Laser Original

Na₂ Near Infrared and Violet Excimer Emissions by Electron Beam Excitation

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A near infrared broadband excimer emission band and an amplified spontaneous emission (ASE) of the Na₂ violet excimer band have been observed by electron beam excitation of a dense sodium vapor. The continuum from 820 to 900 nm is attributed to the Na₂ first bound-free transition band $c^3\Sigma_g^+ \rightarrow a^3\Sigma_u^+$ and the violet excimer band centered at 436 nm is attributed to the Na₂ $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ bound-free emission which was already observed in the optical pumping. The mechanisms for the $c^3\Sigma_g^+$ state formation are proposed to be the three-body collision recombination and the atom-molecule collisional energy transfer. The formation of the $2^3\Pi_g$ state is proposed by a dissociative recombination of Na₃⁺ which is efficiently yielded by electron beam. In addition, a discrete structure band observed on the long wavelength side of the violet bands is believed from the Na₂ $2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ bound-bound transitions.

Key Words: Na₂, Excimer emissions, Near infrared, Violet band, Amplified spontaneous, e-beam excitation

1. Introduction

It is well known that diatomic alkali molecules possess two electronic states which separate at large internuclear distance into two ground state atoms. The lower one in these molecular states is the bound $1^1\Sigma_g^+$ state, in which the spins of the two outermost electrons point in opposite directions. The other state is $3^1\Sigma_u^+$, in which the electron spins are aligned. Although this state has a very shallow van der Waals minimum, it is for the most part repulsive, so emission to the $3^1\Sigma_u^+$ state should be a true continuum. In fact, unstructured bands have been discovered in the spectra of all the alkalis. It is widely believed that these bands do constitute emission to the $3^1\Sigma_u^+$ states although conclusive evidence for this identification does not yet

exist.

Optically pumped alkali dimer lasers have been studied extensively, because alkali dimers are of special interest owing to their simple molecular structure, stability, ease of production and large stimulated emission cross section. Laser oscillations from the $A^1\Sigma_u^+$ and $B^1\Pi_u$ states of sodium dimer by optical excitation have been reported¹⁻⁴⁾. Muller and Hertel⁵⁾ and Krokkel *et al.*⁶⁾ have discussed IR laser from two-photon pumping of high-lying Na₂ state. Dinev *et al.*⁷⁾ reported Na₂ $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ laser emission caused by collisional energy transfer between excited and ground state atoms. In these systems discrete output lines are obtained because they operate on transitions between the strongly bound electronic states.

There have been considerable number of stu-

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dies on Na_2 diffuse bands, being interested in their excimer-type nature⁸⁻¹¹). Such diffuse bands might be developed as possible sources of tunable, high-power lasers¹²). First of all, for the research concerning with the first triplet band transition, Shahdin *et al*¹³). reported the observation of diffuse emission centered at ~ 855 nm in Na_2 excited by a UV laser. Huennekens *et al*¹⁴). also observed an emission located in the range of the lowest triplet transition of Na_2 by populating the $B^1\Pi_u$ state. Recently, Dinev *et al*¹⁵). and Bajic *et al*¹⁶). reported the emission centered at 830 nm which was believed to arise from the Na_2 $c^3\Sigma_g^+ \rightarrow a^3\Sigma_u^+$ transition caused by collisions between two-photon-excited Na (4d) and Na (3s) atoms¹⁵), and by a molecular Raman process or six-wave mixing¹⁶). On the other band, Na_2 violet diffuse band was observed either by one-photon excitation of $X^1\Sigma_g^+ \rightarrow C^1\Pi_u$ or two-photon excitation of $X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+ \rightarrow$ high-lying g state in Na_2 , or one-photon excitation of 3S-3P or two-photon excitation of 3S-4D in the Na atom¹⁷⁻²²). In particular, an observation of small signal gain in the violet band by 350.7 nm CW Kr^+ laser pumping has been reported²³).

To obtain these transition the most fundamental difficulty is due to the absence of an efficient excitation method from the singlet ground state $X^1\Sigma_g^+$ to the upper triplet states. The relevant potential curves of interest are plotted for Na_2 in Fig.1. Laser action with such molecular species, however requires high excited state density and sufficient volume. This should be feasible by electron beam pumping. As a preliminary step toward achieving new tunable and high power excimer lasers in the near infrared and violet, we present the observation of two diffuse bands of Na_2 in 400-460 nm and 820-900 nm regions by e-beam pumping, a preliminary account of which has been given

Fig.1 Potential curves of low-lying states of Na_2 and the corresponding Na atomic states. These curves merely serve to indicate relative positions.

previously²⁴).

