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Infrared Emission Associated with Chemical Reactions on Shuttle and SIRTF Surfaces

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SUMMARY

We estimate the infrared intensities which would be observed by the Shuttle
Infrared Telescope Facility (SIRTF), and which are produced by surface chemistry fol-
lowing atmospheric impact on SIRTF and the Shuttle. Three possible sources of reac-
tants are analyzed: (1) direct atmospheric and scattered contaminant fluxes onto the
Shuttle's surface; (2) direct atmospheric and scattered contaminant fluxes onto the
SIRTF sunshade; and (3) scattered fluxes onto the cold SIRTF mirror. The chemical
reactions are primarily initiated by the dominant flux of reactive atomic oxygen on
the surfaces. Using observations of the optical glow to constrain theoretical
parameters, we estimate for source (1) that the infrared glow on the SIRTF mirror will
be comparable to the zodiacal background between 1-μm and 10-μm wavelengths. We
speculate that oxygen reacts with the atoms and the radicals bound in the organic
molecules that reside on the Shuttle and the Explorer surfaces. We conclude for
source (2) that with suitable construction, a <u>warm</u> (T_S >> 100K) sunshade will produce
insignificant infrared glow. We note that the atomic oxygen flux on the cold SIRTF
mirror (3) is insufficient to produce significant infrared glow. Infrared absorption
by the ice buildup on the mirror is also small.

I. INTRODUCTION

The Shuttle Infrared Telescope Facility (SIRTF) is a highly rated scientific
mission which NASA may operate from the Space Transportation System (STS) or "Shuttle"
in the 1990s. SIRTF is an approximately 1-m diam telescope that is cryogenically
cooled to about 5-10 K so that its sensitivity in the infrared can be increased. Its
prime operating wavelength regime will be in the 2-μm to 200-μm range, and it is
hoped that over much of this range, its photometric sensitivity will be limited by
infrared thermal "noise" from interplanetary dust grains (the so-called "zodiacal
background").

Many molecular vibrational and rotational transitions lie in this wavelength
range; therefore, it is of utmost importance to identify, and if possible, to limit
the infrared radiation which arises from excited molecules in the SIRTF and/or the
Shuttle vicinity. Simpson and Witteborn (ref. 1) have discussed the infrared radia-
tion that is emitted by molecules that are thermally excited, by supersonic collisions
associated with the 7.7 km sec^{-1} atmospheric flow past the Shuttle, and by solar
radiation.

Recent optical observations at wavelengths in the range of 6,000 to 8,000 A from
both the Shuttle and the Explorer satellites indicate an optical "glow" that is
visible centimeters-to-meters from surfaces impacted by the atmospheric wind, and
apparently are correlated to the flux of incoming atmospheric atomic or molecular
oxygen (refs. 2-8). Figure 1 is an optical photograph of the Shuttle glow. The glow
from the Shuttle surfaces seems to be somewhat different from that of the Explorer
surfaces. This is mainly apparent in the measured extent of the glow, ~10 cm on the
Shuttle vs 5 m on the Explorer. This perhaps indicates that different species with

different lifetimes are involved in the two glows. The lifetimes (5×10^{-3} to 3×10^{-4} sec), inferred from the extent of the optical glow, indicate that it is probably caused by transitions (with $\Delta v \gg 1$) in vibrationally excited molecules, although semiforbidden electronic transitions cannot be completely ruled out. The spectra and lifetimes of excited atomic or molecular oxygen do not match those of the species responsible for the glow observed on the Shuttle or the Explorer. Slanger (ref. 8) has postulated that the optical glow may result when the formation (and evaporation) of vibrationally excited OH occurs after there is a surface reaction of the atmosphere oxygen with the hydrogen present on the surface. If the optical glow originates from vibrationally excited molecules, considerable infrared radiation will also be emitted from these newly formed molecules. Langhoff et al. (ref. 9) quantitatively estimate that the near-infrared intensities are to be expected if OH is responsible for the Explorer glow.

This paper discusses the infrared emission associated with chemical reactions on the Shuttle and the SIRTF surfaces. The chemical reactions are initiated by the energetic flux of atmospheric atoms and molecules striking and adsorbing to the surfaces. The possibility of infrared emission from newly formed molecules that are adsorbed to the surfaces as well as those that are ejected from the surfaces are considered. The chemistry on the cold SIRTF mirror, the warm SIRTF sunshade, and the warmer Shuttle surfaces are considered separately. The observations of the optical "glow" are used to constrain the processes of infrared emission. Although we assume that SIRTF will be mounted in the Shuttle bay, the results will also be applied to the possibility that SIRTF will be a free-flyer.

II. PHYSICAL CONDITIONS

Some of the major physical conditions that are relevant to the quantitative analysis of this gas-surface interaction problem are summarized in figure 2. The expected Shuttle altitude for the SIRTF flights is approximately 300 to 400 km. The Shuttle orbital speed is 7.7 km sec^{-1}. The temperature of the Shuttle surface varies from approximately $T_S \cong 200$ K to $T_S \cong 300$ K; the temperature inside the SIRTF telescope is $T_S < 10$ K. Infrared emission will be studied from (1) the direct impact of the atmosphere onto the Shuttle surface, from (2) the direct impact of the atmosphere onto the sunshade, and from (3) the scattered flux of molecules onto the cold SIRTF mirror.

The densities and fluxes of the atmospheric species vary with respect to altitude and thermospheric temperatures (i.e., solar activity), but an upper limit on these parameters can be obtained from the solar maximum values at 300 km as listed in table 1. Other species are either chemically inert or are present in trace amounts. Also tabulated in table 1 is the kinetic energy of impact-per-particle of each species.

The Shuttle outgasses contaminants such as H_2O (23%), N_2 (70%), H_2 (4%), and CO_2 (trace), and collisions with the atmospheric stream lead to a <u>scattered</u> flux of no more than 10^{12} cm^{-2} sec^{-1} oxygen atoms incident upon the outer Shuttle surfaces (refs. 10 and 11 and E. Miller, private communication, 1983). The SIRTF mirror, however, sees a restricted solid angle and the oxygen atoms which strike the inner telescope walls and baffles will stick and freeze, so that the flux of oxygen atoms on the mirror is of order $<10^{10}$ cm^{-2} sec^{-1}. We assume that the flux of the returned H_2O and the N_2 contaminant are approximately this value, and we scale the flux of other atmospheric and contaminant species according to their abundances. In addition to the outgassing contaminants, the combustion products of the thrusters add H_2, N_2, CO_2, CO, and H_2O contamination. During the thruster firing (duration ~1 sec) the fluxes

of returned combustion products are approximately $10^{14} cm^{-2} sec^{-1}$ incident upon the outer Shuttle surfaces. While SIRTF is in operation, the time between firings will be $>10^3$ sec. Time-average fluxes are therefore $<10^{11} cm^{-2} sec^{-1}$. Table 2 summarizes the results.

The density of the Shuttle contaminants peaks at values of $10^9 cm^{-3}$ near the Shuttle's surface. The total density of atmospheric species is also of this order near the surface. Therefore, the mean free path for a collision between two gas particles is more than 1 km. This implies that most outgassing material freely expands from the Shuttle neighborhood and that no significant "ram pressure" region exists above the impact surface since the collision mean free path is so much larger than the Shuttle's size.

III.   GENERAL CONSIDERATIONS OF SURFACE CHEMISTRY

The chemical process of interest involves the impact of atoms and molecules onto a surface where they chemically react with atoms or molecules to form molecules in excited vibrational and/or electronic states. These excited molecules either remain adsorbed to the surface, where they lose their excitation energy to radiation or to the surface, or they escape the surface and thereafter lose their excitation energy to radiation. There are several specific variations to this general picture. The incident particle may react with the surface particle it strikes, in which case the incident energy E_i (as large as ~10 eV for O_2) is available to drive the chemical reaction, and some fraction of that energy may be carried off as kinetic energy, E_k, by the newly formed molecule. Generally, the chemical cross sections are at least an order of magnitude smaller than geometric cross sections so that this process can have, at most, an efficiency of $\lesssim 0.1$.

On the other hand, the incident particle can stick, migrate across the surface, and find a reactive partner. In this case, the energy, E_i, is lost to the surface. The surface particle may be part of the "clean" surface (e.g., paint or Scotchgard), or a Shuttle contaminant which has adsorbed to the surface (e.g., H_2O or thruster fuel), or an atmospheric particle which was previously adsorbed. The newly formed molecules can be ejected by thermal evaporation, or by the conversion of chemical energy to translational energy upon formation. In the former case, the ejection velocity, v_{ev}, is given

$$v_{ev} = 2 \left(\frac{kT_s}{m_i}\right)^{1/2} = 0.19 \left(\frac{T_s}{A_i}\right)^{1/2} km\ sec^{-1} \tag{1}$$

with A_i the atomic mass and T_s in K. In the latter case, the ejection velocity v_{ch} is given

$$v_{ch} = \left(\frac{2E_k}{m_i}\right)^{1/2} = \frac{14}{A_i^{1/2}} \left(\frac{E_k}{1\ eV}\right)^{1/2} km\ sec^{-1} \tag{2}$$

where E_k is the chemical energy transformed to kinetic energy. Hollenbach (Ref. 12) and Hunter and Watson (ref. 13) theoretically model H_2 formation on cold (T < 30 K) surfaces and show that, in this case, $E_k \cong 0.1$ eV. For heavier molecules, E_k is

probably much less (ref. 14). As an example, $v_{ev}(OH) = 0.7$ km sec^{-1}, and $v_{ch}(OH) = 1.1$ km sec^{-1} for $T_s = 250$ K, and $E_k = 0.1$ eV.

The composition of the surface determines a number of important parameters including evaporation times, surface-migration diffusion times, and sticking probabilities. In general, we shall adopt the pessimistic view that sticking probabilities are unity, that diffusion times are sufficiently short, and that evaporation times are sufficiently long so that molecule formation can proceed efficiently. However, we shall consider two types of surface composition: (1) inert surfaces which only adsorb atmospheric and contaminant gases and therefore act as catalysts for reactions between these gases, and (2) chemically reactive surfaces which supply nonadsorbed atoms and molecules for reaction with the striking or the adsorbed particles.

