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CHEMILUMINESCENCE OF NITRIC OXIDE: THE NO ($C^2\Pi$–$A^2\Sigma^+$) RATE CONSTANT

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Abstract—A rocket borne scanning 1/4-m spectrometer was used to observe the night airglow between 1900 and 2300 Å at a resolution of 15 Å. An attitude control system oriented the payload horizontally near apogee (150 km) and pointed the field of view to the north and parallel with the terminator. Progressions from the $\delta(0, v'')$ and $\gamma(0, 0)$ band systems of nitric oxide were observed. The observations of the δ-bands and γ-bands are consistent with the relative intensities produced in the preassociation of ground state atomic oxygen and nitrogen. An observation of the $v' = 0$, ε-band progression is suggested and is consistent with the presence of a resonance fluorescence contribution near apogee. The $A^2\Sigma^+$ (upper level of the γ-bands) can only be populated by cascade from the $C^2\Pi$ state (upper level of the γ-bands) in the preassociation reaction. In the absence of quenching of the $A^2\Sigma^+$ state, the emission rate of the γ-bands can be used as a measure of the C–A transition and thus to deduce the branching ratio to the $A^2\Sigma^+$ state. This branching ratio is estimated to be 0.21 ± 0.04.

INTRODUCTION

The association of a ground state nitrogen atom (N) and an oxygen atom (O) at low pressure leads to the population of $C^2\Pi_{v'=0}$ state of NO among others. This state is formed through the $a^4\Pi$ state, which is directly produced in the association[1]

$$N(^4S) + O(^3P) \rightleftarrows NO(a^4\Pi) \rightleftarrows NO(C^2\Pi, v' = 0) \rightarrow NO(X^2\Pi) + h\nu \quad (1)$$

$$\rightarrow NO(A^2\Sigma^+) + h\nu \quad (2)$$

Only 1 molecule in 33 remains in the $C^2\Pi$ state since the efficiency for dissociation is very large.[2] The u.v. radiation which is emitted in the association reaction arises from the $v' = 0$ level of the $C^2\Pi$ state (δ bands), from the $v' = 0$ and 3 levels of the $A^2\Sigma^+$ state (γ bands), and from the $v' = 0$ to 6 levels of the $B^2\Pi$ state (β bands). The excitation processes for the $B^2\Pi$ levels are complex; however, the excitation process for the $v' = 0$ level of the $A^2\Sigma^+$ state occurs by radiative cascade from the $C^2\Pi$ state and for the $v' = 3$ level by collisional transfer from the $v' = 7$ level of the $B^2\Pi$ state.[1]

Laboratory studies[2,3] have shown that the ratio of the rate constants for the $C^2\Pi$ to $A^2\Sigma^+$ transition with respect to the $C^2\Pi \rightarrow X^2\Pi$ transition is about 0.65 ± 0.13.This ratio implies that the rate for the $C^2\Pi \rightarrow A^2\Sigma^+$ transition is $1.35 \times 10^7\ sec^{-1}$ for a $C^2\Pi \rightarrow X^2\Pi$ transition rate of $2.1 \times 10^7\ sec^{-1}$.[4] Shock tube experiments lead to an oscillator strength for $A^2\Sigma^+ \rightarrow C^2\Pi$ of 0.70,[5] which implies a rate constant of $6.2 \times 10^7\ sec^{-1}$.

The importance of this association process for planetary atmospheres is that estimates of the N and O concentrations can be made and the dynamics monitored. Observations of the spectral distribution of the δ-bands at twilight in the earth's atmosphere[6] were used, in conjunction with model oxygen concentrations, to deduce the N concentrations[7] although the viewing geometry encompassed a range of solar depression angles. Observation of the δ-bands in the nighttime atmosphere of Venus[8] has been utilized to study the presence of odd nitrogen on that planet and was found to require the presence of N_2 there.

