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Observation of $Na_2 2^3\Pi_g$–$1^3\Sigma_u^+$ bound-free emissions generated from Na(3p) in a reactive oxidation process

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Abstract

The chemiluminescent reaction products of the $(Na,\ Na_2) + Br$ halogenation system at concentrations in excess of 10^{12} cm^{-3} are considered. In a purely reaction driven environment evidence is obtained for the formation of the Na_2 $2^3\Pi_g$ excited state and bound-free emission associated with the $2^3\Pi_g - 1^3\Sigma_u^+$ band system. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

At densities which range from 10^{12} to 10^{16} cm^{-3}, the interactions between atomic sodium excited states and small sodium molecules demonstrate surprising consequences. At the highest number densities, these include the first evidence of a Raman pumping [1–6] process induced through chemical reaction. This highly efficient process which appears to involve light scattering from the low lying vibrational levels of ground state sodium dimer, correlates with the Na D-line components (D_1, D_2) formed through the $Na_2 + Br \rightarrow Na^*$ (3P) + NaBr reaction [4–6] (Fig. 1). Equally intriguing is the observation of the optical signatures for the bound-free Na_2 violet emission band systems, onsetting also as the Raman emission features develop in a completely reaction driven environment. In order to observe the chemical formation of the Na_2 violet band systems, accompanied also by Na_2 $B^1\Pi_u - X^1\Sigma_g^+$ emission, we have successfully operated a unique extended path length supersonic expansion source, described in detail elsewhere [5–7] under conditions which produce high concentrations of primarily sodium atoms and dimers. [1]

The violet bands, first observed in 1932 [8], have been the subject of over 30 publications [9] as these features have been observed in absorption and especially in emission following electrical or single- or multiphoton excitation generally at total pressures exceeding 0.1 Torr. In fact, their use as a laser transition has been proposed [10,11] and significant gain has been measured [12]. However, our observation of emission associated with the $Na_2 2^3\Pi_g - 1^3\Sigma_u^+$ and $2^1\Sigma_u^+ - X^1\Sigma_g^+$ transitions, first correctly correlated with the violet bands by Pichler et al. [9], appears to be the first monitoring

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[1] A very small concentration of trimers is also produced in these experiments.

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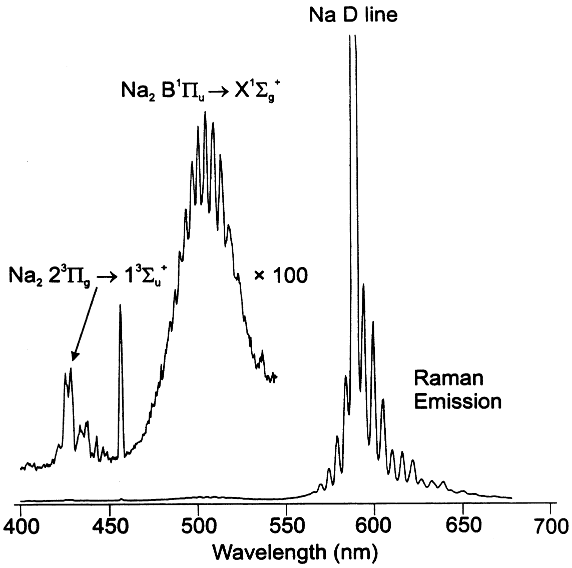

Fig. 1. Survey spectrum of chemiluminescent emission and Raman scattering involving various electronic states of diatomic sodium. The Na_2 $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$ transition corresponds to a triplet–triplet bound-free excimer-like emission process. (Res. – 12 Å, T_{oven} – 875 K, T_{nozzle} – 935 K).

of these band systems associated with (1) a reacting supersonic expansion and (2) a purely chemiluminescent reactive process.