The surface compositions of the SIRTF sunshade (possibly an aluminum oxide or the SIRTF mirror) may provide an example of an "inert" surface. On the other hand, the surface composition of the Shuttle tiles (Scotchgard waterproofing material, a 50-50 mixture of trichloroethane and fluoroalphatic resin) and the Explorer Satellite (probably painted surface) may provide examples of chemically reactive surfaces.

The sticking probabilities of incident molecules or atoms onto a surface depends primarily on the mass ratio, μ, of the incident particle to the surface particle it strikes, the gas-surface binding energy, D, and the energy, E_i, of the incident particle (ref. 15). The sticking probabilities approach unity for $\mu > 1$ and/or for $E_i/D \ll 1$.

Since the SIRTF mirror and the Shuttle surfaces are likely to be covered with ice and organic materials of relatively low mass per atom, the condition $\mu > 1$ approximately holds for most gas-surface interactions of interest with the exception of incident H or H_2. As a first approximation, we make the assumption that all sticking coefficients are unity.

Several timescales are relevant to the process of the ejection of excited, newly formed molecules from surfaces: the timescale t_{ev} for evaporation from the surface, the radiative lifetime (especially the vibrational lifetimes t_{vib} which lead to near-infrared production), and the timescale t_{tr} for transferring the excitation energy to the lattice (e.g., phonon excitation). The evaporation time t_{ev} for a molecule adsorbed with a binding energy, D, to a surface with temperature, T_s, is approximately

$$t_{ev} \cong \nu_0^{-1} e^{D/kT_s} \tag{3}$$

where k is Boltzmann's constant and ν_0 is the vibrational frequency of the adsorbed molecule. Typically, for physically adsorbed species, $D/k \approx 1,000-5,000$ K and $\nu_0 \approx 10^{12-13}$ sec^{-1}. On the warm ($T_s \sim 250$ K) Shuttle surfaces, $t_{ev} < 10^{-7}$ sec, whereas on the cold ($T_s \sim 10$ K) SIRTF surfaces the evaporation times are essentially infinite, and icy surface layers from adsorbed molecules. The radiative lifetimes for vibrationally excited gas molecules are $t_{vib} \approx 10^{-2}$ sec while electronically excited molecules have lifetimes generally $\lesssim 10^{-6}$ sec. The radiative lifetimes for adsorbed molecules may be somewhat shorter. The timescale for transferring excitation energy through various processes to other adsorbed molecules in an icy surface layer and to the underlying surface are discussed in section VI.6. In general the net timescale for transfer is $t_{tr} \lesssim 10^{-5}$ sec.

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In section V, consideration of these timescales leads to an examination of the process of the ejection of excited, newly formed molecules from warn Shuttle surfaces by evaporation followed by infrared emission by the ejected molecule. However, on cold SIRTF surfaces we consider (section VI) three possibilities: (1) the newly formed molecule remains adsorbed to the surface, transfers much of its energy to the surface, but radiates a fraction $\approx t_{tr}/t_{vib}$ in the infrared; (2) the molecule, newly formed from adsorbed reactants, transforms a part of its excitation energy to translational energy and is ejected from the surface; and (3) the collision of an energetic gas particle with a surface reactant results in a chemical reaction and the newly formed excited molecule is ejected as part of the collision process.

IV. UPPER LIMITS ON IR EMISSION FROM SURFACE CHEMISTRY

Before examining the chemical processes on surfaces in sections V and VI, it is instructive to parameterize the problem of IR emission from newly formed molecules that are ejected from surfaces. The basic idea is to calculate the maximum IR intensity produced in the vicinity of a surface by assuming that every particle in an incoming reactant flux forms an excited molecule. Each molecule is ejected from the surface with ΔE of vibrational energy which is radiated into an infrared band of wavelength range, $\Delta\lambda$. To quantitatively calculate a realistic IR intensity, we multiply this maximum intensity by an efficiency factor, η, which is the fraction of incident particles that are actually ejected as excited molecules. The detailed surface chemistry of the later sections, as well as the quantitative measurement of the observed glow, will help to quantitatively estimate η.

A simple and instructive model is shown in figure 3a. A planar flux, F, of particles is incident upon a sphere of radius, r_0. We assume that the particles react on the surface and isotropically eject a flux, F_{ej}, of vibrationally excited molecules from the surface. An efficiency factor, η, can be then defined as

$$\eta \equiv \frac{4F_{ej}}{F} \qquad (4)$$

where η is the fraction of colliding reactants which result in the ejection of excited molecules (the factor of 4 reflects the difference between the impact cross sectional area, πr_0^2, and the surface area, $4\pi r_0^2$, of ejection). The density of scattered excited molecules as a function of distance, r, from the center of the sphere can be written

$$n_* = \frac{F}{4v_{ej}} \eta \left(\frac{r_0}{r}\right)^2 e^{-[(r-r_e)/r_{er}]} \qquad (5)$$

where v_{ej} is the speed of the ejected molecules and $r_{cr} = v_{ej}t_{vib}$ is the e-folding distance a molecule travels before radiating its vibrational energy. The intensity of radiation directed back normal to the surface can then be written

$$I \cong \int_{r_0}^{\infty} \frac{n_* \Delta E \, dr}{4\pi \, \Delta\lambda \, t_{vib}} \qquad (6)$$

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where, as mentioned above, ΔE is the vibrational excitation energy per molecule and $\Delta\lambda$ is the wavelength range of vibrational emission. Performing the integration

$$I \cong 3\times10^{-7} \; \frac{W}{cm^2 \; ster \; \mu m} \; \frac{F_{14}\eta \; \Delta E_{ev}}{\Delta\lambda_{\mu m}} \left(\frac{1}{1 + \dfrac{r_{cr}}{r_0}} \right) \tag{7}$$

where $F_{14} = F/10^{14} \; cm^{-2} \; sec^{-1}$, $\Delta E_{ev} = \Delta E/1 \; eV$, and $\Delta\lambda_{\mu m} = \Delta\lambda/1 \; \mu m$. The maximum occurs for $r_{cr} < r_0$, which corresponds to short radiative lifetimes and emission near the surface. This intensity is to be compared with the zodiacal intensity which ranges between 10^{-10}-10^{-11} W cm^{-2} $ster^{-1}$ μm^{-1} for 1 $\mu m < \lambda < 10$ μm, the wavelength region where most of the vibrational energy of molecules is emitted. Therefore, we can immediately see that the reactive flux of atomic oxygen onto the cold SIRTF mirror ($F_{14} \cong 10^{-4}$) can, at most, produce intensities of the same order as the zodiacal background. However, the direct flux of atomic oxygen onto the outer Shuttle surfaces (including, perhaps, a portion of the inner SIRTF sunshade that is exposed to the atmospheric impact) experiences a flux $F_{14} \sim 1$. Potentially, this flux could lead to large near-infrared backgrounds on the SIRTF mirror. At free-flying altitudes of ≈ 900 km, it will only be during solar maximum that the direct atomic oxygen flux is sufficient ($F_{14} \sim 10^{-2}$) to potentially produce a significant infrared glow.

The direct flux glow creation suggests a somewhat different geometrical model, since the molecules are ejected from the impact surface but radiate to a different surface, the SIRTF mirror. Figure 3b shows a simple geometric model for this case. The distance x_* is the characteristic length along the SIRTF axis where the density of excited molecules, n_*, drops by e. The intensity normal to the SIRTF mirror is then

$$I \cong \frac{n_*(r_d)x_* \; \Delta E}{4\pi \; \Delta\lambda \; t_{vib}} \tag{8}$$

$$I \cong 4\times10^{-7} \; \frac{W}{cm^2 \; ster \; \mu m} \; \frac{F_{14}\eta \; \Delta E_{ev}}{\Delta\lambda_{\mu m}} \left(\frac{r_d}{r_{cr}}\right)^{1/2} \left(\frac{r_0}{r_d}\right)^2 e^{-r_d/r_{cr}} \qquad r_{cr} < r_d \tag{9}$$

$$I = 3\times10^{-7} \; \frac{W}{cm^2 \; ster \; \mu m} \; \frac{F_{14}\eta \; \Delta E_{ev}}{\Delta\lambda_{\mu m}} \left(\frac{r_0}{r_d}\right) \left(\frac{r_0}{r_{cr}}\right) \qquad r_{cr} > r_d \tag{10}$$

where r_d is the characteristic distance from the impact surface to the SIRTF aperture.

First, let us consider the impact area to be the outer Shuttle surface (the geometry is such that the flux onto the outer SIRTF structure is unlikely to eject molecules into the line of sight of the SIRTF mirror). The worst-case geometry is pictured in figure 4, where we estimate $r_d \cong 6$ m and $r_0 \cong 3$ m.

We estimate $r_{cr} = v_{ej}t_{vib} \cong 5$ m. Using equation (9) we find

$$I \approx 3\times10^{-8} \; \frac{W}{cm^2 \; ster \; \mu m} \; \frac{F_{14}\eta \; \Delta E_{ev}}{\Delta\lambda_{\mu m}} \tag{11}$$

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Thus, though the intensity has been reduced somewhat because of the geometry, we still require $\eta < 10^{-3}$ for the intensity to drop below the zodiacal background.

Finally, consider the impact of oxygen atoms on the inner sunshade of SIRTF. Here, $r_0 \cong 1$ m, $r_d \cong 2$ m, and $r_{cr} \cong 5$ m so that equation (10) gives

$$I \cong 3\times10^{-8} \; \frac{W}{cm^2 \; ster \; \mu m} \; \frac{F_{14} \eta \; \Delta E_{eV}}{\Delta\lambda_{\mu m}} \tag{12}$$

Again, a small efficiency $\eta \lesssim 10^{-3}$ is required at Shuttle altitudes so that the infrared "glow" will not exceed that of the zodiacal background. Note, however, that at free-flyer altitudes $F_{14} \leq 10^{-2}$ and a relatively large efficiency of $\eta > 0.1$ is required for significant infrared glow. We discuss the physical processes which determine η in the following sections, and we make quantitative estimates of this efficiency parameter. It will be demonstrated that physical considerations as well as the observational constraints that are provided by the optical glow place likely upper limits of 10^{-3} to 10^{-4} on η.

