INFRARED EMISSION FROM DESORBED NO_2^* and NO^*

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Abstract. Infrared photons from the radiative cascade accompany both the gas-phase NO_2 "continuum" chemiluminescence (which originates from its $^2B_2$ and $^2B_1$ states) and the NO beta bands ($B^2\Pi \rightarrow X^2\Pi$). When these upper electronic states are excited by recombination/desorption at surfaces of low-Earth orbiting spacecraft, similar IR emission spectrums will be observed. The principal NO_2 features (other than the long-wavelength tail of its electronic transitions) are the ν_3 fundamental sequence near 6.2 μm and $\nu_1 + \nu_3$ intercombination bands near 3.6 μm; NO would emit the $\Delta v = 1$ and $\Delta v = 2$ systems above 5.3 and 2.7 μm. Because of the long radiative lifetimes of the upper vibrational states, the infrared radiances in projections parallel to the vehicle surface (which we estimate) are substantially less than those of the visible and ultraviolet glows.

Introduction

We estimate here spatial distributions and relative brightnesses of the infrared afterglows of visible-UV emissions from NO_2 and NO electronically excited in surface recombination reactions. The IR component of the glow off shuttle's silica identified as from NO_2^* by Swenson et al. [1985] would consist of the long-wavelength transitions of the molecule's pseudo-continuum and more slowly emitted discrete vibrational bands of its lowest ($\tilde{X}^2A_1$) electronic state. Recombination of N and O, which in experiments on transition-metal substrates appears to excite selectively and directly the ultraviolet-emitting NO $B^2\Pi$ state [Caubet et al., 1984], would result in similar cascade radiation in the even more slowly emitted vibrational bands of the lower ($X^2\Pi$) state of NO.

NO_2

We proceed following the interpretation [Swenson et al., 1985] that the origin of the orange-red spectrally continuous (at 34Å FWHM resolution) radiation extending a few centimeters off shuttle's windward-directed SiO_2 tile surfaces is NO_2 electronically excited in reactions of NO with O. As pointed out by Kofsky and Barrett [1985], the shift of the peak photon intensity some 1000 cm^{-1} to the red of the glow seen from homogeneous reactions in the laboratory and lower thermosphere can be interpreted as due to (weak) binding of the O atoms to the substrate, insofar as this shift is ~4000 cm^{-1} when the O is bound in "vibrationally excited" O_3 [Kenner and Ogryzlo, 1984], ~7500 cm^{-1} in $O_3(001)$ [Braun et al., 1974], and 8000 cm^{-1} in ground-state O_3 [Clough and Thrush, 1967] where its binding energy is 8500 cm^{-1} or 1.05 eV. Alternatively, the shift to longer wavelengths might be interpreted as due to binding of the NO molecules to the surface (refer to Barrett and Kofsky [these Proceedings]), which would not materially affect the conclusions here.

In view of the only ~1/8-eV red shift, the surface-assisted excitation

reaction can be considered as chemically much more similar to the third (gaseous) body-stabilized NO + O attachment reaction than the NO + O_3 rearrangement reactions, which involve breaking the $O-O_2$ bond. We nonetheless present also the appropriate literature information on the electronic- and vibrational-band emissions that result from the chemiluminescent ground-state ozone reaction, for reasons that will become apparent shortly. The infrared emission wavelengths and the total yields and spatial extents that we derived from the laboratory and theoretical database are summarized in Table 1, and for orientation some potential curves of NO_2 [Paulsen et al., 1970] are reproduced in Figure 1.

Virtually all the gas-phase NO + O recombinations [Kaufman, 1973] but only 7% of the $NO_2 + O_3(\tilde{X}^1A_1)$ rearrangements [Clough and Thrush, 1967] proceed through the $^2B_1$ and $^2B_2$ states. The second column in Table 1 shows the fractions of the photons in the resulting pseudo-continuums terminating on NO_2's $^2A_1$ state that lie at wavelengths above 0.8 μm. We derived these percentages from the measured chemiluminescence spectrums, which tail off toward 3 μm with generally upward curvature [Stair and Kennealy, 1967; Golde et al., 1973] from flat peaks near 0.64 μm [Paulsen et al., 1970; Fontijn et al., 1964] and 1.2 μm [Clough and Thrush, 1967]. In view of the aforementioned observed modest red shift of the glow off shuttle's tiles, very closely half of its electronic-band photons would be at wavelengths above 0.8 μm, the nominal cutoff of the (S-20 response) image intensifier used in the spectrograph. As this longer-wavelength radiation originates from essentially the same distribution of upper states [Clough and Thrush, 1967], the spatial distribution of the near-infrared continuum emission would be similar to that in the orange-red glow. That is, the NIR surface radiances in photon units would be about equal to the visible radiances that have been measured [off silica; the spectral distributions could of course be different off other recombination substrates].

