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Orange Flame from Active Nitrogen and Oxygen in the Absence of a Metal Catalyst Resulting from Collisional Intersystem Crossing into $N_2(B\ ^3\Pi_g)$

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The discovery of an orange flame is reported that appears also at higher pressures of active nitrogen and oxygen without the presence of a metal catalyst unlike previous research in over 30 years. Enhancement of emissions of the first positive band system of nitrogen was observed from various vibrational levels of the $N_2(B\ ^3\Pi_g)$ state. Arguments to identify the species responsible and implications to previous research of this phenomenon of homogeneous excitation and collisional intersystem crossing into $N_2(B\ ^3\Pi_g)$ induced by excited O_2 are presented. Its probing for lasing is suggested.

Introduction

For more than 30 years extensive research work has been carried out on radiationless energy transfer and emissions of radiation attributed to metal surface catalyzed (heterogeneous, in general) formation of species. Such species of great importance also to various applications are excited molecular states of nitrogen,[1−4] oxygen,[5−8] nitric oxide,[2,3,8,9] and nitrogen dioxide.[5,8,10] They are observed in a gas flow of active nitrogen (or nitric oxide to form nitrogen dioxide) and active oxygen premixed or mixed after activation or separately (e.g., as in the study of excited molecular oxygen states) in laboratories on Earth or in space (e.g., the shuttle glow).[11] Also innumerable investigations of the nitrogen afterglow[12] with and without oxygen species have been carried out for more than 100 years for basic research and for a broad spectrum of applications such as atmospheric processes,[12,13] discharges and plasmas,[14] laser excitation,[15] and semiconductor processing.[16] In some of these investigations in the presence of a metal, enhancement of background nitrogen afterglow emissions in the form of a red flame was reported,[1−4] when a mixed stream of nitrogen atoms and discharged oxygen was passed over a metal surface. It was initially[1] ascribed to metal-catalyzed formation of $NO(B\ ^2\Pi)$ from N and O, which upon reacting with N atoms led to red chemiluminescence. However in later work the red flame appeared even when a metal was placed in the active nitrogen flow upstream of the discharged oxygen flow.[17] The observed enhancement of emissions from $v = 6$, 7, and 8 of $N_2(B\ ^3\Pi_g)$ was ascribed[17] to probably excited O_2, more likely $O_2(a\ ^1\Delta_g)$, interacting in the gas phase with $N_2(A\ ^3\Sigma_u^+)$ formed at the metal surface. The red flame could not be observed unless both a metal and discharged oxygen were added to the active nitrogen flow at <1 Torr. Further research on the mechanism of this surface-catalyzed flame was done more recently.[18]

Experimental Section

In the present work the appearance of a bright orange flame is reported from the mixing of active nitrogen and active oxygen gas streams also at much higher N_2 and O_2 pressures and without the presence of a metal for the first time. The flame predominated over the background afterglow emissions and could also be observed with the lab lights on. The flame extended axially in the reactor and had zero intensity near the walls, thus indicating no contribution from heterogeneous wall effects. The active species were generated by flowing nitrogen and oxygen, separately, through 2450 MHz microwave (mw) discharges. The flows were mixed inside a cylindrical flow reactor initially made of Pyrex[19a,b] and later of quartz.[19c] Figure 1 shows a schematic of the apparatus. Gas flows in the range of about 3−10 bar cm^3/s were used. The reactors had an i.d. of 2.0−3.8 cm. The afterglow emissions were observed in variable low resolution (to 3 Å) with spectrometers, filters, and detectors (Ge, Si, and photomultipliers with S-20, S-5, and 605s photocathodes) from IR to UV. Scattered light to the detectors used from the mw discharges used and external sources was eliminated with standard techniques (e.g., by using Wood's horns, black paint, black cloth, etc.). Gratings blazed in the first order at 600 nm and at 1 μm were used. A requirement for the appearance of the orange flame with band intensity I over the background emissions in the nitrogen afterglow with band intensity I_o was the activation of the oxygen species in the oxygen flow entering the reactor. When the oxygen mw discharge was off, the orange flame disappeared. Only the background emissions remained from discharged N_2 mixed with undischarged O_2 with band intensity I_o ($\Delta I = I - I_o$).