2. Experimental Apparatus

A schematic diagram of the present experimental setup is shown in Fig.2. The electron beam supplied by a Febetron 706 electron beam generator installed with a velvet cathode²⁵) had a peak current of 4.5 kA, a beam diameter of 2.0 cm, a pulse width of 3 ns (full width at half-maximum), and an electron particle energy of 500 keV. The electron beam, confined by an externally applied 1.5 kG axial magnetic field (nonuniformity less than 2%), passed through

Fig. 2 Schematic diagram of the experimental apparatus.

the anode foil, a drift section of 15 cm length filled with low-pressure helium and entered into a heat pipe oven containing dense sodium vapor, which was separated from the drift section by a Kapton foil. The heat pipe oven had a diameter of 4.5 cm, a total length of 120 cm, and an active length of 60 cm, which was determined by the distance of the cooling coils. The fluorescence spectrum was observed through a quartz window at the forward end of the cell. Operating temperature of the oven ranged from 400 to 720 °C, corresponding to sodium vapor pressures of 1-125 Torr. Accuracy of temperature control was within ± 2 deg. The cell was filled alternatively with buffer gas of helium, neon, argon, or krypton.

The beam parameters were monitored by color foils and Faraday cups. About 50 % of the peak current emitted by the diode was transmitted into the tube. The observed energy loss in the gas was in good agreement with that predicted by a Monte Carlo calculation²⁶⁾.

For the observation of the first triplet band, the emission from the heat pipe was introduced to an optical multichannel spectrum analyzer (OMA) through a high-pass filter and an optical fiber. The resolution of OMA system was 0.5 nm/channel, when a 600 lines/mm grating and the 30 μm entrance slit were used in the 0.3 m polychromator. In the experiment of the violet band, the spectrum was analyzed with a spectrum multichannel analyzer (SMA) composed of a model IRY-512 detector (Princeton Instrument Inc.). The resolution of SMA system is 0.12 nm/channel with a 1200 grooves/mm grating. The spectrum was corrected for relative detection system efficiency as a function of wavelength. The emission wavelengths were calibrated using a neon spectral lamp and a mercury lamp.

3. Experimental Results

3.1 The near infrared Na_2 $c^3\Sigma^+_g \rightarrow a^3\Sigma^+_u$ excimer emission

Figure 3 (a) shows a Na_2 fluorescence spec-

Fig. 3 (a) Emission spectrum of Na/Na₂ in the region of 550-900 nm excited by electron beam. Cell temperature: 620 °C. Krypton buffer gas pressure: 350 Torr. (b) Na₂ emission spectrum calculated using the potential curves and transition moments of Refs. 8 and 10.

trum observed in the range of 550~900 nm. The buffer gas was 350 Torr krypton and the sodium vapor temperature was 620 °C. It consists of several sharp atomic lines and broad molecular bands. The broad band spreading from 600 to 800 nm shows good coincidence with that observed in optical excitation and assigned as the Na₂ $A^1\Sigma^+_u \rightarrow X^1\Sigma^+_g$ band, which will be abbreviated as the singlet A-X transition in the following part of this paper. In addition, a

strong emission band observed around 800 to 900 nm overlaps with the emission band observed in the previous paper by the excitation of a frequency doubled Nd : YAG laser¹⁴⁾. A drastic difference between the emission spectra observed in the present and the former works is the high relative intensity of the triplet-triplet c-a continuum in the present work. This is explained by assuming that the population density of the $c^3\Sigma^+_g$ state is very high in the present experiments using electron beam excitation. We have concluded that the latter band is the fluorescence due to the lowest triplet-triplet transition, $c^3\Sigma^+_g \rightarrow a^3\Sigma^+_u$ (abbreviated as c-a transition in the following part of this paper), on the reasons given below.