In this paper, we report a measurement of the γ and δ-bands in the night-time thermosphere of the earth, in conjunction with a simultaneous measurement of the atomic oxygen concentration.[9] The relative intensities of the γ and δ band systems are shown to agree with theoretical band strengths and the ratio of the intensities of the two systems is used to infer the rate coefficient for the C to A transition. Analysis of the emission rate vs altitude profile to deduce the atomic nitrogen concentration will be reported at a later date.

A 1/4 m u.v. spectrometer was part of the Michigan Airglow Payload carried by an Aerobee 170 (NASA 13.135) to an altitude of 150 km above White Sands on 2 November 1978. The solar zenith angle was 104°. At apogee, the field of view of the spectrometer was pointed toward the north at a zenith angle of 90° and parallel with the terminator, thereby viewing emissions from a constant time zone. The vertical field of view was 0.32°. This orientation was maintained until 115 km on the downleg.

The relative response of the instrument was determined in the laboratory by adjusting the instrument output with respect to the known branching ratios from a given upper vibrational level of the 4th positive band system of CO and the γ-band system of NO. The accuracy of this relative calibration is estimated to be $\pm 5\%$ with respect to wavelengths. The absolute sensitivity was obtained by viewing an NBS calibrated tungsten strip filament lamp at wavelengths of 2700 and 3200 Å and the accuracy is estimated to be $\pm$ 15%. The slit settings used here have a measured resolution of 15.2 at 2144 Å. The wavelength scan was driven digitally between 1900 and 2300 Å at 2.3 Å/step with the wavelength vs step number determined by viewing a PT hollow cathode discharge lamp. The estimated accuracy is ± 2 Å/step.

SPECTRAL ANALYSIS

Figure 1 gives the results of summing 43 scans obtained while the instrument was viewing in the horizontal position. The response to a constant spectral brightness is represented by the curve. The prominant bands are the $v' = 0$ progression of the δ-band system and the 0,0 band of the γ-band system. There is emission that exceeds the background count (the dashed line) between these bands. The dark count level was 6 counts for 0.574 sec.

The identification of the band systems present was accomplished by constructing synthetic spectra for the NO γ-, δ-, and ε-bands. The molecular constants[10–14] are listed in Table 1. The rotational line strengths for the δ-bands are from Erkovich *et al.*[15] and for the γ- and ε-bands are from Earls.[16] Figure 2 shows the synthetic profile which resulted from this computation. In addition to the normal emissions present from the association reaction, the $v' = 1$ progression of the γ-bands and the $v' = 0$ progression of the ε-bands are present.

When the payload was near apogee, the ultraviolet shadow height of the sun was about 80 km above the rocket. The field of view of the spectrometer in the horizontal direction (12° full angle) included a portion of the sunlight–twilight atmosphere. This fact accounts for the presence of emission from $v' = 1$ and 2 levels of the γ-bands, as well as for contribution to the intensity of the $v' = 3$ and (0, 0) γ-bands. The ε-band system is present also because of resonance scattering of sunlight off the NO molecule.

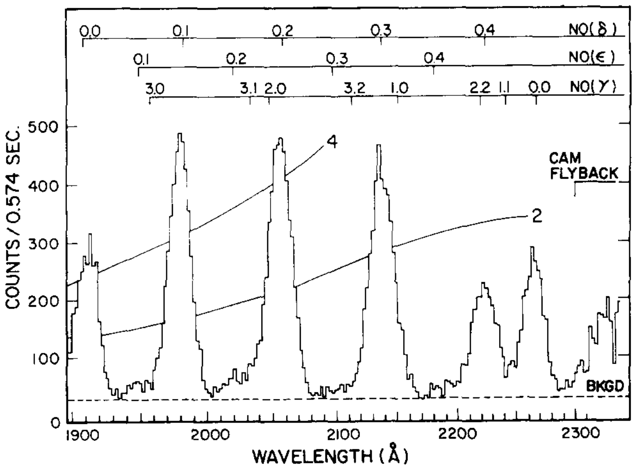

Fig. 1. The nightglow spectrum between 1900 and 2300 Å at a resolution of 15 Å. Forty-three scans are summed which were taken when the viewing direction was parallel to the surface of the earth and the terminator. The absolute instrument response curve is shown in units of 10^6 ph/sec cm^2 (column). The NO band systems are identified.