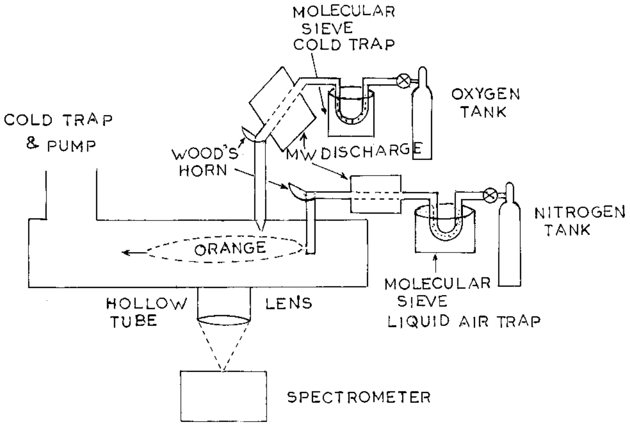

Figure 1. Schematic of the apparatus.

Results and Discussion

A spectroscopic investigation has been conducted of excitation and deexcitation of molecular species in gas mixtures of

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active nitrogen and active oxygen. The investigation concentrated on the first positive band system (1pbs) of nitrogen, $N_2(B\ ^3\Pi_g) \rightarrow N_2(A\ ^3\Sigma_u^+)$, although other band systems (O_2, NO, N_2) were preliminarily examined and further work on them is planned. The extent of the enhancement of emissions depended on the proximity to the mixing region of the active species and the N_2 and O_2 pressure, which was sometimes >20 times higher than that in the past.[17] The enhancement was observed in the flame and downstream from it (by tens of milliseconds). A plot of the relative enhancement $\Delta I/I_o$ of the intensity I_o of radiation from the background 1pbs emissions in the presence of undischarged O_2, which is enhanced by active oxygen to intensity I, vs $N_2(B,v)$ is shown for some cases for observation normal to the flow direction: downstream of the mixing region (over 50 ms in flow time) at 5.5 mbar nitrogen and 0.1 mbar oxygen in Figure 2a; and at higher pressures (15 mbar N_2; 0.9 mbar O_2, at a flow velocity of about 0.2 m/s) closer (<10 ms) to the mixing region, where the flame originated, in Figure 2b. Enhancement from many vibrational levels up to $v = 18$ is shown in Figure 2b for the case of a nitrogen "pink" afterglow. Figure 2a shows no emission from $v \geq 10$ in the present homogeneous gaseous excitation as in the heterogeneous excitation of N_2 species,[17] where emissions from $v \geq 9$ were reported suppressed. This may indicate similar excitation of the precursor species that populate $N_2(B,v)$ in the nitrogen afterglow under the action of active oxygen in both cases. Much higher enhancements than those in Figure 2b were also observed, e.g., even up to ≥50 times higher for emissions from $N_2(B,v{=}6)$. The much larger relative enhancement from $v = 6$ was evident in all cases as in Figure 2. At distances downstream from the discharges (≈0.1 s flow time) and at total pressures up to 10.7 mbar with $1 < N_2/O_2 < 100$ a similar preferential enhancement from $v = 6$ was observed. In some experiments when the O_2 pressure was increased with the N_2 pressure kept constant, the relative increase in the emissions from $v \leq 6$ was larger than that from $v = 11$. Spectra of the 1pbs of N_2 are shown in Figures 3 and 4.

