SPACE SHUTTLE RAM GLOW: IMPLICATION OF NO, RECOMBINATION CONTINUUM

Gary Swenson and Steve Mende

Lockheed Palo Alto Research Laboratory

Stu Clifton

Space Science Laboratory NASA Marshall Space Flight Center

Abstract. The ram glow data gathered to date from imaging experiments on space shuttle suggest the glow is a continuum (within 34 A resolution); the continuum shape is such that the peak is near 7000 Å decreasing to the blue and red, and the average molecular travel leading to emission after leaving the surface is 20 cm (assuming isotropic scattering from the surface). Emission continuum is rare in molecular systems, but the measured spectrum does resemble the laboratory spectrum of $NO_2(^2B_1)$ recombination continuum. The thickness of the observed emission is consistent with the NO_2 hypothesis given an exit velocity of ~2.5 km/sec (1.3 eV) which leaves ~3.7 eV of ramming OI energy available for unbonding the recombined NO_2 from the surface. The NO_2 is formed in a 3-body recombination of $OI + NO + [M] = NO_2 + [M]$, where OI originates from the atmosphere and NO is chemically formed on the surface from atmospheric NI and OI. The spacecraft surface then acts as the [M] for the reaction. Evidence exists from orbital mass spectrometer data that the NO and NO, chemistry described in this process does occur on surfaces of spectrometer orifices in orbit. Surface temperature effects are likely a factor in the NO sticking efficiency and, therefore, glow intensities.

Background

The AE-E satellite was equipped with a Visual Airglow Experiment (VAE) which observed atomic and molecular features in the Earth's airglow layer. Backgrounds in the photometer filter channels were found to have a variability with ram angle. This recognition of a ram background in the AE instrument was first cited by Torr et al. [1977]. These data were reported by Yee and Abreu [1982, 1983]. The data displayed a detectable level of luminosity in the near UV channels of the instrument (3371 Å), with increasing luminosity towards the red wavelengths (7320 Å). The background in all filter channels, when plotted, described a bright ram source, increasing in brightness toward the red wavelengths. The analysis presented suggested the glow extended well away from the spacecraft alluding to the probability that the emitter is a metastable. OH Meinel bands were reported as being a likely candidate species for emission, since the general red character and emission lifetime seemed to fit the evidence. The Yee and Abreu [1982] analysis had found a strong correlation between the ram emission intensity and altitude. The emission intensity closely followed the atomic oxygen scale height above 160 km altitude. Atomic oxygen then is

the probable aeronomical constituent to be a chemical catalyst for whatever process is occurring. Slanger [1983] was among the first to report the OH hypothesis. Langhoff et al. [1983] discussed the simplification of OH to the infrared glow spectrum implied by OH chemistry possibilities.

The DE-B spacecraft was equipped with a high resolution Fabry-Perot Interferometer (FPI). In this instrument, a 7320 Å filter was utilized in series with the Fabry-Perot etalon. Abreu et al. [1983] reported on the background with ram effect associated with this channel. A ram glow was reported and the deduced etalon spectrum showed similarity with the OH spectrum observed in nightglow from the atmospheric limb. The available evidence from these two spacecraft seems to favor the OH hypothesis for the observed glows.

Glow observations have been reported by a number of investigators from shuttle missions STS -3, -5, -8 and -9. Banks et al. [1983] reported glow from Orbiter television and still camera pictures around aft spacecraft surfaces while documenting glows associated with an electron accelerator experiment on STS-3. Mende [1983] and Mende et al. [1983,1984a,b]have documented ram glows associated with STS -5, -8, and 9 using an intensified camera. On the later missions (STS-8 and -9), objective grating imagery of spacecraft glow from the vertical stabilizer depicted a red stuctureless glow [Mende et al., 1984b]. The specral resolution is on the order of 150 Å. On the STS-8 mission it was observed that glows from surface samples including aluminum, kapton, and black chemglaze (a polyurethane black paint typically used in low light level detection instrument baffles) were not equally bright. The surface characteristic and/or the material makeup clearly was shown to affect the glow brightness.