In laboratory gas-phase formation from reactions of NO with O the NO_2, molecules are left with average vibrational energy of about 7000 cm^{-1} after the electronic-band photon has been emitted, in states with ν_3 near 3 and $\nu_1 + \nu_3$ about 5 [Golde and Kaufman, 1974]. In the absence of collisions, as in the near-space environment, these decay by radiating the ν_3 fundamental bands near 6.2 μm [Stair and Kennealy, 1967; Clough and Thrush, 1969] and, with about a factor 10 less probability, a superposition of $\nu_1 + \nu_3$ (each $\Delta v = 1$) intercombination bands (with perhaps some ν_3 overtone) near 3.6 μm [Golde et al., 1973; Golde and Kaufman, 1974; Clough and Thrush, 1969]. Refer to columns 3 and 4 of Table 1, in which we have made an estimate of the broadening to shorter wavelengths of the emission in the complete (unquenched) radiative-relaxation cascade. Corrected for deactivation and artefactual population mechanisms in the laboratory, these bands have intensities proportional to that of the pseudo-continuum as well as the same temperature dependence, which indicates that they originate from upper vibrational states of the lower state of the electronic transitions. Further, the observation that the intensity ratio of the two infrared systems remains constant with concentration of the reactants suggests that they come from the same distribution of upper vibrational states. We estimated the number of photons emitted per recombination from the measured (from the integrated band strengths) radiative lifetimes in the 101 and 001 state listed in Table 1, with the reasonable assumptions that these lifetimes decrease as (vibrational quantum number)$^{-1}$ as

in harmonic-oscillator diatomic molecules and that all of the excitation
is radiated in these two sequences. The estimates for NO + O_3 rearrang-
ement reactions, which in totality result in a somewhat blue-shifted
spectral intensity distribution within the $\nu_1 + \nu_3$ fundamental sequence
[Golde and Kaufman, 1974], refer only to that 7% that proceed through the
$^2B_1$ and $^2B_2$ electronic states and therefore produce (more easily measured,
in the laboratory or spacecraft environment) visible and near-IR photons.

The ν_1 and ν_2 systems of NO_2 above 7.6 and 13.2 μm were below detection
threshold in the laboratory experiments [Clough and Thrush, 1969; Stair and
Kennealy, 1967], which is understandable in view of their low band
strengths; we have included an estimate of the ν_2 fundamental intensity in
Table 1. Clough and Thrush [1969] detected an unidentified weak peak
near 2.5 μm, which appears also to be present (with ~10% of the
amplitude of the underlying continuum) in the spectrum measured by Stair
and Kennealy [1967] (this may be the unidentified feature reported in
absorption in Herzberg's [1945] compilation).

Radiative lifetimes of the principal vibrational states are listed in
the sixth column. Since lifetimes and vibrational spacings decrease
with quantum number in the range excited, the longer-wavelength photons
within each sequence arise from a narrower off-surface layer; furthermore
the shorter-wavelength component in each of the two peaks is in general
emitted after the longer wavelengths, that is, farther away from the
vehicle. In view of the incomplete identification of NO_2's upper vibra-
tional states and lack of quantification of their transition probabilities
and branching, only approximate predictions can be made of the character-
istic emission distances and thus radiances in projections parallel to
recombination surfaces. These lengths are listed in the seventh column
of Table 1, where we have assumed that the NO_2* molecules desorb with
velocities that would result from thermal accommodation (which of course
may not be the case; refer to the presentation by Kofsky and Barrett
[these Proceedings]).

