2 with NO. Therefore, one cannot rely upon this observation to rule out reaction with vibrationally excited O_2 unambiguously. However, Basco and Morse have measured the deexcitation rate of $O_2\,X\,^3\Sigma_g^-\,(3 \leqslant v \leqslant 12)$ by NO_2 and find only a factor of 5 increase in quenching rate coefficient from the lowest to the highest vibrational level measured.[52]

The arguments presented above are strengthened by the fact that the range of radiative lifetimes in the red of the molecule expected to be luminescing, NO_2, is quite large. Lifetimes of NO_2 states excited at about 580 nm have been measured by the Hanle effect[53] and by laser-induced fluorescence[54,55] to range from 20 to 250 μs. If the NO_2 is traveling at about a room temperature average velocity, 3.7×10^4 cm s^{-1}, then a substantial fraction of the molecules in the longer-lived states (if indeed these states are populated) will exit the field of view of the detector before emitting.

Therefore, although there must remain some ambiguity in this argument, the sequential reactions suggested by Harteck[27] or Kenner and Ogryzlo[29] do not seem to be the most likely explanation for the luminescence observed in the conditions of the experiments reported here. An examination of the variation of the intensity (and spectrum) of the deep red luminescence as a function of catalytic metal, using metals of varying recombination coefficient and energy accommodation coefficient[45] would serve to resolve this ambiguity further.

The behavior of the signal with sample temperture history is reminiscent of published descriptions of NO interaction with nickel. Grunze and co-workers report[56] that NO is actually effective in cleaning carbon and sulfur contaminatns from Ni{110}, with a concomitant increase in surface oxygen. They also note that nitric oxide is effective at cleaning carbonaceous impurities from the walls of stainless steel vacuum chambers "during the final stages of bakeout ($\sim$470 K)." They state that during this chamber cleaning process "initially no nitric oxide but high levels of nitrogen, water, and carbon dioxide are detected" by mass spectrometer. Only after carbon and hydrogen contaminants are cleaned from the walls does the $m/e = 30$ signal appear.

Furthermore, published studies of NO and O coadsorption on nickel and ruthenium surfaces reveal that a nondissociated, desorbable state of adsorbed NO develops on the metal surface after sufficient O coverage is obtained.[56–58] Apparently the oxygen (produced in those studies by the dissociative chemisorption of O_2 or NO) binds strongly to the sites active in the dissociation of NO, resulting in an adsorbed NO population which exhibits a weaker metal–NO bond (as ascertained by electron energy loss spectroscopy[57]) and a broad, molecular, temperature programmed thermal desorption spectrum from 300–500 K.[58] Cardillo has interpreted this twofold nature of adsorption sites for NO on metals as owing to differences in the thermochemistry of NO on steps and terraces on the metal surface.[59]

Recall that, in comparison to these two behaviors, luminescence detected in the experiments reported here increased dramatically upon mild heating of the Ni surface, heating which was shown to result in the evolution of carbon dioxide and water from the surface. It is also reasonable to assume that the conditions of these experiments (high flux of O, O_2, and NO) assure at least saturation coverage of O on the nickel surface, if not the presence of a substantial oxide layer. Furthermore, the luminescence was observed over a substrate temperature range at which the residence time of NO would be finite. Therefore, these experiments were carried out under conditions for which some coverage of labile, molecular nitric oxide adsorbate could be expected.

Implicit in the arguments presented above is the assumption that the luminescing species is NO_2. One might initially assume that desorption of NO_2 from a reactive surface might be unlikely, dissociation being the more probable event. Indeed, at submonolayer coverages, NO_2 dissociates on even cold ruthenium surfaces.[60] However, at exposures as low as one "Langmiur"[61] a desorbable molecular adsorbate appears. The coverage threshold for molecular adsorption decreases substantially with oxygen preadsorption. Thus, the idea of desorption of NO_2 from a transition metal surface, under the conditions of these experiments, is not without precedent.