High spectral measurements of the ISO spectrometer on Spacelab 1 show the presence of a red dominated glow [Torr and Torr, 1984]. There are a number of observed emission features which may be part of the natural aurora airglow background environment and therefore may not be part of the shuttle glow.

There is a proposed plasma process for glow production [Papadopoulos, 1983] which involves a two-stream instability between incoming ram and reflected ions. The ion instability sets up an electrostatic wave, which in turn heats the ambient electrons. The pumped-up electrons can in turn excite in situ and ramming constituents. Pumping the electrons to 20+ eV will allow e + X reactions. The energy is sufficient to excite N₂ to 2nd positive, and possibly ionize to 1st negative. A lot of UV emissions could arise with this process whereas the chemical processes postulated are energetically limited to be red and infrared emitters. N₂ first negative (1,0) at 3914 Å and N₂ 2nd positive band at 3371 Å are spectral features expected for this physical process. Detailed calculations have been made by Kofsky and Barrett [1983] regarding the ion instabilities and likely excitation emissions.

Green [1984] recently reviewed the ram glow data and theory for the shuttle environment. The review described the two classes of mechanisms, one being molecular emission from surface collisions and another due to the plasma critical velocity effect. In his discussions, vibrationally excited CO, OH or electronically excited N_2 were postulated as most likely candidates and chemically plausible with the evidence at hand.

More recently, shuttle glow spectrum was reported from STS 41-D with 34 A resolution by Mende et al. [1984c] and Swenson et al. [1985]. These data show the shuttle ram glow to be an emission continuum within the instrument resolution.

The current evidence strongly suggests the glow associated with the ramming atmosphere is a result of NO_2 in recombination [Swenson et al., 1985]. The natural atmosphere is reacting with the 8 km/sec vehicle to produce the phenomenon. The purpose of this presentation is to review the evidence and our current interpretation of the physical processes leading to the glow.

NO, Recombination Chemistry

The picture of spacecraft glow that has evolved includes the optical observations from the space shuttle and Explorer series satellites. we have recently assembled a theory that's consistent with the observations of the shuttle glow spectrum. the theory basically involves the fact that NO forms and sticks on orbiting surfaces (more efficiently on cold ones). NO will react very quickly in 3-body recombination with OI to form NO₂. The surface monolayer of NO is exposed to fast atmospheric OI on ram spacecraft surfaces. Since NO₂ forms with ramming OI, the 5 ev OI also contains enough energy to unbond the formed NO₂ from the surface. NO₂ leaving the surface at 2.3 km/sec can account for the observed e-fold in the stand-off luminous glow from the space shuttle. The bottom part of Figure 1 shows the OI interacting with surface sticking NO to form NO₂. The excited NO₂ which exits the surface gives the red glow.

Wall catalytic formation of NO was observed by Reeves et al. [1960] with laboratory experiments involving NI and OI. Their experiments showed that N('S) + O('P) = NO(B²\pi) forms on the wall and the NO gas phase is formed followed by emission, i.e., NO(B²\pi) = NO(X²\pi) + h ν (beta bands). In their experiments, emission from the excited gas product coming off the wall was observed.

Spectrum of Shuttle Glow

An experiment was operated on several space shuttle missions to provide spatial and spectral distributions of the ram glow associated with the space shuttle Orbiter. The most recent data featured resolved spectrum and imagery of the glow with spectroscopic resolution of 34 Å FWHM between 4000 Å and 8000 Å [Swenson et al., 1985]. The spectrum of the glow on the shuttle tail pod could be clearly separated from reflected light from the Orbiter. The spectrum was taken at 290 km altitude from the ram surface. The spectrum noise was dominated by the ion scintillation in the image intensifier which produces a grain over the entire image of the 30-sec exposure.