2. Observations

The nature of the energy release in the $Na_2 + Br \rightarrow Na^*(3p) + NaBr$ reactive environment as displayed through a Raman-like effect is intriguing in that the Stokes/antiStokes emission features depicted in Fig. 1 begin to dominate at moderately high particle densities. For a pure sodium expansion, they are accompanied by $B^1\Pi_u - X^1\Sigma_g^+$ and Na_2 bound-free emission. By comparison, Fig. 2 demonstrates that the development of emission in these systems at lower densities corresponds to a thermalized $Na_2B^1\Pi_u - X^1\Sigma_g^+$ fluorescence which accompanies a weak Na D-line. As the source flux increases, the relative density of dimers in the reaction zone also increases as we observe (Fig. 2b) collision induced molecular fluorescence associated with the $Na_2A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition superimposed over a very weak Raman-like signal. The $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ molecular fluorescence is distinguished from the Raman-like features by smaller peak separations on the order of ~ 114 cm^{-1} which correspond to vibrational frequencies associated with the Na_2 $A^1\Sigma_u^+$ state.

As the flux continues to increase to the intermediate levels of the pure sodium expansion of Fig. 1 and to the highest fluxes used in these experiments, no Na_2 $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ molecular fluorescence is detected and the emission is dominated by Raman-like scattering. Here, the observed features generated in the reactive environment can exceed all other chemiluminescence by nearly two orders of magnitude (Fig. 1). If the sodium vapor is entrained in argon or helium and this mixture is expanded through the extended slit nozzle, the ratio of the Na_2 B–X fluorescence to the Raman scattering intensity increases. However, if we compare the spectra obtained as one converts from a helium to argon expansion, we observe a quenching and red shifting of the vibrational band intensities associated with the Na_2 $B^1\Pi_u - X^1\Sigma_g^+$ molecular fluorescence which would appear to result from differences in the formation [13] efficiency of the Na_2 B state with argon versus helium entrainment. Further, the bound-free molecular fluorescence which is virtually absent in the helium expansion onsets with argon seeding, albeit not to the extent of that for a pure expansion. This is also demonstrated in Fig. 3 for the highest reactant fluxes obtained in a Na/Ar expansion where the molecular scattering and fluorescence features are accompanied by a cascade of Na atomic emission features.

Previous experimental observations [14–16] suggest that the $B^1\Pi_u \rightarrow X^1\Sigma_g^+$ emission spectrum is produced in one of the following reaction sequences:

$$\begin{aligned} &Na(3p) + Na_2(X^1\Sigma_g^+) \rightarrow Na(3s) + Na_2^*(B^1\Pi_u) \\ &Na_2^*(B^1\Pi_u) \rightarrow Na_2(X^1\Sigma_g^+) + h\nu \end{aligned} \tag{1}$$

$$\begin{aligned} &Na(3p) + Na(3s) + M \rightarrow Na_2^*(B^1\Pi_u) + M \\ &Na_2^*(B^1\Pi_u) \rightarrow Na_2(X^1\Sigma_g^+) + h\nu \end{aligned} \tag{2}$$

where the M in the associative reaction (2) corresponds to a third body whose presence provides a