The time required for the photocurrent to attain steady state after blocking and unblocking the oxygen containing beam is much longer than one would reasonably expect for purely gas-phase or scattering processes. Furthermore, the signal approaches steady state from below. This suggests either than an adsorbed O species is involved or that oxygen prepares some active site for the chemiluminescent reaction. In either case, when the beam is flagged, the reactive sites are apparently blocked at a finite rate by some other species. When the O flux is reintroduced, the blocking contaminant is gradually removed until the steady state is reached. The variation of the "time constant" for reattaining steady state with the excursion from steady state suggests that the surface processes *governing the return to steady state* are not, over all, purely first order.

The time constant for return to steady state exhibits an activation energy in substrate temperature of about 5 kcal/mol. This is close to the 3.5 kcal/mol activation energy measured in this laboratory for the reaction of atomic oxygen with solid, amorphous carbon.[62] The $\sim$200 s time constant for attenuation of the chemiluminescence during O atom beam blocking is of the correct magnitude for poisoning of the surface by a thermalized background contaminant with a partial pressure of $\sim 10^{-9}$ Torr.

These observations lead one to assign the process of chemiluminescence attenuation to contamination of the surface by carbonaceous materials in the chamber residual gas (e.g., carbon monoxide, turbomolecular pump oil, or contaminants from the differential pumping chamber forming an effusive beam into the experimental chamber). The non-first-order return to steady state is more difficult to explain with the kinetic data available. However, it is not difficult to imagine that a surface reaction system potentially involving three species (O, NO, and the poisoning contaminant), perturbed from steady state, might not always proceed in a first-order regime. The fact that the return to steady state seemed more nearly pure first order at higher temperature (where surface coverages of reactants would be lower) is satisfying to the intuition.

In contrast, the *steady-state* luminescence shows apparent first-order dependence on the O atom flux, over a range of NO fluxes. The NO flux dependence is also apparently first order. It must be recognized that these observations are not completely unambiguous proof of the order of the detailed reaction step whereby the luminescing species is produced, since even simple mechanisms of surface mediated reactions can produce a wide range of *apparent* reaction order. However, it can be said that first-order behavior in O and NO is consistent with a surface mediated reaction of O and NO to produce NO_2 under conditions of low surface coverage of reagent(s).

The surface temperature dependence of the luminescence also argues for the participation of an active, adsorbed oxygen atom in the mechanism for luminescence production. Slanger has recently reported[63] measurements of the rate of ultraviolet luminescence of molecular oxygen produced by surface recombination of atomic oxygen on a variety of metal surfaces which had been exposed to substantial fluences of active oxygen. The ultraviolet glow above a Ni catalyst showed a dependence on substrate temperature similar to that shown in Fig. 2(b).

The results reported in this paper are similar to those of Halstead *et al.* who examined the O + NO + Ni reaction in a flow tube.[4,30] The major difference they report is the small, positive temperature dependence of the surface mediated luminescence signal. However, Halstead *et al.* only measured the "orange NO_2^* emission intensity" over a catalyst temperature range of 298–323 K. Their Arrhenius plot of these data (see Fig. 8 of Ref. 4) is similar to the low temperature portion in Fig. 2(b) in the work reported here. This similarity suggests that their conditions resulted in a nickel surface similar to the "aged" surface in this work.

An experiment such as the one reported in this paper cannot, by itself, resolve the many uncertainties which prevail as to the origin(s) and implications of luminescence produced by space vehicle interactions with the orbital atmosphere. Nor is there any intention to claim that this work constitutes a *simulation* of the vehicle glow phenomenon. However, it is interesting to examine the degree to which the results of this work agree with orbital observations.

Figure 10 presents a comparison of the spectrum of luminescence measured for the O + NO + Ni system with two published space flight observations: a spectrum of glow measured[12] near the ram-oriented vertical stabilizer of the space shuttle (STS) and the spectrum of atmosphere-induced luminescence measured on the Atmosphere Explorer (AE) satellite.[11] The STS spectrum has been corrected for detector response, but not for the transmission of the shuttle cabin's rear window through which the spectrum was measured. This correction would increase the long-wavelength end of the spectrum about 30%.[64] The scaling of the spectra is arbitrary. The AE spectrum has been scaled to match the laboratory measurements at about 7500 Å. The STS spectrum has been scaled so that its peak is roughly equal to the O + NO + Ni peak intensity.