Experiments to obtain information on the oxygen and nitrogen species responsible for the 1pbs enhancement included monitoring the concentrations of $O_2(a\ ^1\Delta_g)$ and $O_2(b\ ^1\Sigma_g^+)$ and that of O atoms. The $v = 0 \rightarrow v' = 0$ emissions to $O_2(X\ ^3\Sigma_g^-)$ at 1268 and 762 nm and the NO_2* emission in the presence of NO[20,21] were measured as a function of the oxygen discharge mw power, before and after mixing with nitrogen. These were compared with the corresponding change of the 1pbs enhancement. The $O_2(^1\Sigma)$ signal was very small and could be observed photometrically only without N_2. In a N_2 Lewis−Rayleigh afterglow the 1pbs emission intensity is proportional[12] to $[N]^2$. Therefore, since the observed 1pbs enhancement is nonuniform (Figure 2) even under the normal afterglow conditions (emissions only from $v \leq 12$), it is deduced that it is not the usual N atom recombination that is mainly responsible for this phenomenon. NO β emissions were observed in the mixing region, when oxygen was added upstream of the nitrogen inlet. They disappeared in the mixing region and very close to the oxygen inlet, when oxygen was added downstream of nitrogen, even though 1pbs enhancement was observed there. These results suggest that it is some N_2 species that are responsible for fast collisional intersystem energy transfer to $N_2(B)$ by colliding with active oxygen rather than with excited NO, before N atoms can react with O atoms or recombine by O atoms. Thus from these observations of nonuniform, fast 1pbs enhancement from low/high v of $N_2(B)$, even after times longer than 0.1 s from the discharges, it is surmised that 1pbs enhancement appears by a mechanism of collisional crossing into $N_2(B)$ involving collisions of N_2 species with oxygen species. Energetically possible N_2 species are vibrationally excited N_2, $N_2^\dagger$, metastable $N_2(A)$, and other N_2* species that can be generated