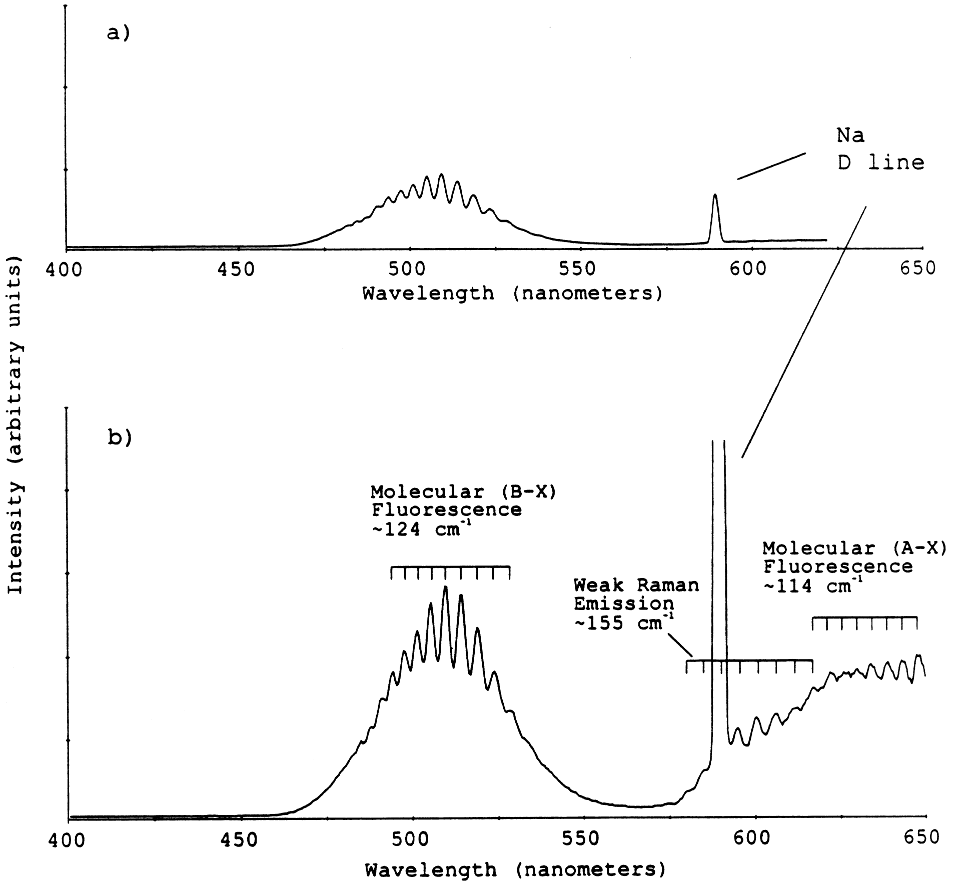

Fig. 2. Survey scans of observed chemiluminescence resulting from sodium/halogen atom interactions at reduced halogen reactant densities. The sodium oven is operated at a temperature close to ~800 K. The relative intensities of the two spectra (a) and (b) are on the same scale.

route to funnel excess energy. The rather large energy defect ($\Delta E \cong 3000$ cm^{-1}) which would be associated with process (1) suggests that this process represents an unlikely mechanism for the observed molecular $B^1\Pi_u \rightarrow X^1\Sigma_g^+$ fluorescence.

At the highest concentrations in the present study, the formation of an excited atom/dimer complex might well enhance the probability that process (1) contributes to the observed Na_2 B–X fluorescence. However, Lam et al. [14] have considered the interaction between Na(3p) and $Na_2(X^1\Sigma_g^+)$ and found the $Na_2A \rightarrow X$ band fluorescence to dominate the B → X band fluorescence for a Na(3p) + $Na_2(X^1\Sigma_g^+)$ collision process. Any evidence for A–X fluorescence appears to be absent in Fig. 3. At lower sodium densities ($\sim 10^{13}$ cm^{-3}) the probability of process (2) is often rather low [14]. Nevertheless, energetics alone suggests that it is more likely that process (2) represents the dominant mechanism for the population of and subsequent chemiluminscence from the $B^1\Pi_u$ state of sodium dimer, particularly at the higher atom number densities present in the current system.

Pichler et al. [9] have used the single mode 351.1 nm excitation from an argon ion laser and optical–optical double resonance via mixed $A_u^1 \sim b^3\Pi_u$ levels to obtain spectra which conclusively demonstrate that the puzzling violet bands arise from the superposition of two distinct continuum emission bands – one singlet ($2^1\Sigma_u^+$–$X^1\Sigma_g^+$), corresponding to the emision from the outer well of the double minimum $2^1\Sigma_u^+$ state, and one triplet