First of all, the strong emission observed in 800 to 900 nm region should not be a bound-continuum transition from the singlet $A^1\Sigma^+_u$ state to the repulsive wall of the ground singlet state $X^1\Sigma^+_g$ ("Millikan's difference potential")²⁷⁾. The fluorescence of this type has been well studied both theoretically and experimentally^{27,28)} and is well known not to include any components longer than 830 nm. It was also reported that this type of emission is accompanied by much stronger bound-bound lines²⁷⁻²⁹⁾. Taking account of the fact that the strong bound-bound lines have not been observed, the A-X bound-continuum emission should be negligible in the present data. On the other hand, it can be shown that the fluorescence spectrum due to the triplet c-a transition should predominate this region by calculating the coefficient of spontaneous emission for $J=55$, which is the most probable value at 620 °C, using the potential values and transition moments given by Konowalow et al^{8,10)}.

Figure 3(b) shows a simulated spectrum of the overlapped c-a and A-X bands by taking into account the lower six vibrational levels of the $c^3\Sigma^+_g$ state and the lower twenty vibrational

levels in the $A^1\Sigma^+_u$ state. It should be noted that the shorter wavelength side of the c-a band is overlapping with the longer wavelength side of the A-X band. The population distribution of the vibrational states was assumed to be non-thermal and a linear surprisal distribution³⁰⁾ was used. The best agreement between the experimental and simulated spectra was obtained, as shown in Fig. 3 (b), by assuming that the population of the $c^3\Sigma^+_g$ state is three times more than that of the singlet A state. The transition energy was shifted by 0.124 eV to bring the peak of A-X band to agree with the present and previous^{27,28)} experimental results. By comparing Fig. 3 (a) and Fig. 3 (b) one can see the strong emission of 800 to 900 nm region is due to the triplet bound-free c-a transition.

In order to investigate how the emission is affected by different buffer gases, we observed the emission spectra under the same condition by replacing the buffer gas from krypton to argon, neon and helium. The results are shown in Fig. 4. If we ignore the atomic lines, all of the observed emission spectra consist of two bands similar to those observed in krypton buffer gas, only the relative intensity of the two bands showing a systematic change, from which it is also evident that the emission band between 830 and 900 nm cannot be attributed to the buffer gas in the heat pipe oven. In the emission spectra of helium buffer gas the A-X band was measured without overlapping with the c-a band, the wavelength of the A-X band head is in agreement with that reported by the optical excitation. The intensity ratio of the c-a to the A-X transition, which will be designated as I_{c-a}/I_{A-X} , drastically decreases from krypton to argon, neon and helium.

It is difficult to give a quantitative explanation of such buffer gas effect on the present experimental results. However, the fact that the

Fig. 4 Spectra observed from electron beam excited Na/Na₂ mixture with buffer gases of Kr (a), Ar (b), Ne (c) and He (d). The vapor temperature was 620 °C and the pressure of the buffer gas was fixed at 350 Torr.

spectrum consists of two bands appearing at the same wavelength region, together with the existence of such a systematic buffer gas dependence, confirms the validity of the present assignment.

We also observed the sodium density dependence of the intensity of the c-a emission by changing the oven temperature in order to investigate the formation mechanism of the $c^3\Sigma^+_g$ state sodium dimers. Figure 5 shows the observed

Fig. 5 Intensities of the diffuse emissions at 848 nm as functions of the temperatures of the cell with different buffer gases of Ne, Ar and Kr. The solid curve indicates the calculated square density of Na from a empirical formula³¹⁾.

temperature dependence of the c-a transition intensity at 848 nm for various buffer gases, together with a plot of the temperature dependence of the square of sodium density. It should be noted that those curves have exactly the same dependence in the low temperature region. This indicates that the main channels of the molecular $c^3\Sigma_g^+$ state production should be a processes in which the rates are proportional to the square of the density of sodium atoms. In the high temperature region the intensity of the c-a transition obviously is separated from the curve of square density of sodium atoms. It might be considered that the free-bound absorption of the $\text{Na}_2 a^3\Sigma_u^+ \rightarrow c^3\Sigma_g^+$ band increases in higher temperature^{31,32)}. These behavior may suggest that the observed triplet c-a emission is coming from the three body collisional processes.