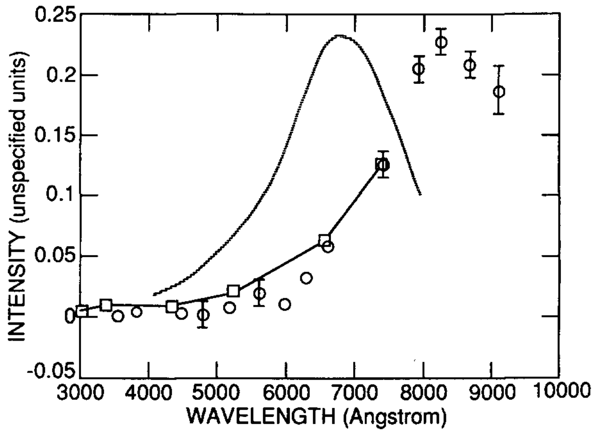

FIG. 10. Comparison of the spectrum of O + NO + Ni chemiluminescence with two published spectra of luminescence which has been ascribed to space vehicle interactions with the atmosphere. circles: this work; squares: luminescence observed on the AE satellite; dashed line: glow near the ram-oriented vertical stabilizer of the space shuttle. See the text for details of the relative scaling of the spectra.

The agreement with the AE spectrum is quite good indeed, although the data are so few that this agreement may be serendipitous. The difference between the AE and STS spectra is not well understood.[65] Ongoing work in this laboratory is directed at examining whether the identity of the substrate (i.e., the thermochemistry of the transient adsorption process) affects the energy disposal in the O + NO + surface reaction, or just the rate.

One of the most dramatic, and frequently discussed aspects of the surface interactions with the low Earth orbit environment is the kinetic energy with which atmospheric particles strike satellite surfaces. Although the kinetic temperature of the atmosphere is not particularly high, approximately 1000 K,[5] the 8 km s^{-1} velocity of an orbiting spacecraft produces relative translational energies of about 5 and 9 eV for atmospheric atomic oxygen and molecular nitrogen, respectively. The work reported here did not involve the use of such high energy collisions.

There is evidence that this relative translational energy is effective in promoting the reaction of atmospheric atomic oxygen with organic polymers frequently used on spacecraft (an effect analogous to the activation barriers observed for reactions of ^3P with hydrocarbons in the gas phase).[31,66] Several of the hypothetical mechanisms for vehicle glow production invoke use of this energy in promoting reactions, or the partitioning of this relative translational energy into internal degrees of freedom of the gaseous products of gas–solid reactions.[14–17] The validity of such notions is by no means proven.

Slanger has argued that the photographs of glow on the fifth flight of the space shuttle (as a function of vehicle attitude) demonstrate that "the interaction of thermal atoms and molecules with the surfaces does not generate the glow, and . . . translational accommodation of fast particles is efficient enough that a single surface collision reduces the kinetic energy below the threshold for glow production."[67] However, Swenson and Mende report that similar photographs from the ninth shuttle flight reveal glow on surfaces at greater than 90° from the velocity vector.[68] They suggest that this glow originates from the thermal flux of atmospheric particles reaching the vehicle surface. Kofsky and Barrett have proposed that observed vehicle glows are brightest on or from ram-oriented surfaces only "because of the greatly enhanced fluxes of air atoms and molecules; if these particles' up-to-10 eV relative kinetic energy plays any part, it would be creating and maintaining sites from which internally excited fragments can be desorbed . . ."[69] Indeed, when one thinks about the role of kinetic energy in governing radical recombination reactions of the residual atmosphere on spacecraft surfaces, it is not immediately clear whether one should compute the reduced mass in a collision based on the space vehicle mass or use the mass of some weakly bound adsorbate on the surface.

It is not within the scope of this paper to resolve this controversy. Such an ongoing debate is briefly described in this discussion only to make the point that the work reported in this paper is not *a priori* irrelevant to the vehicle glow phenomenon on the grounds that the translational energy of the reagents was too low, since the role of kinetic energy in glow production is not conclusively established. Whether the rate of surface-catalyzed recombination of O and NO to form excited NO_2 or the internal state distribution of the NO_2 depends on reagent translational energy is a subject which might merit further research.