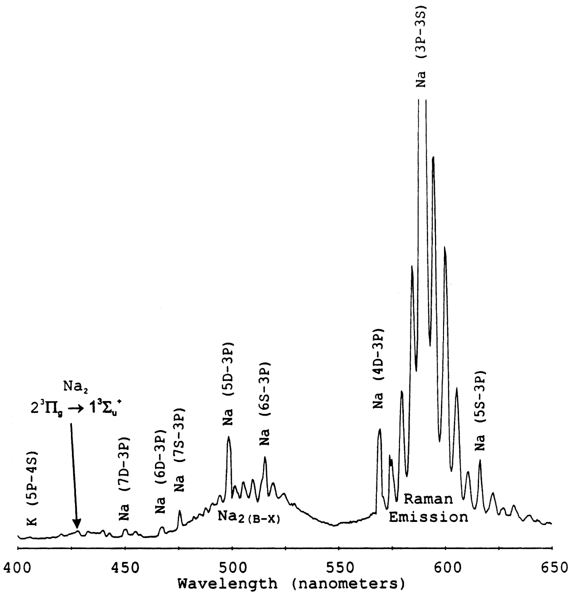

Fig. 3. Chemiluminescent spectrum observed under conditions of highest reactant flux. We observe clear evidence of energy pooling in the Na(3p) state as substantial emission from higher atomic sodium states ($n \geqslant 4$) is present. We also note the appearance of a weak $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$ emission band.

(primarily $2^3\Pi_g$–$1^3\Sigma_u^+$). We have compared the emission features which we observe in an expanded view of Fig. 1 with the data and analysis of Pichler et al. (cf. Footnote 1) and with the spectra obtained by Allegrini et al. [17] generated in a heat pipe oven by pumping the Na D-line transition. We conclude that the features observed in Fig. 1 in the 425–460 nm region, display an intensity distribution closely paralleling that obtained by Pichler et al. [9], which suggests that they result predominantly from the $2^3\Pi_g$–$1^3\Sigma_u^+$ band system (mixing with $3^3\Pi_g$ is possible) with some lesser contribution from the $2^1\Sigma_u^+$–$X^1\Sigma_g^+$ system. It is clear that a bound-free emission from Na_2 has been excited in an exclusively reaction based environment.

3. Discussion

Several mechanisms have been postulated for the formation of the Na_2 $2^3\Pi_g$ excited state [9,14,18]. One such mechanism, involving the associative ionization process is [18]

$$\begin{aligned} &\mathrm{Na(3p)} + \mathrm{Na(3p)} \rightarrow \mathrm{Na}_2^+ + \mathrm{e}^- \\ &\mathrm{Na}_2^+ + \mathrm{e}^- \rightarrow \mathrm{Na}_2^*(2^3\Pi_g) \\ &\mathrm{Na}_2^*(2^3\Pi_g) \rightarrow \mathrm{Na}_2^*(1^3\Sigma_u^+) + h\nu \end{aligned} \tag{3}$$

The results which we have obtained suggest a direct correlation between the available excited Na*(3p) and the formation of the Na_2 $2^3\Pi_g$ state. Both argon and helium supersonic expansions will dilute the formation of the $2^3\Pi_g$ state through energy pooling processes involving the Na(3p) state which can be enhanced by the trapping of resonance radiation associated with the Na 3p → 3s transition. The enhancement of these processes at higher concentrations suggests that mechanism (3) may be operative. Figs. 3 and 4 depict the chemiluminscence observed under the highest bromine atom and sodium fluxes. Here, one observes a significant energy pooling involving the sodium 3p state and a resulting fluorescence from higher atomic sodium states ($n = 4, 5, 6, 7$) by way of the process,

$$\mathrm{Na(3p)} + \mathrm{Na(3p)} \rightarrow \mathrm{Na(ns,\ nd)} + \mathrm{Na\ (3s)} + \Delta E \tag{4}$$

where ΔE represents the energy defect for the pooling interaction indicated. We compare the spectrum of Fig. 4 to the laser excitation spectrum produced by Allegrini et al. [17] under cw laser excitation in a heat pipe oven. Under seeded expansion conditions we observe substantial energy pooling accompanied by the onset of the $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$ emission feature. This feature is even more pronounced under pure expansion conditions where the Na(3p) population is not diluted by argon or helium. The remarkable similarity between the experimental spectra in Fig. 4 would seem to lend strong support to reaction mechanism (3) as the route for production of sodium dimer in the $2^3\Pi_g$ state.