In Figure 2, the spectrum from STS 41-D is plotted and compared with laboratory spectrum of Fontijn et al. [1964] and Paulson et al. [1970]. The laboratory spectrum was produced from 3-body recombination of NO+OI+(M) = NO₂+(M). Continuum emission is not common in molecular systems. NO₂ certainly has the ingredients of composition from the ambient source to be the candidate emitter. The spectrum isn't a perfect fit to the laboratory spectrum by any means, but we attribute this to the temperature at which the spacecraft reaction is taking place as opposed to the laboratory experiments. The laboratory spectrum is typically formed with a recombinant temperature of ~300° K whereas the 5 eV ramming OI characterizes a 60,000° K effective recombinant temperature.

It is well established that NO2 can take on a number of spectral

shapes dependent on the recombinant species and the available internal energy of the recombinant such as found with O_3 (see Figure 3). Figure 3 shows the laboratory recomination spectrum for NO_2 for 3-body curve as well as the spectrum for 2-body recombination with NO and O_3 where the O_3 is vibrationaly excited to different states. The laboratory spectra, again, are all-low temperature spectra. For comparison, we have shown the measured STS 41-D spectrum, which we contend is spectrally different as a result of the ramming OI energy. Golomb and Brown [1975] found laboratory evidence for thermal effects on the spectral shape of the OI recombination spectrum at low temperature (200-350° K) range. They found the intensity of the blue portion of the continuum to decrease with increasing temperature.

Mass Spectrometer Evidence

What evidence do we have that NO forms and sticks on orbiting surfaces in the thermosphere? The best evidence is that reported by the mass spectrometer investigations and what has been observed in NI, NO, and NO₂. Engebretson and Mauersberger [1979] described in detail the response of NO with respect to thermal and orbital parameters for their instrument on AE-C satellite. It's been known since mass spectrometers first flew that most of the atmospheric NI entering the mass spectrometer orifice converts to NO with wall collisions and in fact, a large percentage of the NI signal is deduced from the NO (mass 30) signal in the instruments (see Engebretson and Mauersberger, [1979] and the references cited therein). It's been well established in laboratory experiments that the NI and OI wall reaction form the gas phase NO. Engebretson and Mauersberger [1979] then reported a most interesting phenomenon. They reported that NO was absorbed on the spectrometer walls (with efficiencies higher at low wall temperatures). The top part of the chemistry shown in Figure 1 reflects what has been observed in the mass spectrometer orifice. They observed the gas phase NO, and from temperature and altitude geometry, they deduced that a significant amount of NO was sticking to the wall. The UV emission from surface catalyzed NO in the gas phase has been observed in the laboratory and should be observable on an orbiting ram surface with the proper instrument [Reeves et al., 1960]. Only the NO beta bands are observed in the laboratory (temperatures ~300° K) surface-catalyzed excitation type experiments. What will happen on the spacecraft surface with OI at 5 eV producing the NO is uncertain.

What about the link between the top (NO) chemistry and the bottom (NO₂) chemistry depicted in Figure 1? Engebretson and Mauersberger also noted NO₂ formed in the orifice (most efficienctly at low wall temperatures). In fact, Engebretson (private communication) indicates that this NO₂ is observed in the open ion source configuration of the type used with AE-C but is not as prevalent in closed ion source instruments. This implies that without a source of energetic OI, the NO+OI = NO₂ (gas phase) chemistry does not take place or that wall collision chemistry acts to destroy the NO₂ after it does form.

Surface temperature has been found to be a very important parameter in the effective surface sticking efficiency and NO₂ formation rate in the studies performed by Engebretson and Mauersberger [1979]. The colder surfaces are more efficient for NO to stick, and therefore we could expect a more intense NO₂ emission but lesser NO beta band emission since it is the gas phase NO which emits the beta bands. The warmer surfaces then would tend to emit less NO_2 (red) emission, but more NO (blue beta band) emission.

