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CALCULATION OF SPACE STATION INFRARED IRRADIANCE FROM ATMOSPHERE-INDUCED EMISSIONS

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Introduction

The visible emission observed from the energetic interaction of atmospheric constituents, principally O and N_2, with the material surfaces of objects in low-Earth orbit has been termed Spacecraft or Shuttle glow. Although resolved visible spectra have been taken, the emitters and the responsible excitation mechanisms have not yet been completely understood. Less is known of an infrared component of Shuttle glow. Both the orbital observations of Fazio (1985) using many bandpass radiometers as part of the infrared telescope experiment (IRT), and the ground-based observations of Witteborn raise more questions than they answer. Fazio observed no clear glow and placed an upper bound of 2×10^{11} photons cm^{-2} s^{-1} in the 2 to 3 μm bandpass.

An infrared component to the observed visible ram surface glow seems likely. Many of the species presented as possible sources of Shuttle glow also have electronic or vibrational transitions in the infrared. Even if we neglect products from thruster firings and assume unreactive surfaces, the list of potential radiometers is extensive. These include $CO_2(v)$, $H_2O(v)$, $CO(v)$, $OH(v)$, $NO_2(^2B-^2A)$, and $N_2(B^3\Pi-A^3\Sigma)$. The excitation mechanisms and radiance estimates over the 1 to 10 μm region for each of these species will be discussed.

Model

We have estimated the infrared irradiance of Space Station at an altitude of 460 km. The surface material has been presumed to be non-carbonaceous and inert. The determined number densities of various gases relevant to Space Station from both ambient and outgassing sources are shown in Table 1.

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Table 1. Station Number Densities

Species	Column Density (cm^{-2})	Concentration (cm^{-3})	Fluxes** (molec cm^{-2} s^{-1})
Ambient O	3.45×10^{11}	1.25×10^{8}	1.0×10^{14}
Ambient N_2	2.84×10^{10}	1.03×10^{7}	8.2×10^{12}
Organics	5.7×10^{10}	2.1×10^{7}*	--
H_2O	1.59×10^{10}	5.9×10^{6}*	--
CO_2	1.24×10^{10}	4.6×10^{6}*	--

*Calculated assuming uniform density over a 27m column height.

**Calculated for ambient O, N_2 only using a velocity of 8 km s^{-1}

A model for the production of and emission from infrared active molecules in the Space Station environment has been constructed. The model considers two classes of radiatively active molecular production processes:

(1) Gas phase excitation of molecules in the near Station environment by collision with ambient flux, and;

(2) Surface processes that lead to molecular excitation. We have also considered secondary processes such as energy transfer from surface generated species but we have generally found these processes to contribute negligibly to the total irradiance.

The gas phase processes involve collisions between molecules in the near Space Station environment, principally CO_2, H_2O from cabin leakage and organics from outgassing, with incoming high velocity molecules. At altitudes of 460 km the ambient flux is predominantly O atoms and N_2 molecules. These species impact the station and its outgassed cloud at a relative velocity of about 8 km s^{-1} and therefore have sufficient energy to excite molecular states by direct T-E,V processes, undergo reactive collisions with gas or surface-adsorbed species, or to dissociate (in the case of N_2). Available experimental and theoretical excitation efficiencies and cross sections were used to compute production rates. Where no data were available, estimates for specific rates were made.

The primary results of our analysis are as follows. Incoming O and N_2 molecules impact gaseous CO_2 and H_2O producing vibrational excitation. Fast O atoms also react with water and organic species to form vibrationally excited OH. Considering the cross sections for these processes and the outgassing number densities, most of the incoming ambient flux impacts Space Station surfaces. N_2 impacts with sufficient energy to cause a fraction to dissociate or to populate excited states. Surface formed nitrogen atoms are presumed to remain surface adsorbed where they eventually recombine with another N atom or an O atom. Allowing the N atoms to desorb would principally effect the NO production rate. Organic species in the ambient Station environment will adsorb on Station surfaces where they react with incoming fast O atoms to produce vibrationally excited OH and CO.

The limitations and uncertainties in our treatment are due primarily to the lack of experimental data. The principal uncertainties are in the excitation efficiencies, many of which have yet to be measured. The calculated irradiance levels are therefore believed to be accurate to within only 1 or 2 orders of magnitude. Throughout the course of this study we have sought to identify key reactions/processes requiring experimental investigation.