As the characteristic emission distance of the visible glows so far
measured is about 5 cm [Kofsky and Barrett, 1985], these lengths indicate
that at each altitude (i.e., incident particle flux) the maximum photon
radiances viewing along windward-directed spacecraft surfaces are three
orders of magnitude lower in the NO_2 intercombination-bands sequence near
3.6 μm and two orders of magnitude lower in the fundamental sequence
centered at 6.2 μm. Since the vibrational-band radiation lengths are
comparable to the dimensions of shuttle's surfaces, the outgoing beam has
moderate divergence and thus in projections perpendicular to the surface
the infrared photon radiances would be of the same order as the total radi-
ances in the pseudo-continuum.

These estimates implicitly assume that the surface-catalyzed recombi-
nation proceeds through electronic states of NO_2 only, as in homogeneous
NO + O (+ M) reactions. Direct recombination into vibrationally excited
states of $^2A_1$, as in the NO + O_3 reactions whose chemiluminescence we
have also reviewed here, would of course lead to higher infrared/visible
emission ratios. Similarly, selective depopulation of electronic states
at the surface would increase the relative IR intensities. In such
cases the infrared band sequences would be expected to remain those
identified in Table 1, but with different spectral distributions within
the peaks.

No direct evidence exists for recombination of NO on windward sur-
faces of low-Earth orbiting spacecraft. Nonetheless in view of the
presence of N and O in the incident airstream, the observed recombination
of these atoms into an electronically excited state on several polycrys-
talline metals (albeit not on teflon) at room temperature [Caubet et al.,
1984; Reeves et al., 1960], and the fact that the emission bands observed
in these laboratory experiments are capable of explaining the ultraviolet
component of the Atmosphere Explorer ram glow reported by Yee and Abreu
[1983] (refer to the spectrum in Figure 2, which shows features at the
photometrically-observed 0.280 and 0.337 μm), we proceed with the
exercise of calculating the cascade infrared radiances from $NO^{\dagger}$.

Surface recombination was found to produce directly the $B^2\Pi$ state only
(in a process different from the accepted mechanism of the homogeneous
reaction), as evidenced by the NO β (B→X) progressions. No attempt was
made to measure initial vibrational excitation of, or the rate of recombi-
nation into, the NO ground state. Note that if similar excitation takes
place at exposed spacecraft material substrates this ultraviolet glow
would extend outward less than 1 mm, as the B state's radiative lifetime
is 3.2 μsec; that is, in perpendicular-to-ram surface projections NO
electronic radiation excited only at the optical sensor's surfaces would
be detectable. We derived from the β-band intensities due to the surface
and background gas measured by Caubet et al. [1984] the vibrational
population distribution in NO $X^2\Pi$, which is given with an overview of
the cascade radiation process and the radiative lifetimes of vibrationally-
excited NO(X) in Table 2. The potential curves of NO are shown for
orientation in Figure 3.

These laboratory data show that the average vibrational quantum number
v_2^1 in the lower state is about 7. From this number and the branching
ratios [Billingsley, 1976], we estimate that 5 fundamental-sequence (above
5.3 μm) and 1 overtone-sequence (near 2.8 μm) photons result from each
surface-catalyzed recombination into the NO(B) state. Again due to anhar-
monicity of the ground electronic state, the longer-wavelength IR photons
in each sequence are emitted closer to the surface than the shorter-wave-
length photons. From the radiative lifetimes we find characteristic
radiation lengths of about 1000 cm for each transition (taking the mean
thermal molecular velocity as $\sqrt{(46/30)}$ x 4 x 10^4 cm/sec), so that the
volume from which the vibrational bands are emitted extends some 100 m
forward of the vehicle. Thus the maximum near-parallel IR photon radi-
ances would be many orders of magnitude lower than the UV (β-band)
radiances at each ambient density. Since over that large distance the
$NO^{\dagger}$ beam would have substantial divergence even were it peaked strongly
toward the surface normal (as discussed by Kofsky and Barrett [these
Proceedings]), and at shuttle's operational altitudes little confinement
due to collisions with the atmosphere, the IR radiances in perpendicular
projections would be expected to be somewhat less than the UV photon
radiances.

Over and above its assumption that N + O recombination into NO's B
state can indeed take place on spacecraft ram surface materials, this
derivation assumes that the initial vibrational-state population is the
same as that observed under the laboratory conditions and, more impor-

tantly, that this reaction path is more probable than direct recombination into high vibrational states of NO's ground electronic state. This latter process, which would add to the off-surface infrared glow, can be readily investigated in the laboratory (or space environment) by laser-induced fluorescence methods.