Source Continuity Considerations

Does the source availability account for the luminosity observed in the red glow? At 250 km we observe ~6 kilorayleighs of visible glow when viewing normal to a ram surface (interpreted from e-folding considerations of spacecraft tile surface glows). in other words, ~6.10⁹ photons/cm² sec are observed. The atomic nitrogen population of ~10⁷ [Engebretson et al., 1980] with a spacecraft velocity of 8.10^5 cm/sec yields a nitrogen flux of 8.10^{12} to the surface. The efficiency of producing an NO₂ recombination photon would necessarily be ~1%. This is not unreasonable in NI,OI chemistry. Engebretson and Mauersberger [1979] reported a wall loss probability of NI at >10% per wall collision. If we assume that loss always results in an NO production, an NO monolayer sticking to the surface would be very quickly replaced after an NO molecule is lost from the surface due to ramming OI.

Lifetime and Energy Considerations

What about lifetime and e-folding considerations in the observed luminosity? The lifetime of NO₂ in flourescence is ~70 microseconds according to Schwartz and Johnston [1969]. It was previously reported by Yee and Dalgarno [1983] that the effective e-folding distance an average molecule travels prior to emission is ~20 cm. (This has been reverified on several STS-9 images at Lockheed.) If we assume x = t*v [Yee and Dalgarno, 1983], where x = 20 cm, we would infer that the exit velocity from the surface would be ~2.5 km/sec if NO₂ were the emitter. This corresponds to an effective exit temperature of 10,000° K (1.28 eV). This is ~25% the ram energy of QI; considerably higher than the expected surface temperature of near 300° K. In the process of producing the NO₂ then, total thermal accommodation of the OI does not occur. In summary, the lifetime and energy considerations are reasonable with NO₂ being the emitter. That leaves ~3.7 eV of the initial ramming OI for unbonding the NO₂ from the surface. We expect from the experimental observations of NO and NO₂ variations observed between surface temperatures of 300° K and 400° K by Engebretson and Mauersberger [1979] that the surface bond energy for NO is very small.

Other Considerations and Summary

The mass spectrometer orifice modulation of a surface monolayer of NO fits with the glow observations in principle. If NO can form on an instrument surface, it can also form on other surfaces including the spacecraft skin. It is well understood that the surfaces of the mass spectrometer orifice and that of the shuttle surface are very different. To date, we only have spectrum of the shuttle glow since glows of other emitting material samples have been from small areas at high altitudes and consequently weak to the observing instruments [Mende et al., 1984a,c]. The observed surface samples have been a mixture of insulator and conductor type materials, from all of which a glow emanates. When observing the stand-off glows from these small samples, we do note the e-folding distance is about the same as it is on the Orbiter skin. This suggests to us that the glow is originating from the same chemistry as we observe on the Orbiter. It is this link that lends further credibility to the link between the chemistry observed in the mass spectrometer orifice [Engebretson and Mauersberger, 1979] and that postulated as shuttle ram surface chemistry here [Swenson et al., 1985].

- Some further comments regarding the spacecraft glow are warranted. 1. Conjecture has been that a "dirty" space shuttle is responsible for
- the glow and that because it is dirty, space shuttle is responsible for good for remote studies. We notice that whether data are taken on day 1 or day 9 of a space shuttle mission, the glow intensity seems to be about the same. On the contrary then, the phenomenon is a natural one characteristic of all spacecraft. The edge on view of between 2 and 12 meters of stabilizer and ohms pod surface presents a lot of area to produce glow for cabin or Spacelab module instruments such as the handheld imager. The subtleties of surface temperature and surface type certainly influence the glow intensity. Our theory supports ram glow as a natural phenomenon and by nailing down the physical process, we can extend models to other spacecraft.
- 2. Not all materials glow to the same degree. However, when observing the stand-off distance of other materials, we note that the e-folding distance of intensity from the surface is about the same for all. This supports the same chemistry cited in Figure 1 as likely happening on all surfaces, but the NO sticking efficiency may be important in glow production. Material type is a key to minimizing the effect.
- 3. The glow originating from AE-C, we believe, results from the same chemistry we have cited as being responsible for the glow on the space shuttle. The confusion in comparison, especially from the difference in intensity as a function of angle from the ram direction, very likely relates to the fact that a large portion of the AE-C glow was originating from the instrument baffle as well as from the surrounding spacecraft surface. The baffle glow was not included in the original analysis.