Our model does not treat the fate of unreactive O and N_2 surface collisions. If the accommodation coefficient is small, a large fraction will rebound elastically and will pass through the Station ambient cloud once more. In this event the gas phase emissions may have been underestimated by a factor of two.

The densities of gas phase species have been presumed to be uniform. In fact, a density gradient of specific scale height is a more accurate representation. We have sought to minimize the errors in our approach by using column densities in our calculations rather than volume densities wherever possible.

We have assumed unreactive Station surfaces as well as no external carbonaceous surfaces. We have neglected species and infrared emissions from thruster firings and the effects of solar irrradiance. Surface-enhanced radiative recombination reactions of triatomics such as NO_2 and CO_2 have been ignored. We have neglected all ionic processes. Incorporation of these effects would increase our irradiance predictions.

To determine the observed radiance levels, a simple model has been employed. The extent of Station is assumed to be large relative to the characteristic distances over which radiative emission occurs. Thus, a steradiancy of 2π has been assumed. In order to calculate the irradiance more accurately, a complete description of Space Station dimensions will be needed. To a first approximation, our results may be scaled by the product of the relevant Station surface area and a $1/r^2$ term,

$$\text{Scaling factor} = A/(v\tau)^2$$

where A is the surface area, v is the exit velocity, and τ is the radiative lifetime.

Results

$CO_2(v)$ and $H_2O(v)$ Emission

Since Space Station is moving at roughly 8 km s^{-1} relative to the ambient atmosphere, the interaction of energetic O atoms and N_2 molecules with CO_2 and H_2O from cabin leakage must be considered. There are several published studies of CO_2 and H_2O vibrational excitation by T-V process from fast O atoms and N_2 molecules (Dunn et al., 1973; Schatz and Redman, 1981; Rahbee, 1984; Ryali et al., 1982; Johnson, 1986). The majority of the work is theoretical trajectory analysis and one paper is shock tube data. The accuracy of the collisional cross sections is probably a factor of two. A compilation of the cross sections is shown in Table 2. The flux of vibrationally excited H_2O or CO_2 species is given by the product of the cross section, σ, the flux of reactive species, Φ, and the column density of the target species, α. Since we have assumed a steradiancy of 2π and we are at an altitude in which quenching processes are slow, the radiant intensity is given by,

$$I = 0.5\ \sigma\Phi\alpha \quad .$$

Using the column densities tabulated in Table 1, the photon yields for $CO_2(\nu_2)$ and $H_2O(\nu_1$, ν_2, and $\nu_3)$ have been calculated and are shown in Table 2. Items 1 through 4 show the results for interaction with fast O atoms and 5 to 8 for fast N_2 molecules.

OH Production

The reaction

$$O(8\ \text{km s}^{-1}, 2.6\ \text{eV center of mass}) + H_2O \rightarrow 2\ OH$$

is sufficiently exothermic, 1.9 eV, to produce vibrational and electronic excitation in the OH products. This reaction has been suggested as a possible source of Shuttle glow (Slanger, 1983). The presence of organic compounds in the local Station environment indicates that the more general reaction O + R-H to be most appropriate for consideration here. A reaction (and excitation) cross section of 1×10^{-17} cm^2 has been employed in the radiance calculations for these reactions. The result is shown in Item 9, Table 2.

There is no experimental data for these reactions. Considering the relative abundance of H_2O and organic compounds in Station and Shuttle environment, the rates and products of these reactions represent key uncertainties.

Surface Production of NO(X,v)

The dissociation efficiency of 8 km s^{-1} N_2 molecules impacting a surface is unknown. Reasonable estimates place the dissociation efficiency between 0.1 and 10^{-5}. The upper bound has been set by energetic constraints (assuming small chemisorption energies). Clearly, the nature of the surface should greatly influence the dissociation efficiency and the fate of the atoms (i.e., chemisorbed or reflected). The dynamics of high velocity nitrogen dissociation is an area requiring detailed examination.