However, while process (3) may correspond to the primary mechanism for production of the $2^3\Pi_g$ state of Na_2, another possible mechanism has been postulated by Pichler et al. [9]. This mechanism involves a rapid dissociative recombination process following the reaction sequence:

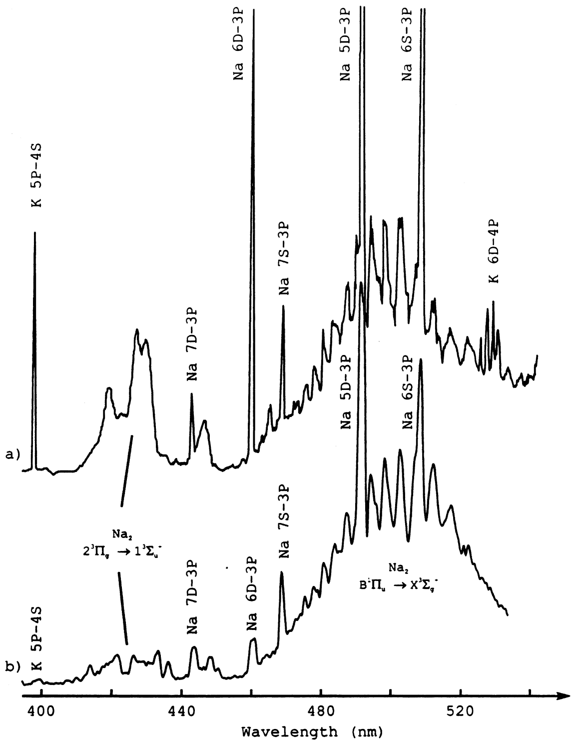

Fig. 4. Comparison of: (a) laser excitation spectrum (from Ref. [14] with (b) the blue emission (400–560 nm) from the experimental spectrum in Fig. 3. Note the onset of the $2^3\Pi_g \rightarrow 1^3\Sigma_u^+$ emission band near 435 nm.

$$\begin{aligned} &Na_3^+ + e^- \rightarrow Na_2^*(2^3\Pi_g) + Na(3s) \\ &Na_2^*(2^3\Pi_g) \rightarrow Na_2(1^3\Sigma_u^+) + h\nu \end{aligned} \tag{5}$$

While the dominant mechanism for formation of the Na_3^+ in the reaction sequence (5) remains unclear, the Na_3^+ ion may be formed from one of the following processes:

$$\begin{aligned} &Na(3p) + Na(3p) \rightarrow Na_2^+ + e^- \\ &Na_2^+ + Na(3s,\ 3p) \rightarrow Na_3^+ \end{aligned} \tag{6}$$

(cf. Ref. [19]).

$$Na(4d, 5s) + Na_2 \rightarrow Na_3^+ + e^- \tag{7}$$

(cf. Ref. [20]).

$$Na_2(C^1\Pi_u) + Na(3p) \rightarrow Na_3^+ + e^- \tag{8}$$

(cf. Ref. [21]).

Klavins et al. [22] have also suggested the production of Na_3^+ via

$$Na_2(A^1\Sigma_u^+) + Na(3p) \rightarrow Na_3^+ + e^- \tag{9}$$

These authors were able to confirm that the sodium trimer ions are produced in associative ionization collisions between sodium dimer and sodium atoms when both colliding partners are in their lowest respective electronically excited states. They also suggest that Na_3^+ can respresent a dominant ion, especially for higher atom/dimer densities, due to its relatively low ionization potential (IP Na $\sim$ 5.14 eV, $Na_2 \sim$ 4.87 eV, $Na_3 \sim$ 3.97 eV) [23–26]. The substantial Na(3p) sodium atom excited state population and the excitation of both the $A^1\Sigma_u^+$ and the $B^1\Pi_u$ sodium dimer states would at lower expansion flux suggest that mechanism (9) can constitute a route for formation of the Na_3^+ ion, consistent also with the data presented in Figs. 3 and 4. Therefore, subsequent recombination, as in process (5), seems to represent an equally likely route for production of the $2^3\Pi_g$ state of the sodium dimer.

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