V. INFRARED EMISSION INITIATED BY CHEMISTRY ON WARM SURFACES

A. Optical Glow on the Shuttle and Explorer Satellites: Constraints on Infrared Emission

One of the first observations which indicated that surface chemistry was producing and ejecting molecules from orbiting spacecraft was the detection of an optical glow by the Visible Airglow Spacecraft Experiment on board the Atmospheric Explorer Satellites AE-C, AE-D, and AE-E (refs. 3 and 4). The spectroscopic instrument used in the observation measured the intensity at 6 wavelengths (2,800A, 3,371A, 4,278A, 5,200A, 6,563A, and 7,320A) with ~20A bandwidth. Besides the spectra, two key observational characteristics of the glow were:

1. "The glow brightness peaks in the forward direction and decreases as the angle of attack ϕ, the angle between the line of sight of the photometer and the satellite velocity vector, increases until it reaches noise levels at about 120 degrees" (refs. 3 and 4). Since the satellite has dimensions of order 1 m, this means that the optical glow extends >1 m from the impact surface. Yee and Abreu (refs. 3 and 4) compare the dependence of the observed intensity with attack angle with a theoretical model in which the excited molecules eject isotropically with a source function proportional to $\cos^3 \phi$, a velocity 2×10^5 cm sec^{-1} and a lifetime $t = 5\times10^{-3}$ sec. The incoming flux ($\alpha \cos \phi$) and the impact energy ($\alpha \cos^2 \phi$) may explain why the initial production rate has a $\cos^3 \phi$ angle of attack dependence (refs. 3 and 4).

2. Above 160 km, the glow brightness decreases exponentially with increasing altitude at the same rate as the atomic oxygen number density, suggesting a production mechanism in which atomic oxygen plays a role. Below 160 km the brightness is no longer directly proportional to the atomic oxygen density. Slanger (ref. 8) suggests it scales with the O_2 density at lower altitudes, where the O_2 density surpasses the O density.

The observations of the glow intensity from the Explorer satellites can be used to derive an efficiency for the production of optical photons. An optical photon

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production efficiency η_{opt} can be defined as the number of optical photons produced per incident colliding reactive particle, i.e.,

$$\eta_{opt} \equiv \frac{F_{opt}}{F} \tag{13}$$

where F_{opt} is the columnar emissivity of optical photons (~5,200-7,300A) detected in the Explorer experiment. Typically $F_{opt} \approx 2\times10^{10}$ photons cm^{-2} sec^{-1} and F (atomic oxygen) $\approx 10^{16}$ particles cm^{-2} sec^{-1} so that $\eta_{opt} \cong 2\times10^{-6}$.

An optical glow has also been observed on the Shuttle (ref. 5) which may have a similar spectrum to the Explorer glow between 5,000A to 8,000A, although very poor spectral resolution prevents a detailed comparison (ref. 6). An apparently major difference between the Shuttle glow and the Explorer glow is that the former extends only 5 to 10 cm from the impact surface, whereas the latter extends several meters. Thus, while the radiative lifetime of the optical excitation from the Explorer was estimated by Yee and Abreu (refs. 3 and 4) to be ≈ 5 ms, the radiative lifetime from the Shuttle is estimated to be ≈ 0.3 ms by Banks et al. Banks (private communication) estimates the limb brightened intensity of the Shuttle's glow to be ≈ 100 k Rayleighs (= 10^{11} photons cm^{-2} sec^{-1}) which translates to a columnar flux in the direction of the impact of $F_{opt} \cong 3\times10^{9}$ photons cm^{-2} sec^{-1}. At the altitude of the glow observation, the atomic oxygen flux is $\cong 1.4\times10^{15}$ cm^{-2} sec^{-1}, resulting in $\eta_{opt} \approx 2\times10^{-6}$. Although the measurement of the intensity and the correction for limb-brightening is approximate, it is rather surprising to note the similarity in η_{opt} (Explorer) and η_{opt} (Shuttle).

The observed optical glow can be used to constrain the infrared intensity produced by the atmospheric impact if we can relate η_{opt} to η. From their definitions we see that

$$\frac{\eta_{opt}}{\eta} = \frac{F_{opt}}{F_{ej}} \tag{14}$$

their ratio is just the fraction of excited molecules which emit an optical photon. If the excitation is electronic, then roughly one optical photon will be omitted for every excited molecule snd $\eta_{opt}/\eta \sim 1$. This appears unlikely, however, because electronic excitations have lifetimes ≤ 1 μsec. If the excitation is vibrational, then it is likely that only a small percentage of excited molecules will radiate optical photons ($\Delta v > 5$, where Δv is the jump in vibration levels in the transition). This fraction depends on the percentage of excited molecules which are ejected in high-v states and the relative lifetimes of these high-v states to optical decay vs infrared decay. Langhoff et al. (ref. 9) treat the spectrum of OH which is equally populated in all v states and with a rotational population given by $T_r = 300$ K (see Fig. 5). OH has been suggested by Slanger (ref. 8) as the newly formed molecule formed after atmospheric O or O_2 impacts the surface. Regardless of the precise identity of the ejected molecule, the OH spectra suggests that, for a vibrationally excited molecule, $\eta_{opt}/\eta \sim 10^{-2}$.

Therefore, the observations of optical glow on the warm impact surfaces of the Shuttle constrain $\eta \sim 2\times10^{-4}$, a number which is perhaps good to within an order of magnitude. The extent of the optical glow of ~10 cm (we note again that this is an order of magnitude smaller than what one would expect from OH) suggests that the scale length for IR emission is $r_{cr} < 1$ m, since the lifetime of low-v states is

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perhaps an order of magnitude larger than the lifetimes of high-v states (ref. 9). Such a low efficiency and small value of r_{cr}, coupled with the geometrical factors discussed in Section IV and incorporated into equations (9) and (10), mean that IR intensity seen by SIRTF from the glow is constrained to $I \leq 10^{-11}$ W cm^{-2} ster μm at 1-10 μm — an intensity comparable to the zodiacal emission. Using the model outlined in figure 4, equation (9), and the parameters above, we schematically compare in figure 6 the expected IR spectrum of the glow (using the OH spectrum as a prototypical spectrum of vibrational emission from molecules) to that of the zodiacal light seen by SIRTF. We briefly discuss below the types of chemical reactions which may lead to the low, observationally constrained efficiency η derived above.

B. Chemistry on Warm Inert Surfaces

An initially inert surface such as that of the SIRTF inner sunshade is exposed to a flux of atmospheric gases and Shuttle contaminants which could, in principle, build up many monolayers of icy surface. This buildup is offset by the thermal evaporation of the adsorbed gases. The condition for maintenance of the initial inert surface is therefore

$$(A_{ss}F_c)^{-1} > t_{ev} \qquad (15)$$

where the left-hand side of equation (15) represents the timescale for a particle to adsorb to a surface site; A_{ss} is the area of a surface site ($\approx 10^{-15}$ cm^2) and F_c is the particle flux. Substitution of the evaporation time, t_{ev}, into equation (15) obtains

$$T_s > \frac{D/k}{\ln(\nu_0/A_{ss}F_c)} \qquad (16)$$

The main adsorbed species (see tables 1 and 2) tend to build up ices of H_2O, CO_2, N_2, and O_2. The binding energies of these molecules on the surfaces of these ices are of order $D/k \approx 1,000-5,000$ K. Using representative values of $D/k \cong 3,000$ K, $\nu_0 = 10^{12}$ sec^{-1}, $A_{ss} = 10^{-15}$ cm^2, and $F_c = 10^{12}$ particles cm^{-2} sec^{-1}, we find that $T_s > 100$ K to prevent ice buildup. This means that a warm SIRTF sunshade (and the Shuttle surfaces) will on the average have no appreciable amounts of adsorbed contaminants, adsorbed atmospheric gases, or ices from, for example, the H_2O vents or the thruster firings. However, surface chemistry can proceed with a tiny fraction of an adsorbed monolayer.
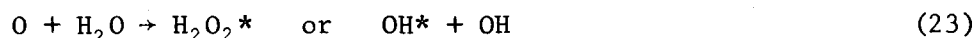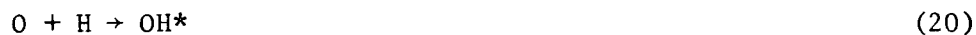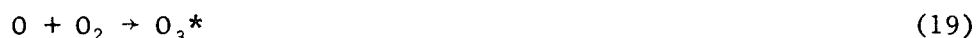
The chemistry on a warm, inert, mostly ice-free surface proceeds in one of two ways: (1) Reactant A strikes the surface, sticks (adsorbs), and migrates across the surface to combine with reactant B, which has previously adsorbed and has not yet evaporated. The maximum flux of evaporating newly formed molecules is then given by the smaller of flux A and flux B. This process is efficient for glancing angles of incident particles, since the impact energy (1/2 mv_i^2 where v_i is the component of velocity normal to the surface) plays no role in the chemical reaction. This contradicts observations of both the Explorer and Shuttle glows, which decrease rapidly in intensity as the angle of attack, ϕ, becomes more glancing. (2) Reactant A directly strikes and reacts with reactant B which is adsorbed to the surface. Since the probability of reaction may scale with the impact energy ($\alpha \cos^2 \phi$), this mechanism is more consistent with the observed dependence of the glow. The probability of a reaction in this case is proportional to the fraction of the surface covered by adsorbed reactant B.

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Although we will consider only the second process in subsequent discussion, there is one possible example of the first process which occurs just after the transient deposition of reactive combustion products from the vernier thrusters. The main chemically reactive species is CO which has a flux of $\sim 10^{14}$ cm^{-2} sec^{-1} during the thruster firing, comparable to the direct flux of O atoms on the Shuttle surfaces. The thruster firing has a timescale of order <1 sec; therefore, <0.1 monolayers CO are deposited on the surface. In approximately 1 sec, an equal number of O atoms strike the CO to form CO_2. Thus, the flux of excited CO_2 molecules is given by

$$F_{ej}(CO_2^*) \lesssim 10^{14} e^{-t/t_0} \text{ cm}^{-2} \text{ sec}^{-1} \tag{17}$$

with $t_0 \sim 1$ sec, assuming that $t_{ev} > 1$ sec for adsorbed CO (i.e., the CO sticks until the oxygen reacts with it). Since SIRTF observations will be made at $t > 10^2$ sec after thruster firings, the emission from excited CO_2 and other molecules formed from combustion products will be negligible. We note that a component of the optical glow could originate from this mechanism, since Banks et al. report an intensification of the glow which extends up until ~ 1 sec after the thrusters fire. Another possibility is that the unburned thruster fuel (monoethylhydrazine) adsorbs and reacts with atmospheric O on this time scale.