We have assumed a dissociation probability of 0.01. On surfaces the recombination of N atoms and O atoms is fast. Since the O atom flux exceeds

Table 2. Calculated Radiance Results

	Emitter	Cross Section or Excitation Efficiency	Transition Energy (cm^{-1})	τ (s)	I(R)**
1.	$CO_2(\nu_3)$	2.8×10^{-19}	2349	2.3×10^{-3}	0.17
2.	$H_2O(\nu_2)$	8×10^{-17}	1595	4.5×10^{-2}	64
3.	$H_2O(\nu_1)$	6×10^{-18}	3652	2.8×10^{-1}	4.8
4.	$H_2O(\nu_3)$	5×10^{-18}	3755	2.5×10^{-2}	4.0
5.	$CO_2(\nu_3)$	1.5×10^{-20}	2349	2.3×10^{-3}	7.6×10^{-4}
6.	$H_2O(\nu_2)$	2×10^{-17}	1595	4.5×10^{-2}	1.3
7.	$H_2O(\nu_1)$	9×10^{-19}	3652	2.8×10^{-1}	5.9×10^{-2}
8.	$H_2O(\nu_3)$	9×10^{-19}*	3755	2.5×10^{-2}	5.9×10^{-2}
9.	OH(v)	1×10^{-17}*	--	$\sim 1 \times 10^{-2}$	36
10.	NO(v)	1×10^{-3}*	--	$\sim 2 \times 10^{-2}$	8000
11.	N_2(B-A)	1×10^{-4}*	9552	$\sim 1 \times 10^{-5}$	400
12.	CO(v)	1×10^{-1}*	--	$\sim 1 \times 10^{-2}$	1×10^4
13.	OH(v)	1×10^{-1}*	--	$\sim 1 \times 10^{-2}$	1×10^4

*Estimated

**Units of Rayleighs, also 0.5 x the total flux of the excited state species. Since the entire vibrational progressions are considered for OH, CO, and NO, frequencies are not shown for these species. In addition, the radiative lifetimes shown for these species are estimates only. Vibrationally dependent values are available in the literature.

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the N_2 flux, the NO flux off the surface may be as high as 2 percent of the incoming N_2 flux,

$$\text{NO flux off} = 1.6 \times 10^{11} \text{ molecules cm}^{-2} \text{ s}^{-1} \quad .$$

If we assume a 300 K thermal exit velocity of 4×10^4 cm s^{-1} then,

$$[\text{NO}] = 4 \times 10^6 \text{ molecules cm}^{-3} \quad .$$

The three states of NO which lie below the dissociation energy are $B^2\pi$, $A^2\Sigma$, and $X^2\pi$ ground state giving rise to beta, gamma, and vibration-rotation bands, respectively. Although neither the $B^2\pi$ nor the $A^2\Sigma$ states directly correlate to the ground state atoms, emission from both states is observed in the surface-enhanced recombination of these species (Dunn et al., 1973). The published account of this work, however, could not rule out energy transfer from N_2^* as the source of NO(A,B). Vibrational excitation of ground state NO should account for a major fraction of the reaction path and the infrared vibration-rotation bands should be prominent in the surface-enhanced recombination of N and O atoms. The fraction of NO which recombines on surfaces with vibrational excitation is unknown and would be a key experimental measurement. For these calculations, we have used 0.10. This fraction was chosen because it is that estimated for CO formed with vibrational excitation from the recombination of C and O atoms on metal surfaces (Tully, 1980; Kori and Halpern, 1983). The radiance estimate for NO(X,v) is shown in Item 10, Table 2.

The CO studies discussed above indicate roughly equal population of all available vibrational levels. Without experimental data for the NO system, equal populations were assumed for this system (in vibrational levels v=1-19, the full extent of our spectroscopic data base).

N_2^* Surface Production

The formation of nitrogen electronic and vibrational excited states from the collision of fast N_2 molecules may occur by direct T-E,V conversion or by dissociation followed by recombination. Neither process has yet been investigated. The only states that directly correlate with the ground state atoms are the $A^3\Sigma$ and $X^1\Sigma$ ground state. Therefore, these are the most likely products. Although the excitation efficiency for $N_2(A^3\Sigma)$ formation has not been directly determined, an estimate may be calculated from the observed Vegard-Kaplan emission intensity as seen on Shuttle by the ISO instrument during the Spacelab 1 mission. The N_2(A-X) emission intensity has been measured as 5 Rayleighs/Angstrom. Assuming a resolution of 10 Angstroms, a field of view depth of 100 cm, and using the Einstein coefficient for the 0 to 6 band, the $N_2(A^3\Sigma, v=0)$ number number density is calculated to be 3×10^6 molecules cm^{-3}. This corresponds to a 2.5×10^{-4} excitation efficiency for $N_2(A,v=0)$ of the incident N_2 flux at 240 km. We have used an efficiency of 1×10^{-3} for the entire state. The N_2(A) flux is therefore,