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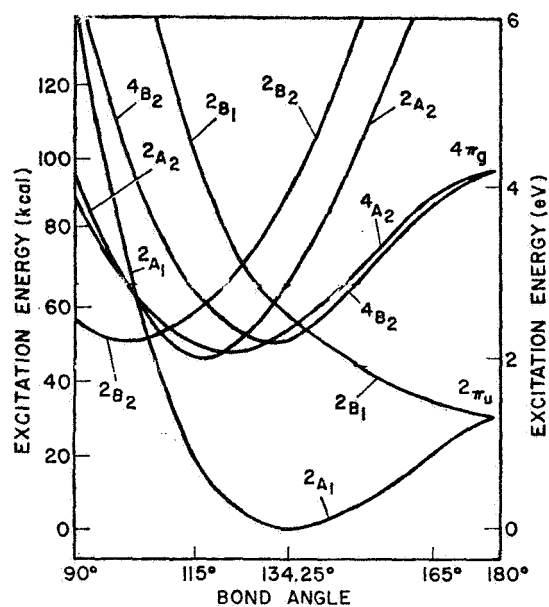
Fig. 1. Electronic energy as a function
of bond angle for several low-
lying states of NO_2 (from Paulsen
et al. [1970]). The bond lengths
are fixed at the equilibrium value
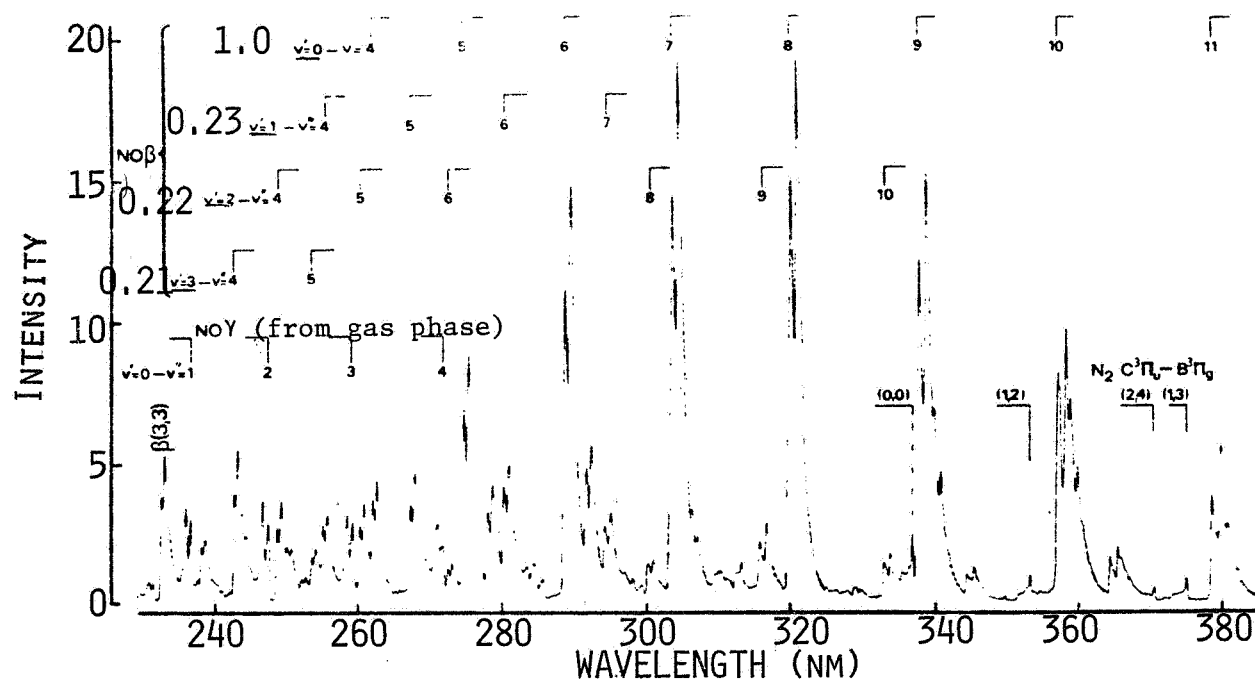for the $^2A_1$ state.