There are certainly some puzzles reported in the literature that do not fit our hypothesis. Torr and Torr [1984] report N2 lst Pos spectrum in apparent ram data in a shuttle-based spectrometer. It is possible that their measurement is contaminated by dayglow or some other natural phenomenon since the experiment was operated during a daylit orbit. It cannot be dismissed however that they possibly observed a baffle or extended ram glow. The Dynamics Explorer B data in the Fabry-Perot channel suggests structure in a narrow region of spectrum of that satellite [Abreu et al., 1983]. Some of the structure was consistent with OH emission spectrum and some was not. The ram glow we attribute to NO₂ in recombination is the near surface glow which e-folds 15-20 cm from the surface.

References

Abreu, V. J., W. R. Skinner, P. B. Hays, and J. H. Yee, Optical effect of spacecraft-environment interaction: Spectrometric observations by DE-B satellite, <u>AIAA-83-CP838</u>, <u>AIAA Shuttle Environment and</u> Operations Meeting, 178, 1983. Banks, P. M., P. R. Williamson, and W. J. Raitt, Space shuttle glow observations, Geophys. Res. Lett., 10, 118, 1983.

Engebretson, M. J., and K. Mauersberger, The impact of gas-surface interactions on mass spectrometric measurements of atomic nitrogen, J. Geophys. Res., 84, 839, 1979.

Engebretson, M. J., J. A. Defreese, and K. Mauersberger, Diurnal, seasonal, and nighttime variations of atomic nitrogen in the equatorial thermosphere, J. Geophys. Res., 85, 2165, 1980.

Fontijn, A., C. B. Meyer, and H. I. Schiff, Absolute quantum yield measurements of the NO-O reaction and its use as a standard for chemiluminescent reactions, J. Chem. Phys., 40, 64, 1964.

- Golomb, D., and J. H. Brown, The temperature dependence of the NO-O chemiluminous recombination, J. Chem. Phys., 63, 5246, 1975.
- Greaves, J. C., and D. Garvin, Chemically induced molecular excitation: Excitation spectrum of the nitric oxide-ozone system, J. Chem. Phys., 30, 348, 1959.
- Green, B. D., Atomic recombination into excited molecular-A possible mechanism for shuttle glow, Geophys. Res. Lett., 11, 576, 1984.
- Kenner, R. D., and E. A. Ogryzlo, Orange chemiluminescence from NO2, J. Chem. Phys., <u>80</u>, 1, 1984.
- Kofsky, I.L., and J. L. Barrett, Optical emissions resulting from plasma interactions near windward directed spacecraft surfaces, AIAA-83-CP838, AIAA Shuttle Environment and Operations Meeting, 198, 1983.

Langhoff, S. R., R. L. Jaffee, J. H. Yee, and A. Dalgarno, The surface glow of the Atmospheric Explorer C and E Satellites, Geophys. Res. Lett., 10, 896, 1983.

Mende, S. B., Measurement of vehicle glow on the space shuttle, AIAA-83-CP838, AIAA Shuttle Environment and Operations Meeting, 79, 1983.

Mende, S. B., O. K. Garriott, and P. M. Banks, Observations of optical emissions on STS-4, Geophys. Res. Lett., 10, 122, 1983.

Mende, S. B., P. M. Banks, and D. A. Klingelsmith, III, Observation of orbiting vehicle induced luminosities on the STS-8 mission, Geophys. <u>Res. Lett.</u>, <u>11</u>, 527, 1984a.

