

INFRARED EMISSION FROM DESORBED NO₂^{*} and NO^{*}

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Abstract. Infrared photons from the radiative cascade accompany both the gas-phase NO₂ "continuum" chemiluminescence (which originates from its ²B₂ and ²B₁ states) and the NO beta bands (B²Π → X²Π). When these upper electronic states are excited by recombination/desorption at surfaces of low-Earth orbiting spacecraft, similar IR emission spectra will be observed. The principal NO₂ features (other than the long-wavelength tail of its electronic transitions) are the ν₃ fundamental sequence near 6.2 μm and ν₁ + ν₃ intercombination bands near 3.6 μm; NO would emit the Δv = 1 and Δv = 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 NO₂ and NO electronically excited in surface recombination reactions. The IR component of the glow off shuttle's silica identified as from NO₂^{*} 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 (X²A₁) electronic state. Recombination of N and O, which in experiments on transition-metal substrates appears to excite selectively and directly the ultraviolet-emitting NO B²Π state [Caubet et al., 1984], would result in similar cascade radiation in the even more slowly emitted vibrational bands of the lower (X²Π) state of NO.

NO₂

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 SiO₂ tile surfaces is NO₂ 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" O₃ [Kenner and Ogryzlo, 1984], ~7500 cm⁻¹ in O₃(001) [Braun et al., 1974], and 8000 cm⁻¹ in ground-state O₃ [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 $\text{NO} + \text{O}$ attachment reaction than the $\text{NO} + \text{O}_3$ rearrangement reactions, which involve breaking the $\text{O}-\text{O}_2$ 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 $\text{NO} + \text{O}$ recombinations [Kaufman, 1973] but only 7% of the $\text{NO}_2 + \text{O}_3(\tilde{X}^1\text{A}_1)$ rearrangements [Clough and Thrush, 1967] proceed through the $^2\text{B}_1$ and $^2\text{B}_2$ states. The second column in Table 1 shows the fractions of the photons in the resulting pseudo-continua terminating on NO_2 's $^2\text{A}_1$ state that lie at wavelengths above $0.8 \mu\text{m}$. We derived these percentages from the measured chemiluminescence spectrums, which tail off toward $3 \mu\text{m}$ with generally upward curvature [Stair and Kennealy, 1967; Golde et al., 1973] from flat peaks near $0.64 \mu\text{m}$ [Paulsen et al., 1970; Fontijn et al., 1964] and $1.2 \mu\text{m}$ [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 $0.8 \mu\text{m}$, 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 $6.2 \mu\text{m}$ [Stair and Kennealy, 1967; Clough and Thrush, 1969] and, with about a factor 10 less probability, a superposition of $\nu_1 + \nu_3$ (each $\Delta\nu = 1$) intercombination bands (with perhaps some ν_3 overtone) near $3.6 \mu\text{m}$ [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 $\text{NO} + \text{O}_3$ rearrangement 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 ${}^2\text{B}_1$ and ${}^2\text{B}_2$ 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 vibrational states and lack of quantification of their transition probabilities and branching, only approximate predictions can be made of the characteristic 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 radiances in the pseudo-continuum.