During the SIRTF observations, however, we ignore the reactions of O with adsorbed contaminants from the thruster firings: they have long since evaporated or have been "chemically" removed. Atmospheric atomic oxygen dominates the flux of reactive species and the important reactions on inert surfaces such as the SIRTF sunshade (and possibly, but less likely, the Shuttle surfaces) are those between atomic oxygen striking adsorbed atmospheric gases or the adsorbed outgas contaminant H_2O.

$$O + O \rightarrow O_2^* \tag{18}$$

$$O + O_2 \rightarrow O_3^* \tag{19}$$

$$O + H \rightarrow OH^* \tag{20}$$

$$O + NO \rightarrow NO_2^* \quad \text{or} \quad NO^* + O \tag{21}$$

$$O + N \rightarrow NO^* \tag{22}$$

$$O + H_2O \rightarrow H_2O_2^* \quad \text{or} \quad OH^* + OH \tag{23}$$

where the star indicates excitation.

Reaction (18) cannot be important in producing an IR glow because the vibrational lifetimes of O_2 are $t_{vib} > 10^5 - 10^6$ sec. Therefore, $r_{cr} \cong 10^{10}$ cm and equation (10) predicts $I \sim 3 \times 10^{-15}$ W cm^{-2} ster^{-1} μm^{-1}, far below the zodiacal background. Essentially, the radiation is greatly diluted because so few O_2 molecules radiate near the Shuttle.

The formation of ozone potentially can be more important than the other reactions because the fluxes of O and O_2 onto the surface far exceed the fluxes of H, NO, H_2O, and N. However, the efficiencies of all these reactions are probably very small because both reactants evaporate from the surface before reacting with each other.

The fluxes of newly formed molecules are calculated under the assumption that surface coverage of the adsorbed reactants is small, and that a direct collision is

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required for a reaction, the mechanism described previously as process (2). The flux of newly formed molecules, $F*$, produced by fluxes F_A and F_B of reactants A and B on a surface is given

$$F* = F_A \alpha_B + F_B \alpha_A \tag{24}$$

where α_A and α_B are the fraction of surface sites occupied by reactants A and B respectively. The fractional surface coverage of reactant X is given when $\alpha_X < 1$,

$$\alpha_X \cong \frac{t_{ev}}{t_c} \tag{25}$$

$$\alpha_X \cong F_X A_{ss} \nu_0^{-1} e^{D_X/kT_s} \tag{26}$$

where $t_c \equiv (F_X A_{ss})^{-1}$ is the collision time for X to hit a site with area A_{ss}. Thus,

$$F* \cong F_B (10^{-27} F_A e^{D_A/kT_s}) + F_A (10^{-27} F_B e^{D_B/kT_s}) \tag{27}$$

where we have substituted $A_{ss} = 10^{-15}$ cm^2 and $\nu_0 = 10^{12}$ sec^{-1} and the quantities in parentheses, α_A and α_B, cannot exceed the minimum of 1 and F_A/F_B (for α_A) and F_B/F_A (for α_B). Putting in "typical" values $D_X/k = 3,000$ K, $T_s = 250$ K, the fluxes in table 2 appropriate to Shuttle altitudes, and letting $F* = F\eta$ in equation (12), we obtain $I(O_3*) \cong 10^{-15}$ W cm^{-2} ster^{-1} μm^{-1}, $I(OH*) \approx 10^{-17}$ W cm^{-2} ster^{-1} μm^{-1}, $I(NO_2*) \approx 10^{-18}$ W cm^{-2} ster^{-1} μm^{-1}, $I(H_2O_2*) \approx 10^{-16}$ W cm^{-2} ster^{-1} μm^{-1}, and $I(NO*) \approx 10^{-16}$ W cm^{-2} ster^{-1} μm^{-1}. These results apply to the reactions initiated by direct impact on the sunshade. All these intensities are substantially below zodiacal light intensities, but they are exponentially sensitive to the uncertain values of the binding energies, D.

However, the production of OH*, NO$_2$*, NO*, and H$_2$O$_2$* is limited by flux conservation to the fluxes of H, NO, N, and H$_2$O respectively:
$I_{max}(OH*) \leq 6\times10^{-11}$ W cm^{-2} ster^{-1} μm^{-1}, $I_{max}(NO_2*) \leq 6\times10^{-12}$ W cm^{-2} ster^{-1} μm^{-1}, $I_{max}(NO*) \leq 1.4\times10^{-10}$ W cm^{-2} ster^{-1} μm^{-1}, and $I_{max}(H_2O_2*) \leq 3\times10^{-10}$ W cm^{-2} ster^{-1} μm^{-1} (see table 2 and eq. (12)). The worst case is the formation of O$_3$ on the sunshade, where intensities of 4×10^{-9} W cm^{-2} ster^{-1} μm^{-1} are possible if D_O/k or $D_{O_2}/k \gtrsim 7,000$ K and SIRTF is at low Sortie altitudes. We note that at free-flyer altitudes, the atmospheric fluxes of O, O$_2$, N, and NO, and the scattered flux of H$_2$O are reduced by factors $>10^2$, which proportionately reduces $I_{max}(O_3*, NO*, NO_2*,$ and $H_2O_2*)$.

However, by constructing the sunshade from materials with D_O/k and $D_{O_2}/k \ll 7,000$ K, evaporation rather than ozone production will occur. Such a surface would likely evaporate the other reactants mentioned above as well. It should be noted that the Explorer surfaces, as discussed below, do not form appreciable amounts of O$_3$ by this mechanism so that engineering such surfaces will not be difficult.

The production of the optical glow by this mechanism can now be considered (e.g., assume the Shuttle and Explorer surfaces to be relatively inert). We find for example, that D_O/k or $D_H/k \gtrsim 6,500$ K would result in the optical glow from OH production. Similar values of D for the reactants which form O$_3$, NO$_2$, H$_2$O$_2$, or NO could also produce intensities of order of the optical glow. These values of D are higher

than typical estimates, and we consider a more likely production mechanism for the optical glow in the following section. Furthermore, the formation of OH is the only likely glow candidate, especially for the Explorer data, where the glow intensity was seen to scale with the atomic oxygen flux F_O. Equation (27) demonstrates that the formation mechanism envisioned here scales with the product $F_A F_B$. Therefore, only OH production will scale roughly with F_O, because F_H is relatively constant in the thermosphere where the low mass of hydrogen provides a large scale height.

If the Shuttle glow originates from the chemical reaction of adsorbed atmospheric O and H atoms (which we feel is unlikely because of the high D values involved, and because the vibrational lifetimes of OH do not match the lifetimes estimated by Banks et al. for the Shuttle glow), the glow intensity will be a very sensitive function of T_S, the Shuttle surface temperature (see eq. (27)). The glow should rapidly decrease in intensity with increasing temperature, T_S, which drives evaporation of reactants. For instance, normalizing to provide the observed optical glow at $T_S = 250$ K, we find that the glow diminishes by a factor of 10 at $T_S = 275$ K. The lack of variation in the Explorer data under conditions where surface temperature variations likely exceeded ±25 K indicate that in this case, at least, this mechanism is inoperant.

C. Chemistry on Chemically Active Surfaces

We define a chemically active surface as one which provides one of the reactants in the formation of the excited molecule. For example, a surface which is largely composed of organic molecules will have an abundance of hydrogen atoms which may react with the flux of atmospheric oxygen to form OH. The reaction probability, η, is then simply the fraction of oxygen atoms which combine with chemically bonded surface atoms or radicals rather than, for example, bouncing off the surface or adsorbing and later evaporating. Since all that is needed is $\eta \sim 2\times10^{-4}$ to produce the optical glow, this mechanism appears to be a reasonable possibility.

Several features of this mechanism are noteworthy:

1. This chemical erosion process removes material from the surface at a rate

$$R_E = m_s \eta F \cong 2\times10^{-14}\left(\frac{m_s}{m_H}\right)\eta_{-4}F_{14} \text{ gm cm}^{-2} \text{ sec}^{-1} \tag{28}$$

where m_s is the mass of the surface atom or radical removed per reaction, m_H is the hydrogen atom mass, and $\eta_{-4} = \eta\times10^{-4}$. Assuming that $m_s/m_H \sim 1$, that the density of the surface material is about 1 gm cm^{-3}, and that $\eta_{-4}F_{14} < 10$, we obtain a surface erosion rate of $\lesssim 2\times10^{-13}$ cm sec^{-1} or $\lesssim 0.1$ μm/yr. Negligible material is removed in the lifetime of the Shuttle or the Explorer. The Scotchgard or painted surfaces could easily supply the reservoir of atoms or radicals.

2. The intensity of the glow is critically dependent on the surface materials and on the existence of a chemically bonded reservoir of atoms and radicals. The sunshade, for example, could be designed so that its surface would provide very few reactants to feed this mechanism.

3. Different surface materials could lead to the production of different molecules with different radiative lifetimes, an effect noted when comparing the Shuttle and the Explorer glows.

4. The reaction of oxygen with an atom or radical already bonded in a large molecule will likely require an activation energy. This activation energy can be supplied by the impact energy, which depends sensitivitly ($\alpha \cos^2 \phi$) on the angle of attack. Such a dependence is indicated in the Explorer data, and (less quantitatively) in the Shuttle data.

5. The intensity of the glow will scale with the atomic oxygen flux, as observed in the Explorer data.

6. The glow intensity would be insensitive to the surface temperature.

For these reasons, we tentatively identify this mechanism as the one which produces the optical glow on the Shuttle and the Explorer surfaces.

VI. INFRARED EMISSION AND ABSORPTION INITIATED BY CHEMISTRY ON COLD SURFACES

As discussed in section IV, the particle flux on the cold surfaces is very small and produces at most an average intensity comparable to the zodiacal background. It is, however, still of some interest to study the chemistry taking place on the cold surfaces in some detail, in order to identify contaminating molecules. In particular, it is conceivable that the radiation is emitted in a smaller wavelength region than had been assumed when equation (7) was derived. In that case, the intensity of the glow in the restricted wavelength region might be higher than the zodiacal background. More stringent constraints on the infrared glow, in particular on η (see eq. (7)) and on the expected infrared characteristics of the "icy" layer will be useful.