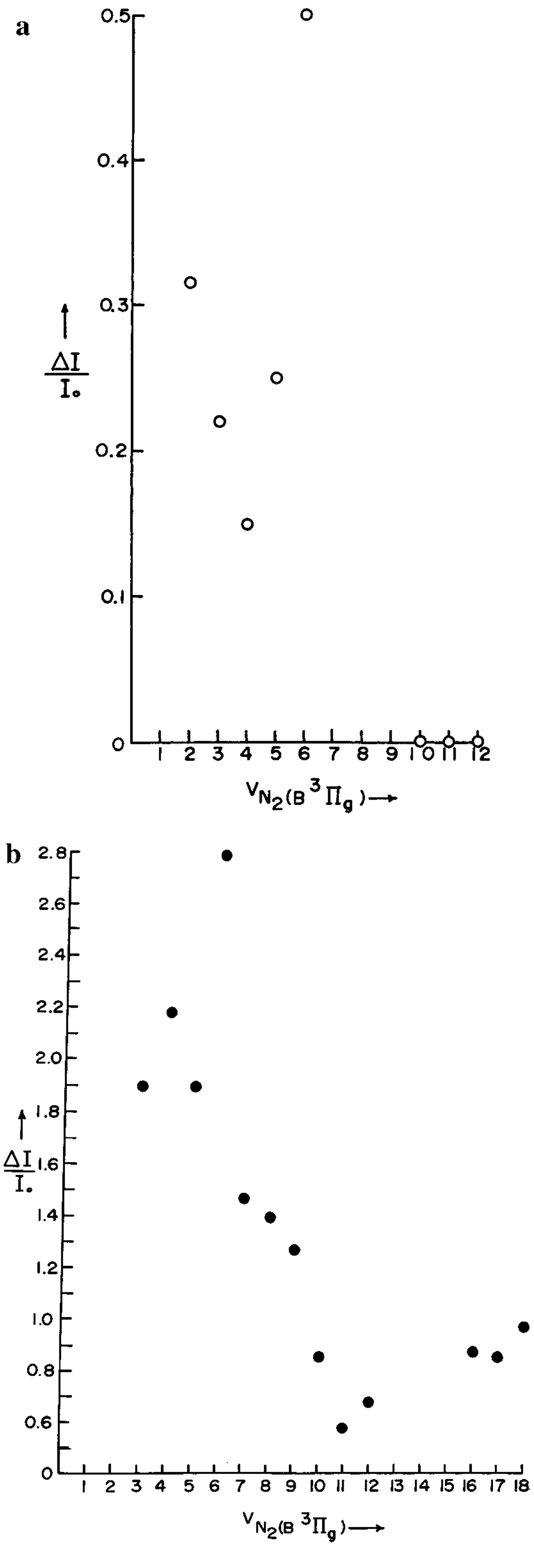

Figure 2. Relative enhancement of first positive band system (1pbs) emissions of N_2 from a gas mixture of discharged nitrogen and separately discharged oxygen in a flow reactor. I represents N_2 1pbs band intensity. I_o represents N_2 1pbs band intensity, however, from a gas mixture of discharged nitrogen as above and undischarged oxygen in the same flow reactor. $\Delta I = I - I_o$. (a) Downstream of the mixing region. $P_{N_2} = 5.5$ mbar. $P_{O_2} = 0.1$ mbar. (b) Near the mixing region of a "pink" nitrogen afterglow (extending visually downstream almost to the oxygen inlet) with oxygen. $P_{N_2} = 15.0$ mbar. $P_{O_2} = 0.9$ mbar. The maximum absolute deviation of intensities was 10%.