CONCLUSIONS

The results and discussion presented above can be summarized as follows. A deep red luminescence has been observed when O and NO are directed at an oxidized polycrystalline nickel surface. The luminescent intensity exhibits a complicated dependence on substrate temperature. The intensity of the glow depends strongly on the state of the surface, being enhanced by the removal of carbon-containing surface contaminants. The time required for the glow to reach steady state when the oxygen beam is nearly instantaneously blocked and then opened is several seconds. The steady-state luminescence appears to be first order in O and NO. The intensity of the luminescence is many times greater than one would expect for simple, known gas-phase reactions in the O + NO system, and indeed the conditions of the experiment were selected to minimize the importance of gas-phase reactions. All of these attributes provided strong evidence that the luminescence arises from some product of the surface-mediated reaction of O and NO, which suffers interference from background contaminant(s) in the system.

The spectrum of the luminescence, the reagents in the system, and the similar work of Halstead *et al.* suggest that the luminescing species is electronically excited NO_2.

The results presented in this paper provide substantial support for the notion[18–20,25] that the heterogeneous reaction of O and NO under conditions in which gas-phase reactions are expected to be negligible can be a contributor to vehicle glows observed in low Earth orbit.

Clearly the sort of reaction system examined in this work is quite complex, and there is a wealth of detail yet to be revealed in it. Continuing investigations of the O + NO + solid system in this laboratory are being directed toward gaining a better understanding of the mechanism(s) responsible for the observed luminescence by more carefully examining the reagent flux dependence of the luminescence signal, obtaining more highly resolved spectra of the luminescence, and examining the interaction of O and NO on other and better controlled substrates.

ACKNOWLEDGMENTS

The authors wish to thank G. Eng, T. L. Hayhurst, R. F. Heidner, M. M. Hills, and A. T. Pritt for many useful discussions during the course of this work. This work was supported by the Aerospace Sponsored Research program.

[1] G. Mannella and P. Harteck, J. Chem. Phys. **34**, 2177 (1964), and references cited therein.
[2] L. S. Brown and S. L. Bernasek, J. Chem. Phys. **82**, 2110 (1985).
[3] B. Halpern and M. Kori, in *Gas Phase Chemiluminescence and Chemi-ionization*, edited by A. Fontijn (North–Holland, New York, 1987), p. 327.
[4] J. A. Halstead, N. Triggs, A.-L. Chu, and R. R. Reeves, in *Gas Phase Chemiluminescence and Chemi-ionization*, edited by A. Fontijn (North–Holland, New York, 1987), p. 307.
[5] A. E. Hedin, C. A. Reber, G. P. Newton, N. W. Spencer, H. C. Brinton, H. G. Mayr, and W. E. Potter, J. Geophys. Res. **82**, 2148 (1977).
[6] G. S. Arnold and D. R. Peplinski, 13th Space Simulation Conference, NASA Conference Publication 2340, 1984(b), pp. 150–168.
[7] L. J. Leger, I. K. Spiker, J. F. Kuminecz, T. J. Ballentine, and J. T. Visentine, AIAA Shuttle Environment and Operations Meeting, Washington, D. C., AIAA paper #83-2631-CP, 31 October–2 November, 1983.
[8] L. J. Leger, J. T. Visentine, and J. K. Kuminecz, AIAA 22nd Aerospace Sciences Meeting, Reno, NV, AIAA paper 84-0548, January, 1984.
[9] G. S. Arnold, D. R. Peplinski, and R. R. Herm, SD-TR-82-81, The Aerospace Corporation, El Segundo, CA, 30 September, 1982.
[10] P. M. Banks, P. R. Williamson, and W. J. Raitt, Geophys. Res. Lett. **10**, 118 (1983).
[11] J. H. Yee and V. J. Abreu, Geophys. Res. Lett. **10**, 126 (1983).
[12] S. B. Mende and G. R. Swenson, AIAA paper #85-0475, AIAA 23rd Aerospace Sciences Meeting, Reno, NV, 17 January, 1985.
[13] J. H. Yee and A. Dalgarno, Proceedings of the AIAA Shuttle Environment and Operations Conference, October 31–November 2, 1983, Washington, D.C. pp. 191–197.
[14] T. G. Slanger, Geophys. Res. Lett. **10**, 130 (1983).
[15] B. D. Green, Geophys. Res. Lett. **11**, 576 (1984).
[16] T. Shimazaki and M. Mizushuma, Proceedings of the AIAA Shuttle Environment and Operations II Conference, November 13–15, 1985, Houston, TX, pp. 79–87.
[17] K. Papadopoulos, Radio Sci. **19**, 576 (1984).
[18] M. R. Torr, P. B. Hays, B. C. Kennedy, and J. C. G. Walker, Planet. Space Sci. **25**, 173 (1977).
[19] R. R. Reeves, NASA Induced Shuttle Luminosity Meeting, McLean, VA, 8 October, 1982.
[20] G. Swenson, S. Mende, and S. Clifton, Proceedings of the Second Workshop on Spacecraft Glow, NASA CP 2391, May 6–7, 1985, pp. 35–45.
[21] B. D. Green, G. E. Caledonia, and T. D. Wilkerson, J. Spacecraft **22**, 500 (1985).
[22] B. D. Green and E. Murad, Planet. Space Sci. **34**, 219 (1986).
[23] J. L. Barrett, I. L. Kofsky, and E. Murad, Proc. SPIE **687**, 28 (1986).
[24] I. L. Kofsky and J. L. Barrett, J. Spacecraft **24**, 133 (1987).
[25] G. R. Swenson, S. B. Mende, and E. J. Llewellyn, Nature **323**, 519 (1987).
[26] M. F. Golde, A. E. Roche, and F. Kaufman, SRCC Report #187, Uni-