A. Chemistry on Cold Surfaces

The chemistry which takes place on cold surfaces (T_s = 10 K) such as the SIRTF mirror depends critically on the energy accommodation of the impinging species because part of the excess kinetic energy may be used to overcome energy barriers. (We shall call such processes "hot" chemistry.) We will first discuss the possibility that energy accommodation is fast, implying that only activationless reactions can take place ("cold" chemistry). These reactions primarily occur as mobile-adsorbed species roam the surface to find suitable reaction partners. On the basis of laboratory experiments on diffusion in low-temperature matrices, it is expected that only H, N, and O are mobile on an icy surface at 10 K (Tielens and Hagen, in preparation). Because of flux considerations, only the latter need to be considered in the diffusion-limited surface chemistry. The reactions of interest in the "cold" chemistry are listed in table 3. Reactions of atoms and of atoms and radicals are expected to have no activation energy barriers. The reaction of O with CO and O_2 have been added since these reactions are known to occur at 10 K in solid matrices (Tielens and Hagen). The resulting composition of the "icy" layer is given in table 4 where we have assumed that all reaction products remain on the surface.

We will now discuss the possibility that part of the excess kinetic energy of the impinging species can be used to overcome activation barriers for reactions. In table 5 we list possibly important reactions and their activation energy for the "hot" chemistry. Collisional dissociation of saturated molecules is likely to be unimportant. All of the activation barriers in table 5 are less than the kinetic energy of an impinging O atom. It is unlikely, however, that all of the kinetic energy can be used to overcome the activation barrier. Part of the kinetic energy may, for example,

be lost through (inelastic) scattering collisions on the surface. In particular, H_2 present on the "icy" surface may absorb a large fraction of the kinetic energy of the impinging species. Probably only the reactions of O atoms with O_3, H_2, and H_2O are of some importance. Furthermore, it should be noted that the cross sections ($\cong 10^{-16}$ cm^{-2}, ref. 16) for these reactions are generally down by a factor of 10 when compared to the geometrical cross sections ($\cong 10^{-15}$ cm^{-2}). Finally, part of the kinetic energy of the oxygen atom will result in center-of-mass translational energy of the reaction products and cause their evaporation. The composition of the "icy" layer as given in table 4 seems, therefore, still reasonable, although the mole fraction of H_2O and O_3 is perhaps somewhat overestimated.

B. Infrared Absorption Characteristics of the "Icy" Layer

The infrared absorption characteristics of the icy layer are given in table 6. In two weeks of operation a total column density of H_2O of 1.2×10^{16} cm^{-2} will accumulate on the mirror. The column densities of other species scale according to table 4. The integrated strength of the OH stretching band is then about 2.4 cm^{-1}. The width of the band is 320 cm^{-1} (ref. 17) and the optical depth is approximately 8×10^{-3}. The optical depth in the CO_2 is negligible ($\sim 10^{-3}$). N_2 is a homonuclear diatomic molecule and its bands are therefore infrared-inactive.

C. Infrared Emission from the "Icy" Layer

The cold chemistry described in section A will leave a newly formed molecule on the "icy" surface in an electronically and/or vibrationally excited state. In this section we will discuss the fate of this excitation energy, in particular the possibility that part of the reaction energy may emerge as infrared radiation.

The energy of an electronically excited molecule can decay through a large number of radiative and radiationless channels involving combinations of electronic, vibrational and phonon transitions. Thermoluminescence experiments on photolyzed low-temperature matrices indicate that a considerable fraction of the electronically excited molecule will decay radiatively to a vibrationally excited state in a lower lying electronic state (ref. 18 and Tielens and Hagen). Little energy is expected to flow into center-of-mass translational energy during electronic decay (Tielens and Hagen).

Vibrationally excited molecules can decay through several channels, for example, (1) radiative decay, (2) delocalized lattice modes, (3) local phonon modes, (4) intramode conversion, and (5) energy exchange with neighboring molecules (refs. 19 and 20). In this section we are mainly interested in radiative decay since it leads to the emission of an IR photon. It should be noted that processes (4) and (5) do not destroy the vibrational excitation, they merely transfer it from one vibrational mode within a molecule to another, or to another molecule.

Which of these decay channels dominates depends on the relative rates. Typically radiative decay rates are $\sim 10^2$ sec^{-1} (or $t_{vib} \sim 10^{-2}$ sec). For hydrogenated diatomics, transfer to local rotational modes is fast (10^3-10^7 sec^{-1}; ref. 19). The same is true for the lowest vibrational mode of hydrogenated polyatomic molecules. For other vibrational modes in these molecules, intermode conversion and intramode cascading dominates. Typical relaxation timescales are of the order of a few nanoseconds (ref. 20). For nonhydrogenated molecules inside a matrix, transfer to local rotational modes is slow (10^{-2} – 1 sec; ref. 19), because of the large barrier to rotation. On

the surface, barriers against rotation will be greatly reduced, thus facilitating transfer to local rotational modes. The rates could be up by a factor of 10^2 (Tielens and Hagen). It seems, however, that the transfer through multipolar-multipolar inter-action of the vibrational quantum to a neighboring molecule will dominate the vibra-tional relaxation. The rate of this process will depend on the energy mismatch of the two levels involved and the concentration of the acceptor. For CO a rate of 10^{11} sec^{-1} (mole fraction)$^{-1}$ has been measured for the resonant transfer process (ref. 21). For transfer from CO to CH_4, the rate is still $4 \times 10^{+4}$ sec^{-1} (mole fraction)$^{-1}$ despite an energy mismatch of 500 cm^{-1}. In view of the composition of the "icy" layer (table 4), the vibrational levels of the molecules involved, the large dipole moment of H_2O, and the hydrogen bonding capacity of H_2O, it seems likely that most of the vibrational quanta, available upon formation of a molecule, will end up in the lowest mode of H_2O and possibly CO_2 in a time $t_{tr} \leq 10^{-5}$ sec. Transfer from these modes to the local phonon bath is expected to be rapid. Consequently only few ($\sim t_{tr}/t_{vib} < 10^{-3}$) of these quanta will escape as IR radiation. It should be noted that the zodiacal background is approximately a factor of 10 brighter in this wave-length region than it is in the one around 3 µm. This tends to make the infrared glow from molecules in the "icy" surface even less of a problem.

Substitution of $\eta \sim 10^{-3}$ and $F_{14} \sim 10^{-4}$ into equation (7) results in $I \cong 3 \times 10^{-14}$ W cm^{-2} ster^{-1} µm^{-1}, several orders of magnitude lower than the zodiacal light background. We can therefore safely ignore IR radiation from _adsorbed_ newly formed molecules on the SIRTF mirror surface.

D. Infrared Emission from Molecules Ejected from Cold SIRTF Surfaces

As discussed in section VI.C, part of the reaction energy may emerge as center-of-mass translational energy of the newly formed molecule. This may lead to ejection of vibrationally hot molecules which decay radiatively in the gas phase above the surface. In this case, the fraction of the reaction energy radiated in the IR may be of order unity. It is of some interest, therefore, to consider the possibility of ejection of newly formed molecules in some detail. Two different cases will be considered.

1. Molecule ejection following cold chemistry. In this case, the newly formed molecule is in a highly excited vibrational state and has little center-of-mass trans-lational energy. Matrix isolation studies of energy transfer in low-temperature matrices show that the energy is transferred quantum for quantum, and that the energy gap begween initial and final channel is what primarily controls the energy flow (refs. 19 and 20). The large energy gap between vibrational quanta ($\sim 2,000$ cm^{-1}) and local center-of-mass translational quanta (~ 100 cm^{-1}) ensures a small rate of transfer of vibrational-to-translational energy. Furthermore, the energy gap between local center-of-mass translational quanta and the phonon modes of the matrix material will be small. Therefore, the energy transfer from local center-of-mass translational energy to the phonon mode is expected to be fast, and ejection of newly formed molecules is likely to be unimportant.

It should be noted, however, that the energy transfer rate not only depends on the energy gap, but also on the coupling between the energy channels. In the labora-tory experiments on energy transfer inside matrices, the energy transfer to local center-of-mass translational modes may have been hampered relative to its main com-petitors — local rotational modes and radiative modes — because of the matrix sur-rounding the vibrational molecules. On the surface, decay to local center-of-mass translational modes could conceivably be much faster than anticipated on the basis of

the available experiments. No estimate of this effect is available. The evaporation of newly formed molecules from surfaces has been studied theoretically in a slightly different context (refs. 13, 14, and 22). These classical calculations (of the probability of evaporation of a newly formed H_2 molecule from an interstellar grain surface) show that the H_2 molecule will be ejected, but only barely. Heavier molecules are not expected to be ejected upon formation (ref. 14). It should be noted that these calculations neglect all energy channels other than local center-of-mass translational modes and delocalized lattice modes. The probability of ejection is therefore maximized. It seems likely, therefore, that the fraction of newly formed molecules which evaporate is small in this case. As seen in equation (7) with $F_{14} < 10^{-4}$, even an efficiency as high as $\eta \cong 0.1$ leads to IR intensities < zodiacal background.

2. Molecule ejection following hot chemistry. As mentioned in section A, it is possible that kinetic energy of the oxygen atom (~5 eV) can be used to overcome an activation barrier. In particular, O atoms may react with H_2O and O_3 (table 5). The reaction products are likely to retain some of the kinetic energy of the O atom as center-of-mass translational energy and immediately eject from the surface. Part of the kinetic energy will go into vibrational and rotational excitation of the product molecules. Subsequent radiative decay in the gas phase will produce IR photons. As mentioned in section V.A, the probability for hot chemistry to proceed is at least an order of magnitude smaller than the probability for scattering off of the surface. Thus, $\eta < 0.1$ and the intensity of IR emission is less than the zodiacal background (see eq. (7)).