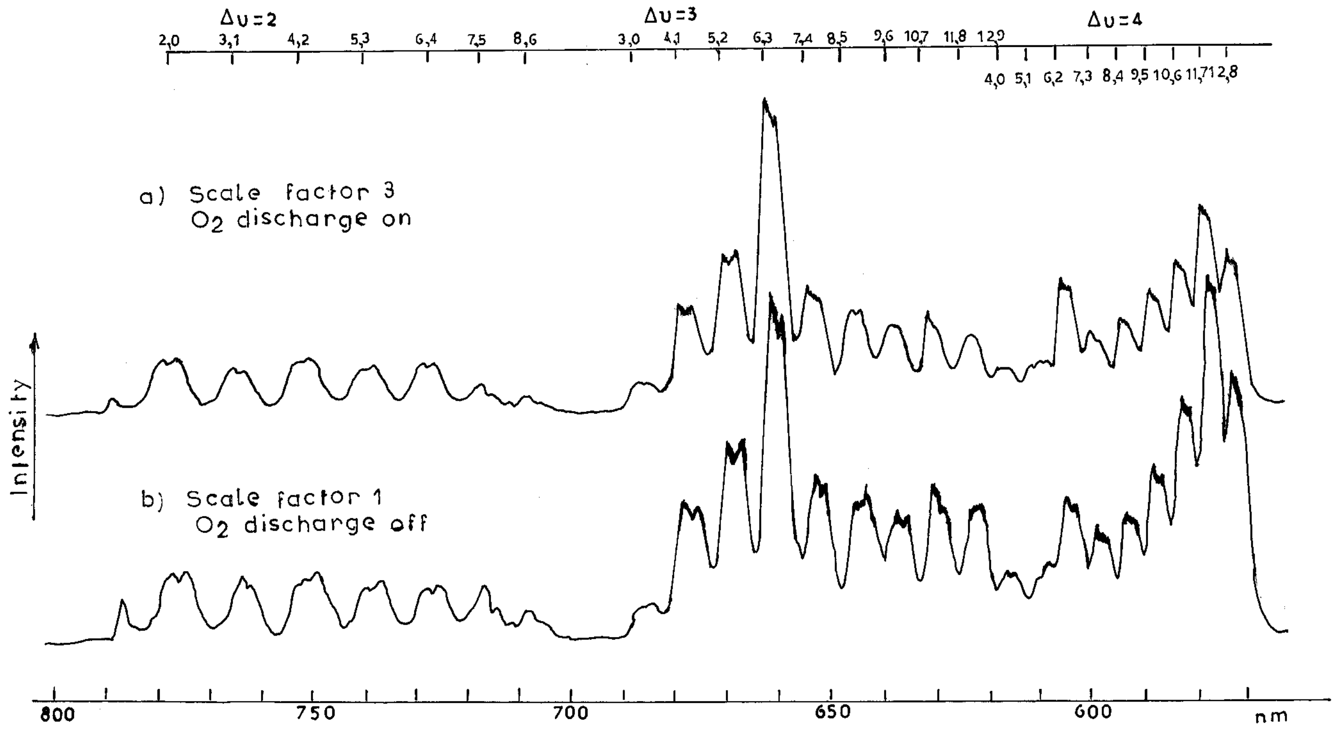

Figure 3. Emission spectra showing the $\Delta v = 2$, $\Delta v = 3$, and $\Delta v = 4$ band sequences of the first positive band system (1pbs) of $N_2(B\ ^3\Pi_g \rightarrow A\ ^3\Sigma_u^+)$. The vibrational levels of each band in a 1pbs sequence are shown over each band with the $N_2(B\ ^3\Pi_g)$ vibrational level of each band shown first. The spectra were obtained by adding (a, top spectrum) discharged oxygen to a "pink" nitrogen afterglow with a scale factor of 3 and (b, lower spectrum) undischarged oxygen to the same "pink" nitrogen afterglow with a scale factor of 1. In both cases $P_{N_2} = 12.0$ mbar and $P_{O_2} = 0.7$ mbar. The spectra are not corrected for grating and detector nonuniform spectral response.