Mende, S. B., G. R. Swenson, and K. S. Clifton, Preliminary results of the Atmospheric Emissions Photometric Imaging Experiment (AEPI) on Spacelab 1, Science, 225, 191, 1984b.

Mende, S. B., G. R. Swenson, K. S. Clifton, R. Gause, L. Leger, and O. K. Garriott, Space vehicle glow measurements on STS 41D, Submitted to J. Spacecraft and Rockets, 1984c.

Papadopoulos, K., On the shuttle glow, SAI Report 84-147-WA, 1983.

Paulsen, D. E., W. F. Sheridan, and R. E. Huffman, Thermal and

- recombination emission of NO₂, <u>J. Chem. Phys.</u>, <u>53</u>, 647, 1970. Reeves, R. R., G. Manella, and P. Harteck, Formation of excited NO and N₂ by wall catalysis, <u>J. Chem. Phys</u>., <u>32</u>, 946, 1960.
- Schwartz, S. E., and H. S. Johnston, Kinetics of nitrogen dioxide fluorescence, J. Chem. Phys., <u>51</u>, 1286, 1969.
- Slanger, T. G., Conjectures on the origin of the surface glow of space vehicles, <u>Geophys. Res. Lett.</u>, 10, 130, 1983.
- Swenson, G. R., S. B. Mende, and K. S. Clifton, Ram vehicle glow spectrum: Implication of NO₂ recombination continuum, Geophys. Res. Lett., <u>12</u>, 97, 1985.

- Torr, M. R., P. B. Hays, B. C. Kennedy and J. C. G. Walker, Intercalibration of airglow observations with the Atmospheric Explorer Satellites, <u>Planet. Space Sci.</u>, 25, 173, 1977.
- Torr, M. R., and D. G. Torr, Atmospheric spectral imaging, <u>Science</u>, <u>225</u>, 169, 1984.
- Vanpee, M., K. D. Hill, and W. R. Kineyko, <u>AIAA J. (Am. Inst. Aeronaut.</u> <u>Astronaut.)</u>, 9, 135, 1971.

Yee, J. H., and A. Dalgarno, Radiative lifetime analysis of the spacecraft optical glows, <u>AIAA-83-CP838</u>, <u>AIAA Shuttle Environment and</u> <u>Operations Meeting</u>, <u>191</u>, 1983.

Yee, J. H., and V. J. Abreu, Optical contamination on the Atmospheric Explorer-E satellite, Proceedings of the SPIE, <u>338</u>, 120, 1982.

Yee, J. H., and V. J. Abreu, Visible glow induced by spacecraft-environment interaction, <u>Geophys. Res. Lett.</u>, <u>10</u>, 126, 1983.



Fig. 1. A schematic representation of the chemistry believed to be responsible for spacecraft ram glow. Starting at the top, the ramming OI and NI intercept a spacecraft surface and form NO, some of which sticks to the surface and some of which escapes in the gas phase. The NO which sticks to the surface is subjected to ramming OI which forms a 3-body recombination with the surface [M] to create NO₂. The escaping NO₂ radiates the red continuum observed on ram surfaces. [See Swenson et al., 1985.]



Fig. 2. The spectrum of spacecraft glow compared with that of the laboratory spectrum measured in laboratory experiments by Fontijn et al. [1964] and Paulsen et al. [1970]. A spectral blend produced by spectrally e-folding the measured spectrum with lifetime data of Schwartz and Johnston [1969] is also plotted.



Fig. 3. The NO₂ recombination spectrum for 3-body recombination [Vanpee et al., 1971], and for 2-body recombination with upper state 03 [Kenner and Ogryzlo, 1984], as well as vibrationally excited 03 [Greaves and Garvin, 1959]. The STS 41-D spectrum is plotted as a dashed curve and the Atmosphere Explorer data are plotted [Yee and Abreu, 1983]. It is noted that the laboratory spectrum of recombination can take on a large range of spectral shape dependent on the state of the recombinant constituents.