VII. SUMMARY AND CONCLUSIONS

We have estimated the IR intensities seen by SIRTF and produced by surface chemistry following atmospheric impact on the Shuttle and SIRTF. These intensities are compared with the zodiacal intensity of $I \cong 10^{-10}-10^{-11}$ W cm^{-2} $ster^{-1}$ μm^{-1} from wavelengths of 1-10 μm. The chemical reactions are apparently initiated by the dominant flux of reactive atomic oxygen on the surfaces, and a general equation (7) was derived which estimated the intensity of IR emission produced as a function of the atomic oxygen flux F_O, the efficiency η of forming vibrationally excited molecules, and various atomic parameters. Three possible sources have been analyzed: (1) direct atmospheric fluxes and scattered contaminant fluxes onto the Shuttle surface; (2) direct atmospheric fluxes and scattered contaminant fluxes onto the SIRTF sunshade; and (3) scattered fluxes onto the cold SIRTF mirror.

1. The Direct Impact Flux onto Warm Shuttle Surfaces. The flux of atomic oxygen can be at most ~5×10^{14} cm^{-2} sec^{-1} onto the direct impact surfaces of the Shuttle, which lie a distance $r_d > 6$ m from the SIRTF aperture. Equation (11) gives the expected IR intensity for such a geometry in terms of F_O, η, r_d, and atomic parameters. The key atomic parameter is the lifetime t_{vib} of the excited molecule, which determines r_{cr} — the characteristic distance over which the molecule radiates in the IR. The observations of the optical glow observed on the Shuttle suggest $\eta \approx 2 \times 10^{-4}$ and $r_{cr} \sim 1$ m. From these numbers we estimate an IR (1 μm - 10 μm) glow — associated with the optical glow — which will provide an intensity of $<10^{-11}$ W cm^{-2} $ster^{-1}$ μm^{-1} onto the SIRTF mirror, an intensity comparable to the zodiacal background (see fig. 6). This calculation assumes that vibrationally excited molecules produce the optical glow; if electronic excitation is responsible, the infrared intensity is several orders of magnitude smaller. We speculate that atmospheric oxygen reacts with atoms and radicals bound in the organic molecules residing on Shuttle and Explorer surfaces.

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2. Direct Impact Flux Onto Chemically Inert Warm SIRTF Sunshade. No substantial amounts of contaminants will freeze to the sunshade surface because the high surface temperature ($T_s > 100$ K) will ensure evaporation. Therefore, the formation of IR-active molecules must involve reaction with small surface coverages of adsorbed atmospheric or contaminant molecules. The formation of O_2 produces insignificant IR flux because the long lifetimes of vibrationally excited O_2 ensure geometrical dilution of the intensity to well below zodiacal values. The formation of O_3 can be minimized by engineering sunshade surfaces with low adsorption energies $D/k < 6,500$ K for O and O_2. The Explorer surfaces are examples of such surfaces since the optical intensity from efficient O_3 formation would be brighter than that observed and would scale as the product of the atomic oxygen and molecular oxygen fluxes, instead of the observed scaling with atomic oxygen alone. The formation of OH is possible, but the maximum flux of excited molecules is then limited by the H atom flux, which lies a factor $\sim 10^3$ below the oxygen flux. This alone means $I \lesssim 10^{-10}$ W cm^{-2} ster^{-1} μm^{-1}. However, it is likely that most H and O atoms evaporate before combining. Again $D/k < 6,000$ K for H and O ensures this. Thus, the sunshade could potentially produce an IR background which is larger than the zodiacal background, and care must be taken to use materials with low binding energies for adsorption of O, O_2, and H, and to use IR cancellation methods such as chopping. If SIRTF is a free-flyer at altitudes of ~ 900 km, the formation of OH could still be a problem if O adheres, since the H atom flux changes little from 300 to 900 km.

3. Scattered Flux onto the Cold SIRTF Mirror. The atomic oxygen flux $F_O \cong 10^{10}$ cm^{-2} sec^{-1} onto the cold mirror is approximately four orders of magnitude less than the direct flux onto the warmer surfaces. The potentially strongest source of IR emission is the production of excited molecules that are initiated by the impact of the O atom onto a molecule or atom adsorbed on the surface and followed by immediate ejection of the newly formed molecule. The efficiency of this process is $\eta \lesssim 0.1$ and the resultant IR intensity $I \lesssim 3 \times 10^{-12}$ W cm^{-2} ster^{-1} μm^{-1}, less than the zodiacal background. Infrared emission from adsorbed molecules on the mirror is negligible, because of the fast transfer of vibrational excitation energy to the surface. Infrared absorption by the ice buildup on the surface is also small.

The most likely explanation for the optical glow near the Shuttle surface is the reaction of an atmospheric oxygen atom with an atom or radical bound to the organic molecules applied to Shuttle or Explorer surfaces. This explanation seems consistent with the observed intensities, the observed dependence of intensity on angle of attack, and the observed correlation with atmospheric atomic oxygen in the Explorer data. The short lifetime (t $\sim$ 0.3 msec) for the Shuttle glow when compared to the lifetimes (t $\sim$ 5 msec) for the Explorer glow supports the argument that different molecules are produced. The OH molecule, with a lifetime of ~ 5 msec, is a candidate for the Explorer glow. The Shuttle glow has such a short lifetime, in fact, that it is possible that metastable electronic, rather than vibrational excitation, is involved. In terms of the possible Shuttle IR glow, we take the worst case assumption that the excitation is vibrational. Another less likely explanation for the Shuttle glow is that OH is formed by the reaction of atmospheric O and H atoms incident upon their adsorbed partner. If this were the case, the glow intensity is very sensitive to the Shuttle surface temperature. Finally, the observed intensification of the optical glow for ~ 1 sec after thruster firings may be the result of the combustion product CO or possible unburned thruster fuel being adsorbed to the surface and removed by reaction with atmospheric O.

The physics and environment involved in the Shuttle glow problem are sufficiently complex so that quantitative theoretical analysis is difficult. We have tried to outline above a theoretical overview of the problem, to make order of magnitude estimates, and to place upper limits on certain quantities using general physical principles. In the end, however, the question of the intensity and extent of the infrared Shuttle glow will be best answered by direct observation, and we urge that such measurements be made.

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TABLE 1.- ATMOSPHERIC CONSTITUENTS AT 300 km
DURING SOLAR MAXIMUM

Species	Density, cm^{-3} [a]	Flux, cm^{-2} sec^{-1}	Kinetic energy, eV
O	6.2×10^8	4.8×10^{14}	4.74
O_2	1.6×10^7	1.2×10^{13}	9.47
N_2	2.6×10^8	2.0×10^{14}	8.29
H	2.9×10^5	2.2×10^{11}	.30
NO	2.4×10^4	1.8×10^{10}	8.88
N	6.0×10^5	4.6×10^{11}	4.14

[a]Shimazaki (private communication, 1983).

TABLE 2.- SCATTERED FLUXES ONTO SURFACES

Species	Source [a]	Flux onto SIRTF mirror, cm^{-2} sec^{-1}	Flux onto Shuttle surface, cm^{-2} sec^{-1}
O	A	10^{10}	10^{12}
O_2	A	2.5×10^9	2.5×10^{11}
N_2	A, C, O	10^{10}	10^{12}
NO	A	10^7	10^9
N	A	10^7	10^9
H	A	5×10^6	5×10^8
H_2	C, O	10^9	10^{11}
H_2O	C, O	10^{10}	10^{12}
CO	C	10^9	10^{11}
CO_2	C, O	10^8	10^{10}

[a]A = atmosphere, C = combustion, O = outgas.

TABLE 3.- "COLD" REACTIONS

$$O + O_2 \rightarrow O_3$$
$$O + NO \rightarrow NO_2$$
$$O + CO \rightarrow CO_2$$
$$O + O \rightarrow O_2$$
$$O + N \rightarrow NO$$
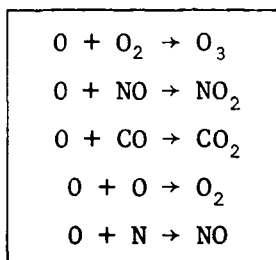
TABLE 4.- COMPOSITION OF
"ICY" LAYER USING
"COLD" CHEMISTRY

Species	Mole fraction, %
H_2O	38
CO_2	4
N_2	38
O_3	19
NO_2	.04

TABLE 5.- "HOT" REACTIONS

Reaction	Activation energy, eV
$O + H_2O \rightarrow OH + OH$	0.79
$O + CO_2 \rightarrow CO + O_2$	2.3
$O + NO \rightarrow N + O_2$	1.7
$O + N_2 \rightarrow NO + N$	3.3
$O + O_3 \rightarrow O_2 + O_2$	.21
$O + H_2 \rightarrow OH + H$	.49

TABLE 6.- INFRARED ADSORPTION CHARACTERISTICS
OF THE "ICY" LAYER

Species	Vibrational frequency, cm^{-1}	Vibrational wavelength, μm	Integrated strength,[a] $cm\ molecule^{-1}$
H_2O	3360	2.98	2.0 (-16)
	1640	6.10	7.4 (-17)
	745	13.4	5.0 (-17)
CO_2	2337	4.28	1.0 (-16)
	655	15.3	7.0 (-18)
N_2	---	---	---
O_3	1100[b]	9.09	4.0 (-19)
	1030[b]	9.71	1.4 (-17)
	695[b]	14.4	7.4 (-19)
NO_2	2900[c]	3.45	2.5 (-19)
	1610[c]	6.21	6.1 (-17)
	749[c]	13.4	

[a]Strength from gas phase data (ref. 23), except for H_2O which is taken from reference 17.

[b]Xe matrix.

[c]H_2 matrix.