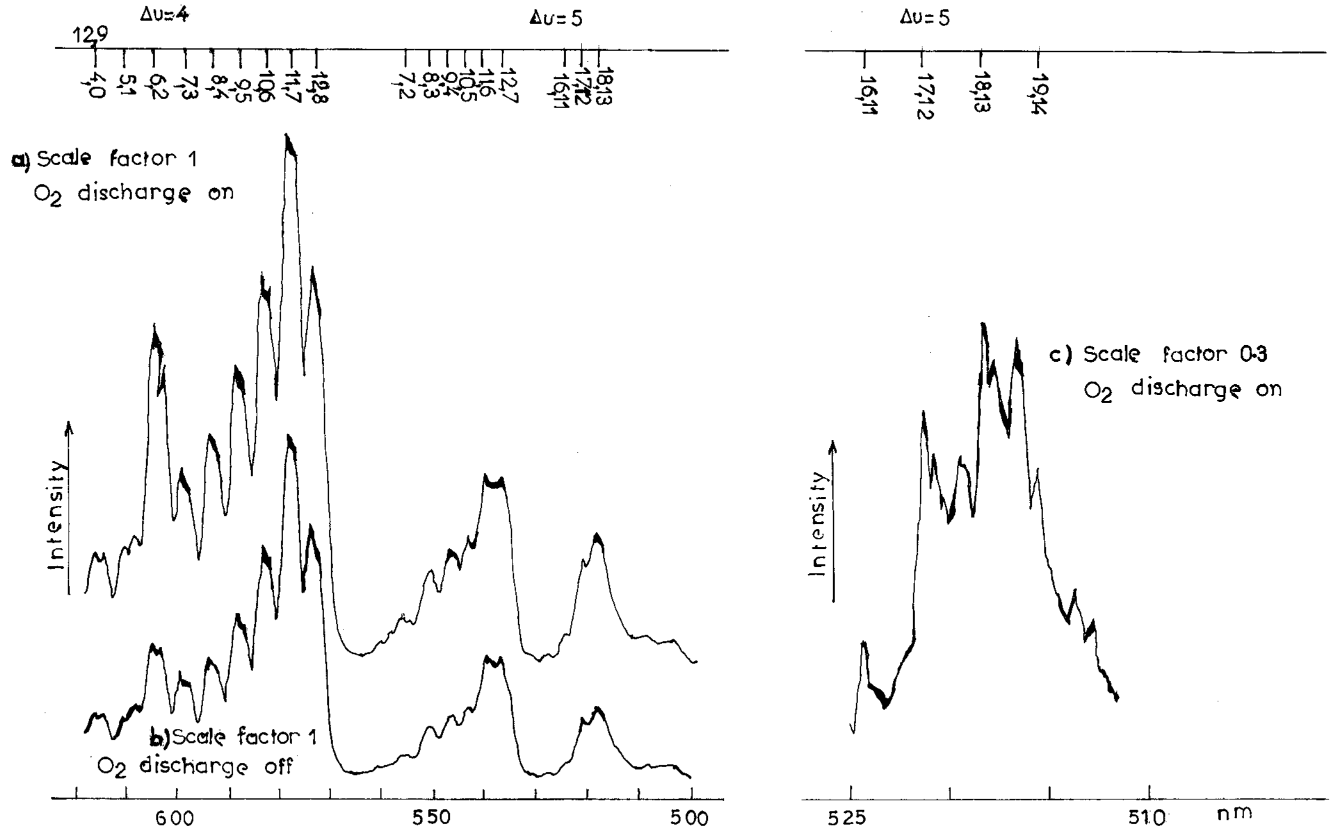

Figure 4. Emission spectra showing the $\Delta v = 4$ and $\Delta v = 5$ band sequences of N_2 1pbs with (a, top spectrum) and without (b, lower spectrum) discharged oxygen with a scale factor of 1 and the rest of the experimental conditions the same as those in Figure 3. On the right side (c) the emission spectrum with discharged oxygen is shown for some high-v $\Delta v = 5$ bands at higher resolution with a scale factor of 0.3. $P_{N_2} = 10.3$ mbar and $P_{O_2} = 0.3$ mbar.

in the N_2 afterglow and may cross into the $N_2(B)$ state or are coupled to $N_2(B)$ like $N_2(W\ ^3\Delta_u)$, $N_2(B'\ ^3\Sigma_u^-)$ and $N_2(A'\ ^5\Sigma_g^+)$.[12]

The intensity of emission from a large flame appeared to optimize by the eye at low mw power of the oxygen discharge and high mw power of the nitrogen discharge. The latter observation was confirmed by quantitative measurements on the intensity of various 1pbs bands. The comparison of the quantitative effect of the change of the oxygen discharge mw power on the excited O_2 concentration and on the 1pbs intensity led to the following results: it showed that the initial concentration of $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ changed similarly to the observed 1pbs intensity, in contrast to [O], which changed rather proportionally to NO emissions (with the flame on). In an experiment discharged oxygen was passed through a piece of quartz tubing with a ring of mercuric oxide film (for O atom removal) in it and subsequently through a ≈5 cm piece of Tygon tubing, before entering the reactor. No change in the orange flame was observed. Spectral scans with and without the mercuric oxide showed no significant changes in visible 1pbs emissions. That O atoms are unlikely to cause this 1pbs enhancement results also from the observations that the flame intensity appeared to optimize at low O_2 discharge mw power (i.e. at low O concentration), as mentioned earlier, and that the O_2 addition to the N_2 afterglow does not change the $N_2(B)$ distribution significantly. However in such a gas mixture there are already O atoms, as expected from the chemical reactions of O_2 with species in the N_2 afterglow and as evidenced by NO* emissions, but no 1pbs enhancement has been observed. $O_2^\dagger$ (vibrationally excited) is considered unlikely since it may be excited in active N_2 without leading to 1pbs enhancement. Also, when active oxygen flowed through glass wool (for O_2 vibrational relaxation), there was no effect on the flame. It is concluded that electronically excited O_2, O_2*, is the likely candidate for this phenomenon with $O_2(^1\Delta)$ the most likely one, because of the very low concentration and the faster quenching rate of $O_2(^1\Sigma)$ (or of another O_2* state).

About 25 years ago $N_2(A)$ was considered the main N_2 state involved in populating $N_2(B)$ in the nitrogen afterglow in general[12] and in its surface-catalyzed excitation, in particular.[17] However, after the discovery of the optical transitions and the indicated collisional coupling of $N_2(B\leftrightarrow W)$[12,13] and during the gradual extension of the available knowledge on the chemical kinetics and dynamics of the quenching of metastable $N_2(A)$ by atoms such as $N(^4S)$ and $O(^3P)$ and molecules such as O_2,[12,21−24] there has been a shift away from $N_2(A)$.[22] This shift turned in favor of $N_2(W)$[18] as the main state responsible for collisional intersystem crossing into $N_2(B)$. This occurred not only for N_2 metal-catalyzed excitation[18] but also for a low-altitude aurora[13] and relaxation with coupling of $N_2(B)$.[25−27] This shift may have led to the indicated unawareness about the possible fast $N_2(A) + O_2$* interaction that may interfere in the determination of the rate coefficient of the reaction $N_2(A) +$ O,[21,23−24] although such an interaction had already been proposed for a fast energy transfer process induced by $O_2(^1\Delta)$ that populates $N_2(B)$.[17]