versity of Pittsburgh, Pittsburgh, PA, May, 1973, and references cited therein.

[27] P. Harteck and R. R. Reeves, Discuss. Faraday Soc. **37**, 82 (1964).

[28] B. A. Thrush, C. J. Halstead, and A. McKenzie, J. Phys. Chem. **72**, 3711 (1968).

[29] R. D. Kenner and E. A. Ogryzlo, J. Chem. Phys. **80**, 1 (1984).

[30] A.-L. Chu, R. R. Reeves, and J. A. Halstead, J. Phys. Chem. **90**, 466 (1986).

[31] G. S. Arnold, D. R. Peplinski, and F. M. Cascarano, J. Spacecraft **24**, 454 (1987).

[32] E. J. Murphy and J. H. Brophy, Rev. Sci. Instrum. **36**, 294 (1979).

[33] D. R. Miller and D. F. Patch, Rev. Sci. Instrum. **40**, 1566 (1969).

[34] J. P. Doering, E. E. Gulcicek, and S. O. Vaughan, Chem. Phys. Lett. **114**, 334 (1985).

[35] J. P. Doering and S. O. Vaughan, J. Geophys. Res. **91**, 3279 (1987).

[36] M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald, and A. N. Seyverud, *JANAF Thermochemical Tables Part II, Cr-Zr*, 3rd ed. (American Chemical Society and American Institute of Physics for the National Bureau of Standards, Washington, D.C., 1986).

[37] G. Herzberg, *Molecular Spectra and Molecular Structure*, 2nd ed. (Van Nostrand, New York, 1950), Vol. I, pp. 558–559.

[38] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1966), Vol. III, pp. 602.

[39] Anonymous, Hamamatsu Corporation, Middlesex, NJ, Product Bulletin T80-12-5.

[40] F. Kaufman, in *Chemiluminescence and Bioluminescence*, edited by M. J. Cormier, D. M. Hercules, and J. Lee (Plenum, New York, 1973), p. 83.

[41] K. H. Becker, W. Groth, and D. Thran, Chem. Phys. Lett. **15**, 84 (1978).

[42] T. Kasai, T. Masui, H. Nakaner, I. Hanasaki, and K. Kuwata, Chem. Phys. Lett. **56**, 84 (1978).