These estimates implicitly assume that the surface-catalyzed recombination proceeds through electronic states of NO_2 only, as in homogeneous $\text{NO} + \text{O}$ (+ M) reactions. Direct recombination into vibrationally excited states of ${}^2\text{A}_1$, as in the $\text{NO} + \text{O}_3$ 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 surfaces 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 polycrystalline 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 $\text{B}^2\Pi$ state only (in a process different from the accepted mechanism of the homogeneous reaction), as evidenced by the NO β ($\text{B}\rightarrow\text{X}$) progressions. No attempt was made to measure initial vibrational excitation of, or the rate of recombination 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 $\text{X}^2\Pi$, 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 anharmonicity of the ground electronic state, the longer-wavelength IR photons in each sequence are emitted closer to the surface than the shorter-wavelength photons. From the radiative lifetimes we find characteristic radiation lengths of about 1000 cm for each transition (taking the mean thermal molecular velocity as $\sqrt{(46/30)} \times 4 \times 10^4$ 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 radiances 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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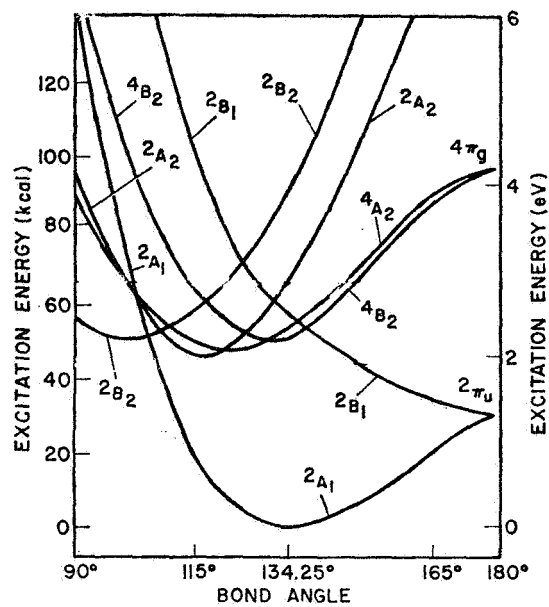


Fig. 1. Electronic energy as a function of bond angle for several low-lying states of NO_2 (from Paulsen et al. [1970]). The bond lengths are fixed at the equilibrium value for the 2A_1 state.

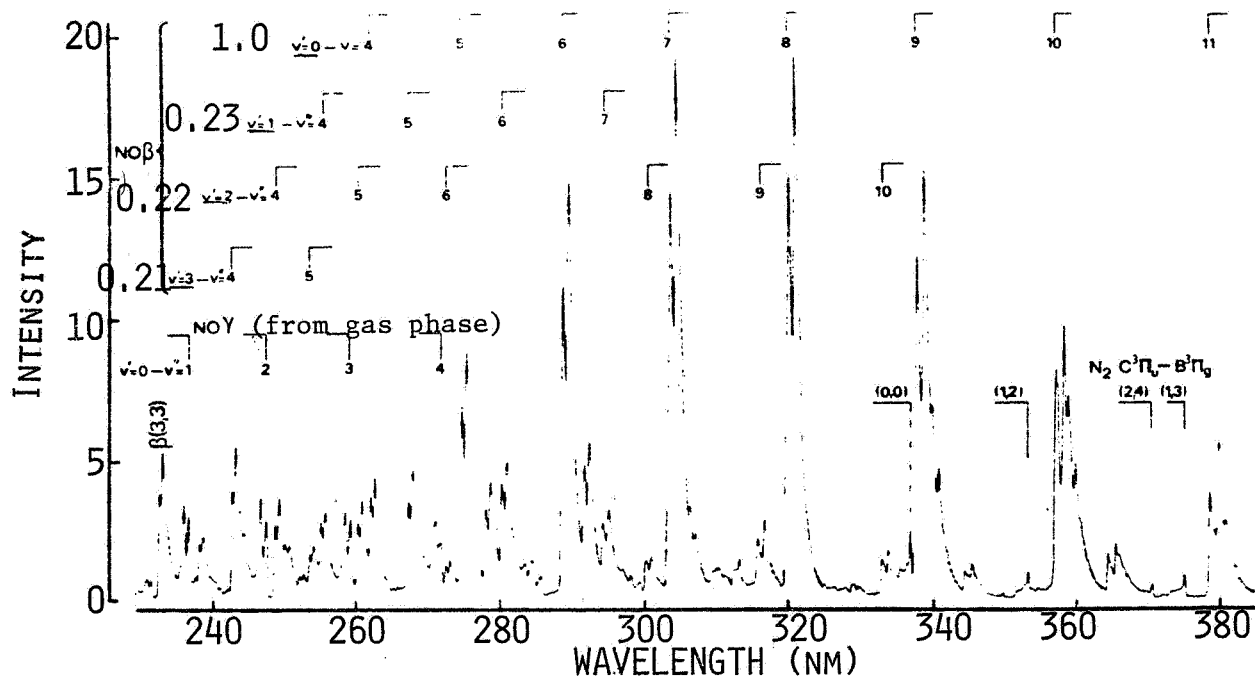


Fig. 2. NO chemiluminescence from N- and O-atom recombination at a polycrystalline Ni surface (from Caubet et al. [1984]). The relative initial vibrational-state populations in NO(B) are shown at upper left.