However experiments have shown two components in $N_2(B)$ fluorescence decay.[25−28] Also recently the results of molecular beam one-collision crossing into $N_2(B,v)$[28] showed (from the different 1pbs spectral distributions at two beam flight-times) that there are at least two species that populate $N_2(B)$ by collisional intersystem crossing: one (or more) of shorter and another one (or more) of longer lifetime. They were ascribed to $N_2(W)$ and $N_2(A)$ on the basis of their shorter and longer lifetime, respectively. The experimental results in Figure 4 of Ottinger and co-workers[28] show their 1pbs $\Delta v = 3$ sequence in the N_2 afterglow spectrum of an active nitrogen molecular beam, before undergoing any collision. The sequence is almost identical (except for some shift in their wavelength for each band, presumably due to inadvertent error) to that of an aurora spectrum.[13] This would be expected of similarly (electron impact) excited N_2 at similar fluorescence times, before long fluorescence or any collisions change it. However after one collision in passing through O_2 or NO or N_2, etc., the molecules in the beam are reported to show (no spectrum for O_2 is shown) large enhancement of their emission with the largest one from $N_2(B,v{=}6)$, as in this work. The spectral distribution after one collision with N_2 also shows that the longer lifetime species ascribed to $N_2(A)$ cross into $N_2(B,v)$ for all $v \leq 12$; however, they cross faster for $v = 6$ and 4. These levels have a small energy gap with the $N_2(A,v'{=}16)$ and $N_2(A,v'{=}13)$. The shorter lifetime species ascribed to $N_2(W)$ appear in the spectrum to cross into $N_2(B,v)$ significantly at least for $v = 5$, 6, and 7. These $N_2(B)$ levels are close to the $N_2(W,v'')$ ones for $v'' = 6$, 7, and 8. Therefore the $N_2(A)$ state cannot be excluded; both $N_2(A)$ and $N_2(W)$ are probably involved in this excitation of $N_2(B)$. Nevertheless, involvement also of some other species cannot be excluded. Such species are $N_2^\dagger$, through its reported reaction with $N_2(A)$[29a] and other N_2* states, as mentioned previously, especially for excitation of $N_2(B,v{>}12)$ induced by O_2*. Collisional intersystem crossing from $N_2(B)$ into $N_2(B')$[27b] and from $N_2(a\ ^1\Pi_g)$ into $(a'\ ^1\Sigma_u^-)$[29] as well as the absorption[29c] and laser-induced fluorescence[29d] after earlier failure[29c] for $N_2(C''\ ^5\Pi_u) - (A'\ ^5\Sigma_g^+)$ were directly observed recently. The previous arguments for this collisional energy transfer lead to the next possible equation for the mechanism $O_2{*} + N_2{*} \rightarrow N_2(B,v) + O_2'$, where O_2' may be ground state O_2 or excited O_2; N_2* or $N_2^\dagger$ may act as a third body.