Figure 1.- The optical glow photographed on STS 3 is seen extending approximately 5 to 10 cm to the right of the tail and engine cowling. The horizontal streak is the nightglow of the terrestrial atmosphere.
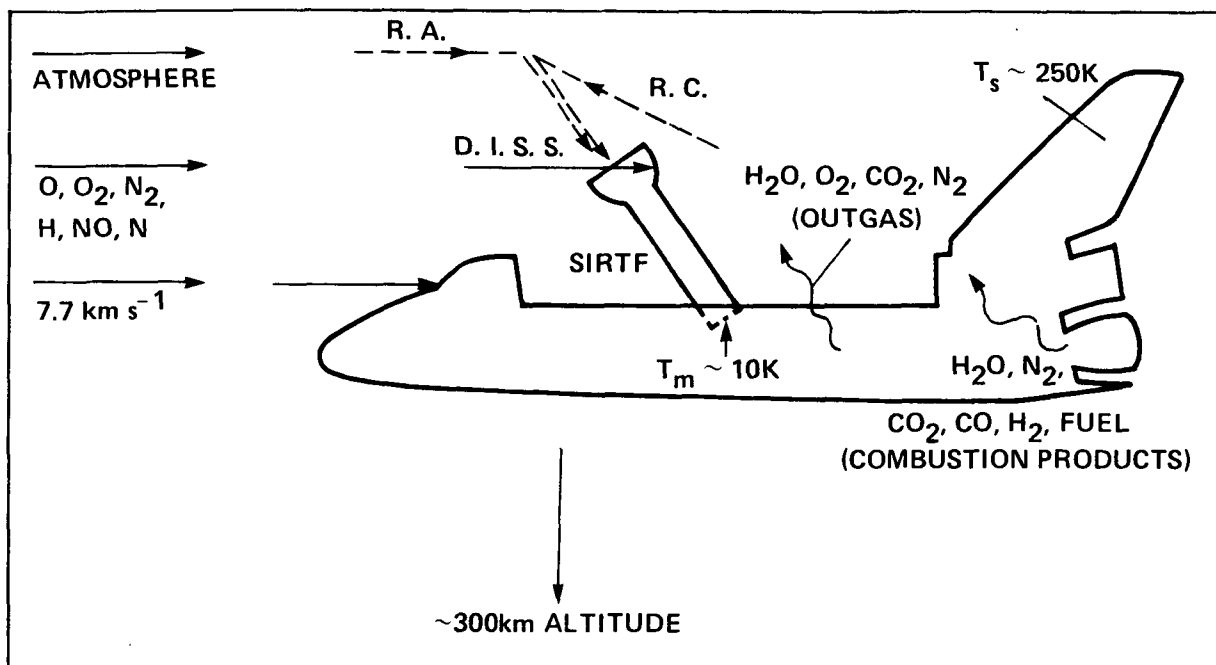
ATMOSPHERE

R. A.

R. C.

$T_s \sim 250K$

D. I. S. S.

$O, O_2, N_2,$
H, NO, N

H_2O, O_2, CO_2, N_2
(OUTGAS)

SIRTF

7.7 km s^{-1}

$T_m \sim 10K$

$H_2O, N_2,$

$CO_2, CO, H_2,$ FUEL
(COMBUSTION PRODUCTS)

$\sim$300km ALTITUDE

Figure 2.- The environment of the Shuttle and SIRTF is schematically drawn, showing
chemical fluxes of interest. The temperature, T, of the SIRTF mirror is approxi-
mately 10 K; the temperature T_s of the Shuttle is about 250 K; the Shuttle alti-
tude is approximately 300 km. The atmosphere is composed primarily of O, O_2, N_2,
H, NO, and N which strikes SIRTF and the Shuttle at 7.7 km sec^{-1}. We explore
infrared emission initiated by the direct impact of the atmosphere on the Shuttle
(D.I.S.H.), the direct impact of the atmosphere on the inside of the SIRTF sunshade
(D.I.S.S.), and by the reflected or scattered flux of atmospheric (R.A.) or con-
taminant (R.C.) molecules onto the SIRTF mirror and sunshade. Contaminants include
the outgas products H_2O, O_2, CO_2, and N_2 as well as combustion products H_2O, N_2,
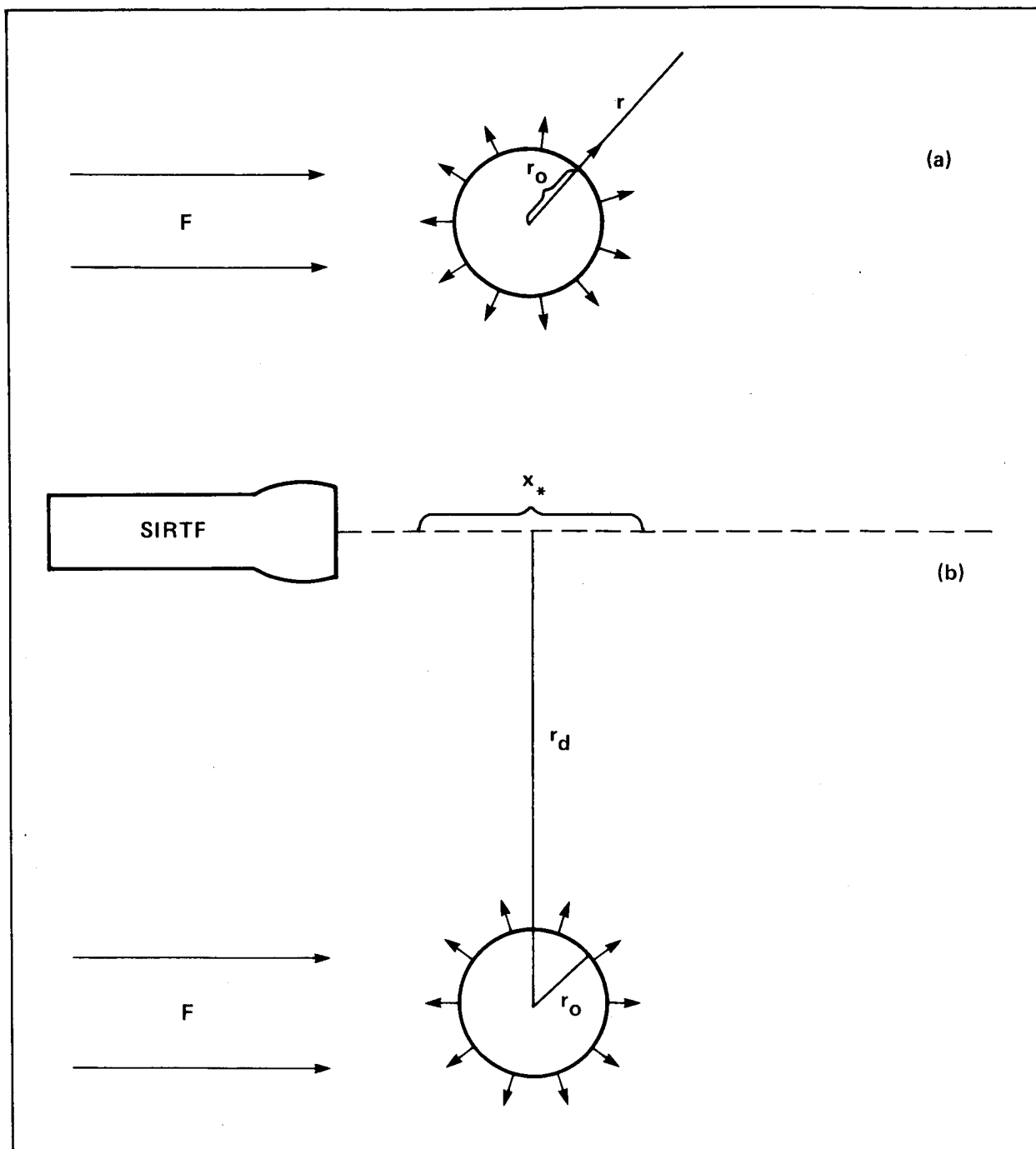CO_2, CO, H_2, and unburnt fuel.