[43] K. Honma and O. Kajimoto, J. Chem. Phys. **81**, 3344 (1984).

[44] C. K. Lam, Institute for Aerospace Sciences, University of Toronto, UTIAS Report No. 212, 1976.

[45] G. A. Melin and R. J. Madix, Trans. Faraday Soc. **67**, 198 (1971).

[46] W. F. Sheehan, *Physical Chemistry* (Allyn and Bacon, Boston, 1970), p. 950.

[47] R. D. Kenner and E. A. Ogryzlo, Int. J. Chem. Kinet. **12**, 501 (1980).

[48] R. D. Kenner and E. A. Ogryzlo, Can. J. Chem. **61**, 921 (1983).

[49] R. D. Kenner and E. A. Ogryzlo, Chem. Phys. Lett. **103**, 209 (1983).

[50] T. G. Slanger, W. K. Bischel, and M. J. Dyer, Chem. Phys. Lett. **108**, 472 (1984).

[51] F. J. Lipscomb, R. G. W. Norrish, and B. A. Thrush, Proc. R. Soc. London Ser. A **233**, 455 (1956).

[52] N. Bosco and R. D. Morse, Proc. Soc. London Ser. A **334**, 553 (1973).

[53] R. Bylicki, H. G. Weber, H. Zscheeg, and M. Arnold, J. Chem. Phys. **80**, 1791 (1984).

[54] V. M. Donnelly and F. Kaufman, J. Chem. Phys. **66**, 4100 (1977).

[55] O. Cheshnovsky and A. Amrirav, Chem. Phys. Lett. **109**, 368 (1984).

[56] M. Grunze, G. Strasser, and O. Elshazly, J. Vac. Sci. Technol. A **4**, 2396 (1986).

[57] T. W. Root, G. B. Fisher, and L. D. Schmidt, J. Chem. Phys. **85**, 4679 (1986).

[58] F. Bozso, J. Arias, C. P. Hanrahan, J. T. Yates, R. M. Martin, and H. Metiu, Surf. Sci. **141**, 591 (1984).

[59] M. J. Cardillo, Langmuir **1**, 4 (1985).

[60] U. Schwalke, J. E. Parmeter, and W. H. Weinberg, Surf. Sci. **178**, 625 (1986).

[61] A "Langmuir" is a colloquial, approximate unit of fluence. It is the fluence of atoms or molecules which strike the surface of a solid exposed to a gas in thermal equilibrium at 10^{-6} Torr pressure for 1 s. For small molecules at room temperature, this fluence corresponds roughly to one monolayer coverage for unit sticking probability.

[62] G. S. Arnold and D. R. Peplinski, AIAA J. **24**, 673 (1986).

[63] T. G. Slanger, MP 86-130, SRI International, Menlo Park, CA, 7 July, 1986.

[64] G. B. Swenson, Lockheed Palo Alto Research Laboratories (private communication).

[65] Dalgarno *et al.* have argued that apparent differences in the AE and STS spectra should not be surprising, inasmuch as the viewing geometries of the two measurements are dramatically different. The STS measurement is the spectrum of emission from a luminescent layer localized within 10–20 cm of the shuttle vertical stabilizer surface. The AE photometer views out from the surface of the vehicle, and therefore measures the spectrum of the whole column of gas leaving the vehicle surface. Furthermore, one expects that the surface materials exposed to the atmosphere on the two vehicles to be different. Thus the chemiluminescent reactions giving rise to the observed glows, or indeed the energy disposal in a given reaction, may very well be different on the two vehicles. See A. Dalgarno, J.-H. Yee, and M. Lecompte, Proceedings of the Second Workshop on Spacecraft Glow, NASA CP2391, May 6–7, 1985, pp. 52–62.

[66] G. S. Arnold, D. R. Peplinski, AIAAJ. **23**, 1621 (1985).

[67] T. G. Slanger, Geophys. Res. Lett. **13**, 431 (1986).

[68] G. R. Swenson and S. B. Mende, Geophys. Res. Lett. **13**, 509 (1986).

[69] I. L. Kofsky and J. L. Barrett, Planet. Space Sci. **34**, 665 (1986).