Interference of this excitation may more or less have affected previous research. For example, all values of rate constants for the reaction of O atoms (from discharged oxygen) with $N_2(A)$ (from discharged nitrogen, or from excitation transfer to N_2 by Ar metastables) may be affected, if indeed $N_2(A)$ interacts with O_2* in this phenomenon, because O_2* is formed along with O atoms in (and outside) the discharge. This should be taken into account also in (upper) atmospheric models[23] or anywhere such $N_2(A)$ interactions matter. Such reactions of O atoms produced even from the reaction NO + N may be affected by this collisional excitation due to potential $O_2(^1\Delta)$ formation in heterogeneous recombination of O atoms.[30] Speculative estimates of possible error up to 30% from the interaction of $N_2(A)$ with $O_2(^1\Delta)$ in some cases were reported[21,23,24] for the rate constant of the reaction $N_2(A) + O$. The error may be even higher. It depends on how fast, compared to O_2, O_2* may interact with $N_2(A)$. All values reported for the rate constants for the chemical reaction $N + O_2(^1\Delta)$ studied[31−33] in N_2 afterglows may be at most upper limits, if this reaction occurs at a significant rate, because of the possibility of interference of the energy transfer between $O_2(^1\Delta)$ and $N_2(A)$ or some other N_2* species. This energy transfer has also probably caused the too large increase in background emissions and affected the results reported[24,34] in the study of the reaction of $N_2(A)$ with O from discharged oxygen.

Further Discussion and Conclusion

A flame and/or a simple enhancement of N_2 afterglow emissions caused by active oxygen were also reported in the past in other experiments.[1−4,17,18,35−37] They show aspects of the same basic phenomenon reported here, i.e., enhancement of the 1pbs due to collisional intersystem excitation transfer into $N_2(B)$ induced by collisions with apparently excited O_2. However, in all of the previous works the ocurrence of the 1pbs enhancement was related to some different factor, namely, either to the presence of a metal at <1 Torr, or only to the mixing region of the discharged O_2 and N_2 streams during some of the

TABLE 1: Summary of Research Work That May Have Been Affected by This Excitation to $N_2(B\ ^3\Pi_g)$

	reference
1. rate of interaction between $N_2(A\ ^3\Sigma_u^+)$ and O	21, 23, 24, 34
2. rate of interaction between N and $O_2(a\ ^1\Delta_g)$	31−33
3. exclusion of the role of $N_2(A\ ^3\Sigma_u^+)$ in populating $N_2(B\ ^3\Pi_g)$	13, 18, 22, 25−27
4. mechanism of the $N_2(B\ ^3\Pi_g)$ vibrational redistribution	35

photometric attempts to determine the rate constant of the $O_2(^1\Delta)$ reaction with N atoms in the N_2 afterglow,[36,37] or to the effect of O (and H) atoms[35] in the study of the vibrational redistribution of N_2(B). This was reported to occur only at a N_2 pressure of 0.01−1.0 Torr and was considered to be in agreement with earlier work.[3] However, it is contrary to the work later revised[17] and to results in this work. For this reason or for some other unknown reason(s) this homogeneous intersystem crossing into N_2(B) apparently induced by collisions between N_2* and excited O_2, as evidenced by nonuniform enhancement of N_2 1pbs emissions in a broad range of total pressure and N_2/O_2 ratios, remained unnoticed. It has probably affected several investigations[38] summarized in Table 1, as a recent reinterpretation[39] of experimental results[21−24,31−35] also shows, and it should be taken into account in all pertinent applications. This reinterpretation[39] provides additional support for the role of N_2(A) and O_2* in this excitation. It might even help shed more light on, if not elucidate, the mechanism of the nitrogen afterglow in general and that of the $N(^4S)$ recombination in particular, which are not yet fully resolved,[12,29] for example, by determining the populating and depopulating effect of O_2* on various N_2* states. It was previously conjectured that by variation of the N_2 and O_2 pressure, similar precursor(s) may have been formed in the homogeneous and the heterogeneous N_2 excitation. Much higher N_2 pressures were also used in these experiments compared to <1 Torr used in the past.[17] Through these two factors, i.e., pressure and variability of composition, it may be possible to find conditions for partial or total population inversion and high intensities for a visible laser by employing this phenomenon, i.e., this homogeneous collisional intersystem excitation transfer into $N_2(B,v)$ induced by O_2*. In fact it was reported that low v $N_2(A,v)$ states predominate[24] over higher ones (e.g., $v = 0$, 1 over $v = 3$) at high pressure and react with O_2 (and O) slower than higher v states.[21,24,34] Near IR lasing of pure N_2 1pbs and of other bands has been reported.[15] There is no visible N_2 1pbs laser or chemical laser.[40]

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