$$N_2(A^3\Sigma) \text{ flux} = 8 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$$

and

$$[N_2(A^3\Sigma)] = 2 \times 10^5 \text{ molecules cm}^{-3} \quad .$$

The N_2(A) state is long-lived, $\tau = 2s$, and may be quenched by the other species also in Station environment. The quenching of N_2(A) by NO to form NO(A) is rapid, 6×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Since we are in a region where quenching is slow, the photon emission rate will be identical to the NO(A) formation rate,

$$\text{NO(A) formation rate} = (6 \times 10^{-11})(2 \times 10^5)(4 \times 10^6)$$
$$= 48 \text{ molecules cm}^{-3} \text{ s}^{-1} \quad .$$

For a column height of 27m, an irradiance of 6.5×10^{-2} Rayleighs is calculated. Compared to the other processes shown in Table 2, however, these values are small. Since the NO(A) formation rate is low, NO(X,v) production from NO(A,v) radiative cascade will be negligible.

Considering the low number densities at this altitude, secondary energy transfer processes such as described above are calculated to be insignificant in comparison to direct excitation processes. Since the yields from these mechanisms scale as the square of the number densities, such mechanisms may become important at lower altitudes or during transient events that significantly increase local densities such as attitude adjustment or trimming maneuvers.

First positive emission has been observed in the recombination of nitrogen atoms on metallic surfaces (Brennan and McIntyre, 1982) and has been suggested as one of the emitters in Shuttle glow (Green, 1984). Since the $B^3\pi$ state of N_2 does not correlate to the ground state atoms, the mechanism for populating this state by surface-catalyzed atom recombination is unclear. Owing to the uncertainty in this process, we have assumed an excitation efficiency of 10^{-4} for this process. The results for this system are shown in Item 11, Table 2.

CO, OH Surface Production

Even with non-reactive surfaces, we expect near unity sticking coefficients for organic molecules. Once on the surface the organic species may react with incoming O atoms to produce CO and OH in their ground and vibrationally excited states (the electronic excited states are also possible but are not considered since this study is limited with IR radiators). The flux of organic material assuming molecular effusion onto the surface is given by,

$$\Phi = 0.25\ \rho v$$

where ρ is the ambient density of organic species and v is the thermal velocity of the ambient organics (taken as 4×10^4 cm s^{-1}). Since the O atom flux is three orders of magnitude in excess of the organics, the product CO and OH fluxes have been taken as equal to the incoming organic flux. The resulting CO and OH fluxes are therefore,

$$\text{CO flux} = 2 \times 10^{11} \text{ molecules cm}^{-2}\text{ s}^{-1}$$

$$\text{OH flux} = 2 \times 10^{11} \text{ molecules cm}^{-2}\text{ s}^{-1} \quad .$$

Assuming an exit velocity of 4×10^4 cm s^{-1}, the resulting concentrations area,

$$[CO] = [OH] = 5 \times 10^6 \text{ molecules cm}^{-3} \quad .$$

The radiance calculations have been performed assuming an excitation probability of 0.10. The results are shown in Item 12 and 13, Table 2. The surface produced OH(X,v) is predicted to exceed the gas phase production by a factor of 200. The surface production rates have not been measured and thus represent a key uncertainty since these processes are likely to produce significant IR emissions at Station altitude.

Total Irradiance Results

A composite spectrum of all the major emitting species is shown in Figures 1 and 2. Figure 2 shows the data from Figure 1 on log scale. The spectra for the diatomics were calculated using a spectral generation code.

The CO_2 and H_2O spectra were generated by converting all rotational lines on the HITRAN tape for these species from absorption strength to emission intensity. The band averaged Einstein coefficients agreed with published values to generally within 10 percent, verifying our methodology.

Each spectrum was produced separately then added together point by point to generate the composite spectrum shown in Figures 1 and 2. The intensity units are Rayleighs/µm. The resolution element has been chosen to be constant at 100 Angstroms.