Figure 3.- Schematic drawings of flux F of atmospheric gases incident upon Shuttle surfaces, represented schematically as a sphere of radius r_0. In (a) the basic geometry is sketched with r the distance from the center of the sphere. This configuration may readily apply to the glow seen by SIRTF from the scattered flux incident upon the mirror itself. In (b) a geometry is sketched in which the impact flux occurs at a distance r_d from the SIRTF line-of-sight. The parameter x_* is the pathlength of excited molecules.
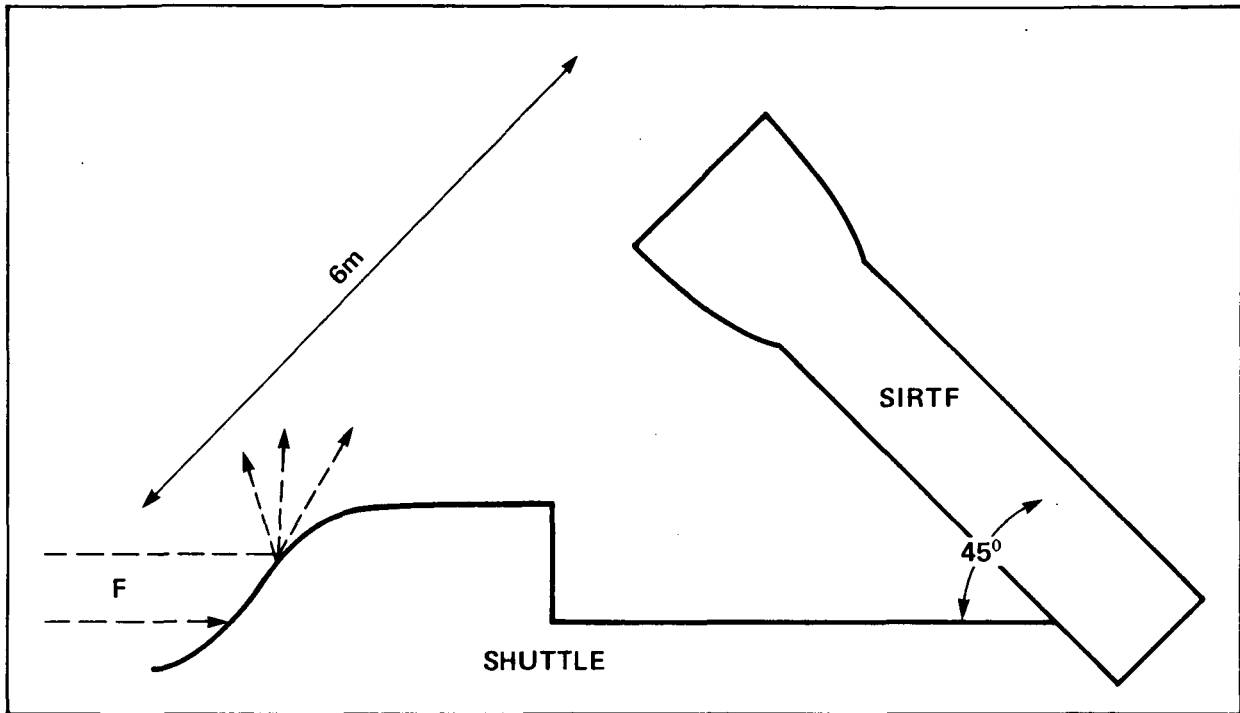
Figure 4.- The worst case configuration for SIRTF observing the infrared glow associated with the observed optical glow is schematically shown. The atmospheric flux F impacts a minimum distance of about 6 m from the SIRTF line-of-sight. This configuration can be modeled with figure 3b, using $r_d \sim 6$ m and $r_o \sim 3$ m.
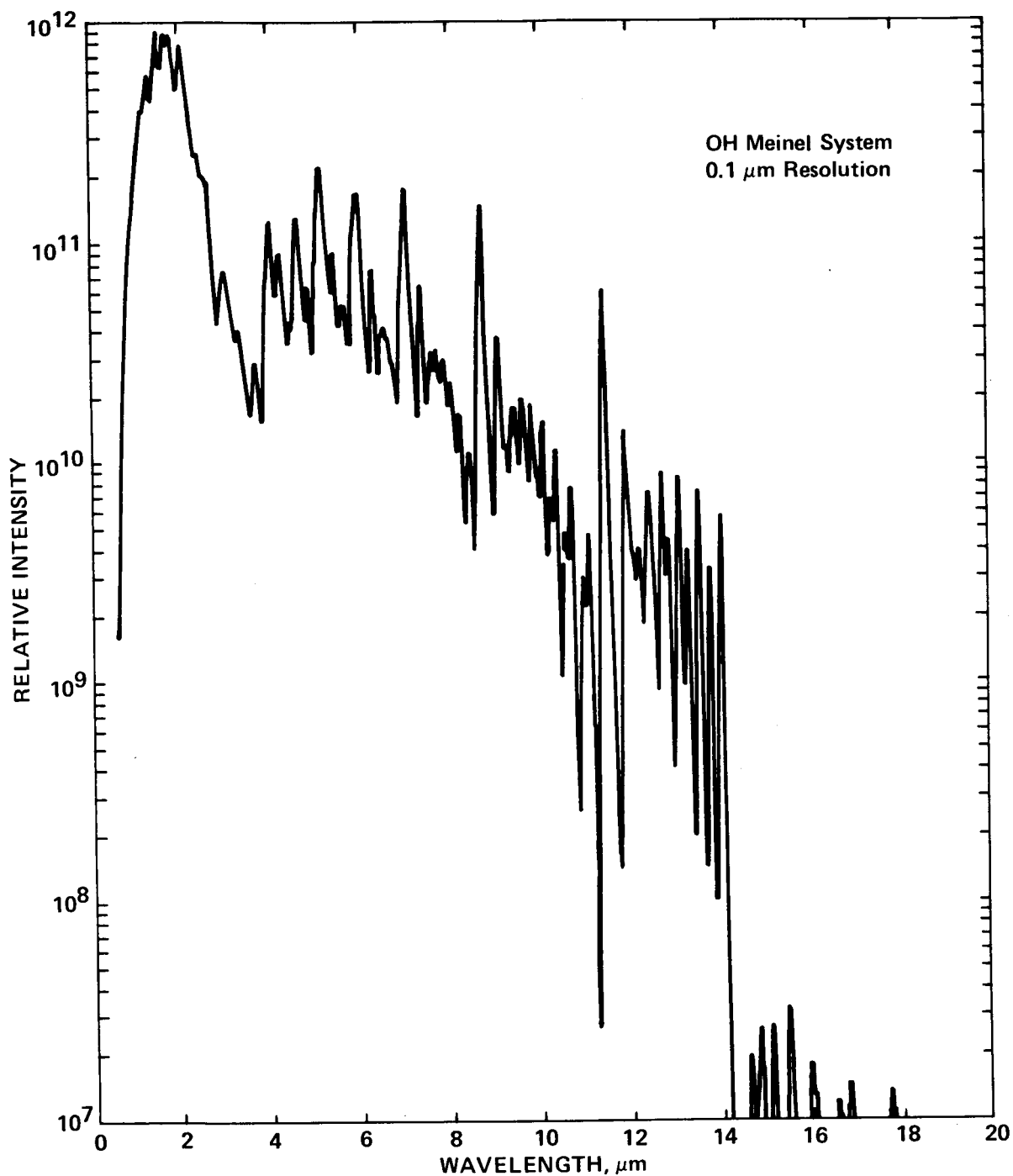
Figure 5.- The emission from OH molecules equally distributed in the vibrational
   levels of the ground electronic state, with rotational temperature T_R = 300 K
   is shown (ref. 9). The assumed spectral resolution is 0.1 μm.
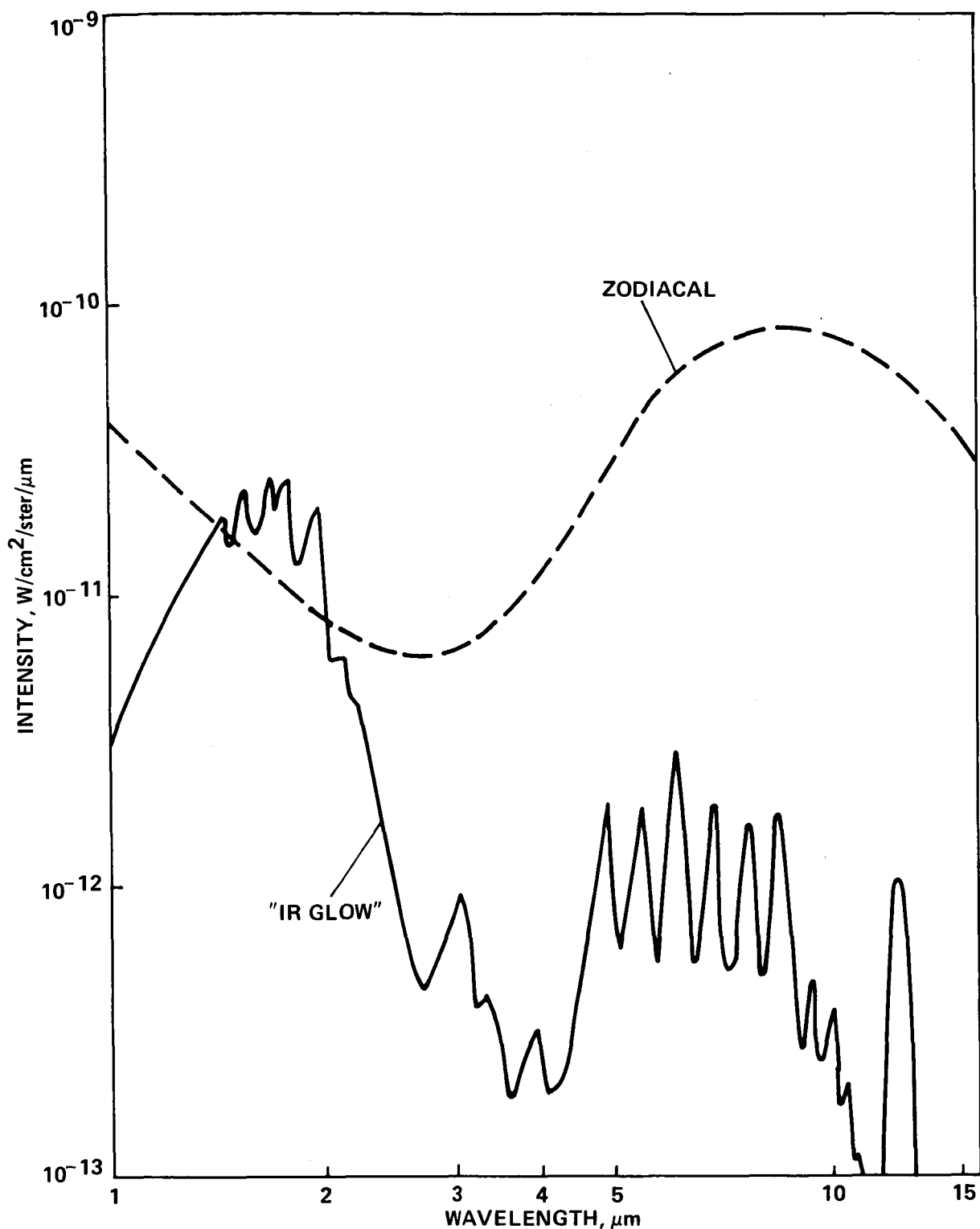
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Figure 6.- The zodiacal light intensity, assuming observation 90° from sun on the
    ecliptic, is crudely plotted with the dashed line as a function of wavelength.
    (The intensity drops by a factor of ~3 for observations perpendicular to the eclip-
    tic.) The expected IR glow intensity is schematically shown with the solid line
    marked "IR glow," calculated using the assumptions outlined in the text. The pre-
    cise shape of the spectrum, sketched here assuming the OH spectrum from figure 5,
    is quite uncertain since OH may not be responsible for the Shuttle glow (see text).

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16. Abstract

We estimate the infrared intensities which would be observed by the Shuttle Infrared Telescope Facility (SIRTF), and which are produced by surface chemistry following atmospheric impact on SIRTF and the Shuttle. Three possible sources of reactants are analyzed: (1) direct atmospheric and scattered contaminant fluxes onto the Shuttle's surface; (2) direct atmospheric and scattered contaminant fluxes onto the SIRTF sunshade; and (3) scattered fluxes onto the cold SIRTF mirror. The chemical reactions are primarily initiated by the dominant flux of reactive atomic oxygen on the surfaces. Using observations of the optical glow to constrain theoretical parameters, we estimate for source (1) that the infrared glow on the SIRTF mirror will be comparable to the zodiacal background between 1-μm and 10-μm wavelengths. We speculate that oxygen reacts with the atoms and the radicals bound in the organic molecules that reside on the Shuttle and the Explorer surfaces. We conclude that for source (2) that with suitable construction, a _warm_ ($T_S \gg$ 100 K) sunshade will produce insignificant infrared glow. We noted that the atomic oxygen flux on the cold SIRTF mirror (3) is insufficient to produce significant infrared glow. Infrared absorption by the ice buildup on the mirror is also small.

17. Key Words (Suggested by Author(s)) Infrared glow Shuttle SIRTF Surface chemistry Atomic oxygen	18. Distribution Statement Unlimited Subject Category - 88
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