Fig. 2.   NO chemiluminescence from N- and O-atom recombination at
a polycrystalline Ni surface (from Caubet et al. [1984]).
The relative initial vibrational-state populations in
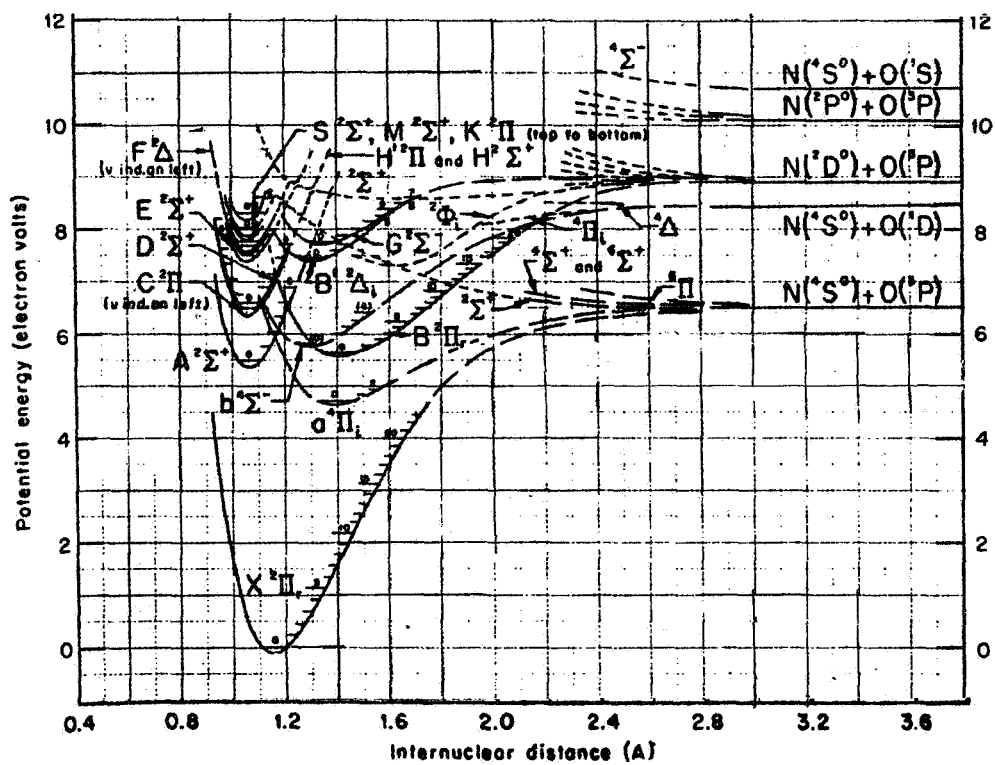NO(B) are shown at upper left.

Fig. 3.   Potential energy curves for NO.

TABLE 1. NO_2 INFRARED RADIATIONS

Gas-phase reaction	*	Wavelengths, μm +HWHM	Band	Photons/per electronic transition	Radiative lifetimes, sec	Lifetime x 4×10^4 cm/sec, cm
NO + O + M	0.45	3.6 +0.35, -0.25	$(\nu_1 + \nu_3)$ each $\Delta v=1$ sequences, some $2\nu_3$	0.24 +0.1	0.0078 near 3.5 μm (101→000, 0.077)	300
NO + O_3(X)	0.93	3.55 +0.24, -0.13		0.37	~0.002 near 3.7 μm $(\nu_1 + \nu_3 \approx 4)$	60-80
Both of above		6.2 +0.35	ν_3 fundamental	3 (O) 4 (O_3)	0.0066 (001→000)	250, to 60 at longer wavelengths
		13.2 +1	ν_2	$\sim 10^{-3}$		
		7.6	ν_1	$\sim 10^{-2}$		
		2.5 +0.13	unidentified	$\sim 10^{-3}$		

*Fraction of electronic-band photons at wavelengths >0.8 μm in the gas-phase reactions.

TABLE 2.   NO INFRARED RADIATIONS

Reaction Sequence		Wavelengths	Photons/ Reaction
$N + O \xrightarrow{\text{Surface}} NO\ (B,v_1')$;		2.7 - 3.1µm (overtone)	1
$NO(B) \longrightarrow NO(X,v_2')$; + β bands;		5.3 - 5.9µm (fundamental)	5
$NO(X,v_2') \longrightarrow NO(X,v_2'-1,-2)$ + vibrational bands cascade			

Initial Vibrational State v_2' of $NO(X^2\Pi)$