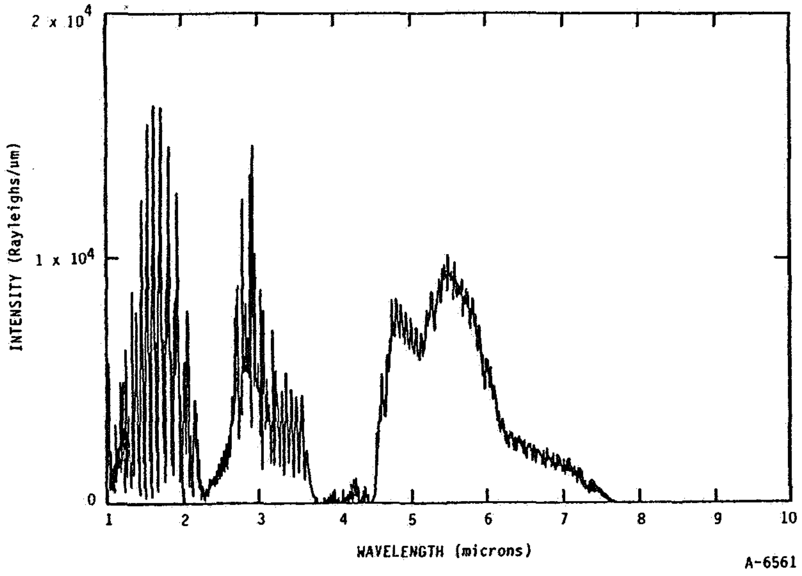

Fig. 1. Predicted Station IR irradiance.

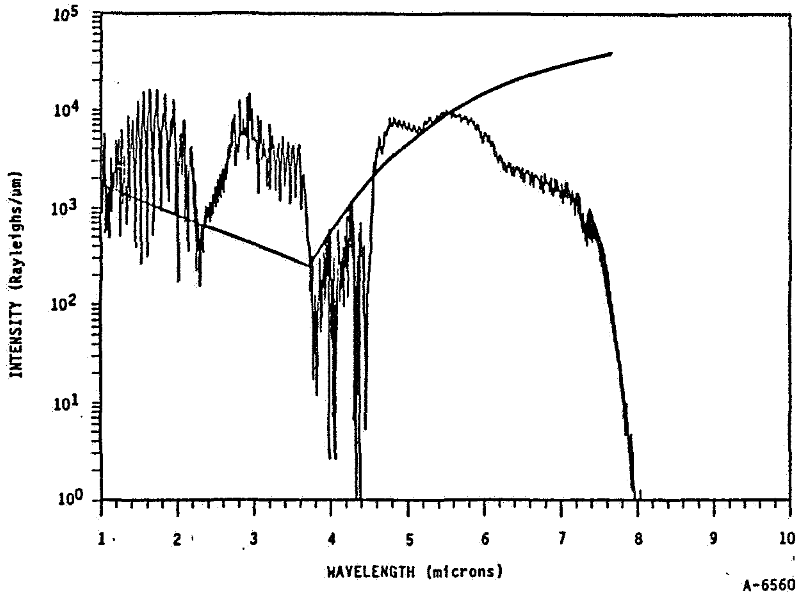

Fig. 2. Prediction Station IR irradiance, log scale.

Conclusions

Figures 1 and 2 show that the observed irradiance is predicted to be non-uniform over the 1 to 8 μm region. No irradiance has been predicted for wavelengths longer than this. In order to properly interpret these results they should be compared to anticipated background levels. Zodiacal light on the ecliptic in the 1 to 2, 2 to 3, and 3 to 4 μm bands have been calculated to be 1000, 500, and 300 Rayleighs, respectively (these values have been adjusted for the 2π steradiancy of our model). Figure 2 shows the predicted irradiance in comparison to the zodiacal background. The results in Figures 1 and 2 equal or exceed these predicted background levels, indicating that the Space Station IR background from atmosphere-induced emissions may be a problem of consequence.

The total irradiance shown in Figures 1 and 2 is dominated by surface processes. These are, unfortunately, the processses that are subject to the greatest uncertainty owing to the lack of experimental data. We have previously outlined our basic assumptions. Our irradiance results are estimated to be accurate to within 1 or 2 orders of magnitude. Improved estimates will require results from a detailed experimental and theoretical program.

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