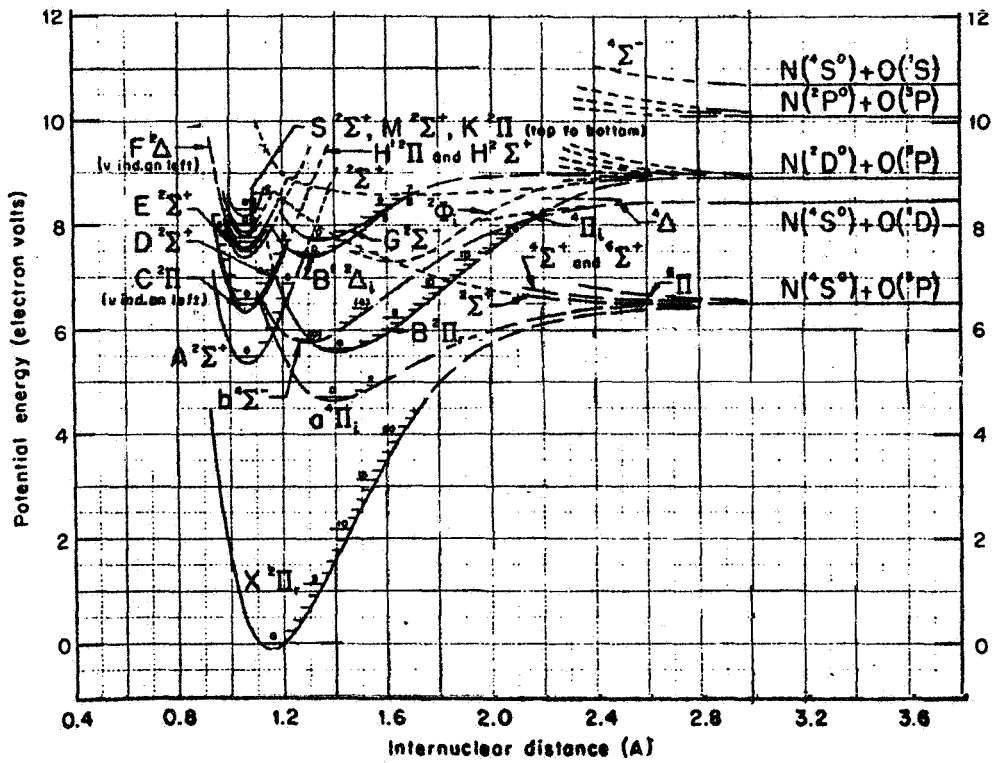


Fig. 3. Potential energy curves for NO.

TABLE 1. NO₂ INFRARED RADIATIONS

<u>Gas-phase reaction</u>	<u>*</u>	<u>Wavelengths, μm ±HWHM</u>	<u>Band</u>	<u>Photons/per electronic transition</u>	<u>Radiative lifetimes, sec</u>	<u>Lifetime x 4 x 10⁴ cm/sec, cm</u>
NO + O + M	0.45	3.6 +0.35, -0.25	(ν ₁ + ν ₃) each Δν=1 sequences, some 2ν 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 (ν ₁ + ν ₃ ≈ 4)	60- 80
Both of above		6.2 +0.35	ν ₃ fundamental	3 (0) 4 (0 ₃)	0.0066 (001→000)	250, to 60 at longer wavelengths
		13.2 +1 7.6 - 2.5 +0.13	ν ₂ ν ₁ unidentified	~10 ⁻³ ~10 ⁻² ~10 ⁻³		

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

TABLE 2. NO INFRARED RADIATIONS

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