Table 1. Molecular constants for NO.

STATES	B_e	α_e	T_e	D_e	A	ω_e	$\omega_e X_e$	$\omega_e Y_e$
(a) $A^2\Sigma^+$	1.9948	0.0183	43906.4	5.4×10^{-6}	0	2374.3	16.1	-0.046
(b) $C^2\Pi$	2.002	0.030	52128.8	$4.\ \times10^{-6}$	3	2395.0	15.0	0.00
(c) $D^2\Sigma^+$	1.9917	0	53021.5[(e)]	0	0	2327.0	23.0	0.00
(d) $X^2\Pi_{3/2}$	1.7276	0.0178	121	5.57×10^{-6}	123.26[(a)]	1903.68	13.970	-0.0012
$^2\Pi_{1/2}$	1.6816		0			1904.03		

(a) Taken from Ref. 10; (b) from Ref. 11; (c) from Ref. 12; (d) from Ref. 13; (e) calculated from Ref. 14.

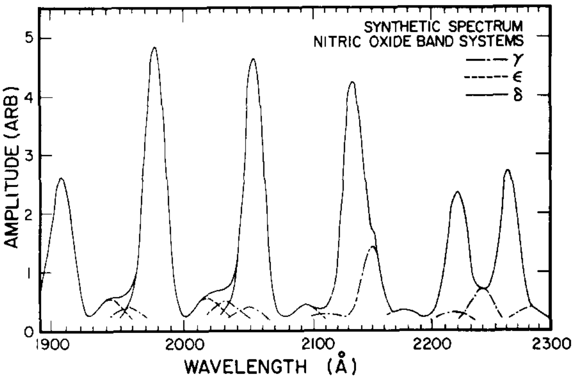

Fig. 2. The synthetic spectrum of the NO band systems has been constructed to fit the data of Fig. 1.

The relative intensities of the individual vibrational transitions within the observed band systems are listed in Table 2. The accuracy is ±10% for δ-bands and ±20% for others. Also listed are the relative band strengths calculated by using Franck-Condon factors[17,18] and observed in the laboratory.[19,20] The laboratory accuracy is estimated to be ±30%. The agreement amongst the set of numbers is therefore quite good.

The total intensity from a vibrational level within a band system was obtained by summation of the observed band intensities with allowances for bands outside the scan range. Table 3 gives these results for the three band systems of NO that were observed. The contribution to these intensities from resonance fluorescence is given and was calculated for the γ-bands by using relative vibrational level populations deduced from both the g-factors calculated by Cravens[21] and the spectral intensity measurements reported by Pearce.[22] The remaining intensities are produced by the association reaction.

The $v' = 0$ level of the $A^2\Sigma^+$ state is populated by cascading from the $v' = 0$ level of the $C^2\Pi$ state; thus, the intensity of the γ-bands, in the absence of quenching, represents the intensity of the $C^2\Pi \rightarrow A^2\Sigma^+$ transition. Consequently, the ratio of the sum of the γ-bands for $v' = 0$ to the sum of the δ-bands for $v' = 0$ will give the branching ratio to the $A^2\Sigma^+$ state. The intensities in Table 3 give $\bar{\omega}_{C\text{-}A} = 0.21 \pm 0.04$ where $\bar{\omega}_{C\text{-}A} = I_{CA}/(I_{CA} + I_{CX})$. Taking the transition probability of the $C^2\Pi$-$X^2\Pi$ transition to be $2.1 \times 10^7\ \text{sec}^{-1}$[4] and using the branching ratio deduced here (0.21), the transition probability for the $C^2\Pi$-$A^2\Sigma^+$ transition is calculated to be $(5.6 \pm 1.5) \times 10^6\ \text{sec}^{-1}$.

DISCUSSION

The branching ratio from the $C^2\Pi$ state to the $A^2\Sigma^+$ state deduced in this experiment (0.21) may be compared with the value 0.38 deduced from the laboratory experiments of Groth *et al.*[3] and 0.41 deduced by Callear and Pilling.[2] The source of the discrepancy with Groth *et al.* is in their assumption of a constant instrument response at wavelengths less than 2300 Å. Their reported relative intensities for the δ-bands below 2300 Å do not agree with the relative intensities listed in Table 2. However, if adjacent bands at wavelengths longer than 2300 Å are used to calculate the branching ratio, then a branching ratio of 0.24 is obtained, which is in good

Table 2. Relative band strengths for the δ, ε, and γ bands of NO.

Band System	v', v"	λ(Å)	Calculated Values*	Laboratory Measurements†	This Study
δ	0,0	1909	0.67	-	0.68
	0,1	1980	1.00	1.00	1.00
	0,2	2055	0.84	0.84	0.74
	0,3	2135	0.52	0.64	0.47
	0,4	2220	0.27	0.20	0.21
ε	0,1	1947	1.28	1.60	1.25
	0,2	2020	1.00	1.00	1.00
	0,3	2097	0.64	0.56	0.58
	0,4	2179	0.33	0.24	0.25
γ	3,0	1958	0.82	0.68	0.80
	3,1	2033	1.00	1.00	1.00
	3,2	2112	0.19	0.18	0.20
	3,3	2197	0.16	0.14	0.20
	3,4	2286	0.39		0.40

*Franck-Condon factors from Ref. 17 are used for the ε and δ bands; values from Ref. 18 are used for the γ bands. †Data from Ref. 1 are used for the ε and δ bands and from Ref. 20 for the γ bands.

Table 3. Band intensities for summed spectra in the units 10^6 photons/cm^2-sec.

		Intensity Total	Resonance Fluorescense	Preassociation Reaction
δ - bands	v' = 0	$I_\delta^0 = 478$	0	478
ε - bands	v' = 0	$I_\varepsilon^0 = 39$	39	0
γ - bands	v' = 0	$I_\gamma^0 = 170$	40	130
	= 1	$I_\gamma^1 = 45$	45	0
	= 2	$I_\gamma^2 = 11$	11	0
	= 3	$I_\gamma^3 = 26$	11	15

agreement with the ratio derived from this work. It is not at all clear why the results of Callear and Pilling are different from those reported here. Their experiment is apparently straightforward. In the NO fluorescence experiment, the changes in the intensities of the γ-bands are monitored as a function of the changes in δ-band fluorescence caused by changing the source intensity for steady-state conditions in the system.

The work of Young and Sharpless[1] suggests the γ- and the δ-bands are of "comparable intensity" at low pressure. The work reported here suggests a ratio of 0.27. Young and Sharpless did their work in nitrogen and it has been shown[2] that N_2 suppresses predissociation of the δ-bands and enhances the γ-band emission.

Examination of dayglow spectra[22,23] suggests that the total intensity of the ε bands relative to the (1, 0) γ-band is less than 0.30. This ratio is about 25% of the value observed in this experiment. Furthermore, the intensity ratio of the $v' = 3$ to the $v' = 0$ γ-bands is 0.12 or about 3 times the ratio deduced from laboratory experiments.[20] It should also be noted that a portion of the background emission may be from the Lyman–Birge–Hopfield bands of N_2. Observation of these bands at night was reported recently.[24] Consequently, no firm conclusions about the presence and intensities of band systems other than $\delta(v'=0)$ and $\gamma(v'=0, 1)$ band systems can be drawn.

The transition probability for the $C^2\Pi \rightarrow A^2\Sigma^+$ transition deduced here, $(5.6 \pm 1.5) \times 10^6\ sec^{-1}$, is smaller by a factor of 2.5 than the laboratory value of $(1.35 \pm 0.27) \times 10^7\ sec^{-1}$. Problems associated with the laboratory determination have been discussed.

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