3.2 The $\text{Na}_2 2^3\Pi \rightarrow a^3\Sigma_u^+$ violet band excimer emission

A typical fluorescence spectrum of the violet

Fig. 6 Emission spectrum in the spectral region from 410 to 460 nm for electron-beam-excited Ar/Na/Na₂ mixtures. Cell temperature: 515 °C. Argon buffer gas pressure: 200 Torr. The resolution of SMA was 0.12 nm/channel.

bands (400-460 nm) excited by the electron beam is shown in Fig.6. The resolution of SMA was 0.12 nm/channel. The buffer gas was 200 Torr of Ar and the Na vapor temperature was 515 °C. The peak of the emission is centered at 436 nm. Two weaker features are seen at about 452 nm and 428 nm. The fluorescence spectrum beyond 460 nm consists of the Na₂ B-X band (460-565 nm), the A-X band (600-820 nm), the first triplet band $c^3\Sigma_g^+ \rightarrow a^3\Sigma_u^+$ (see discussion above) and several Na atomic resonance lines.

The spectral positions of the two peaks of 436 and 452 nm agree approximately with the positions of the spectral features observed with optical pumping¹⁷⁻²³⁾; however, in contract to a fact that the long wavelength peak of 452 nm was almost the same in intense with the peak of 436 nm in the previous works which were observed in low pressure optical pumping, the short wavelength peak at 436 nm had the dominate intensity in the present experiment. One of the most pronounced features of the broad diffuse band in the 415-438 nm region is obviously blue-

Fig. 7 The fluorescence spectra in (a) the 420-442 nm, and (b) the 445-460 nm regions from electron-beam-excited Ar/Na/Na₂ mixtures. Temperature 515 °C and argon buffer gas pressure 200 Torr. The resolution of SMA was 0.05 nm/channel.

shaded. For reasons given below, we conclude that only the 436 nm band is the emission from the bound-free triplet-triplet transition, $2^3\Pi_g \rightarrow a^3\Sigma_u^+$.

First of all, the spectra of the 436 nm and 452 nm regions were observed in a higher resolution. Figure 7 shows an observed result in (a) the 420-442 nm, and (b) the 445-460 nm regions from electron-beam-excited Ar/Na/Na₂ mixtures. The resolution of SMA was 0.05

nm/channel. The spectrum in Fig.7 (a) still presents a smoothing continuous structure, but the 452 nm region in Fig.7 (b) appears some discrete peaks which can be attributed to vibration-vibration transitions from bound states. On the other hand, the fluorescence spectrum arising from the triplet $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ transition should not include any components longer than 440 nm; this can be shown by calculating the Franck-Condon factors (FCF's) of the $J=50$ rotational state in the Na₂ $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ emissions, which is the most probable value for a temperature of 515 °C, by using the potential curves given by Jeung^{33,34}. The result also shows that emissions are almost due to the transitions to the $a^3\Sigma_u^+$ continuum, especially for the lower vibrational levels of the $2^3\Pi_g$ state. One can see that the Na₂ $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ transition has very large Franck-Condon densities because of the nice overlap of the lower vibrational transitions³⁵, similar to that which occurs in the B-X systems of the rare-gas-halides, as the KrF spectrum³⁶. The transition from the $3^3\Pi_g$ to $a^3\Sigma_u^+$ state is also expected to lie near this wavelength region²³, which has a calculated wavelength of 425 nm from $v'=0$ of $3^3\Pi_g$ state, but it is expected much weaker than the $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ transition because the FCF's of the $3^3\Pi_g \rightarrow a^3\Sigma_u^+$ are smaller and spread. Figure 8 shows a simulated spectrum of the Na₂ $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ band by taking into account of the lower fifteen vibrational levels of the $2^3\Pi_g$ state. The population distribution of the vibrational states was assumed to be non-thermal and a linear surprisal distribution³⁷ was used. It was clearly exhibited that the $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ transition has a main peak at 435 nm and has a broad blue-shaded diffuse feature in the 410-440 nm region, which are in good agreement with the observed result (see Fig. 6). It should be noted that the $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ calculated spectrum has not to in-

Fig. 8 The simulated spectrum of the Na_2 $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ band by using the potential curves given by Jeung^{33,34)} and taking into account of the lower fifteen vibrational levels of the $2^3\Pi_g$ state.

clude any components longer than 440 nm.

By comparing Figs. 8 and 6 one can see the broad blue-shaded band extending from 415 to 438 nm corresponds to the bound-free $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ continuum. Our fluorescence spectrum should consist of many transitions originating from various vibrational levels of the $2^3\Pi_g$ state, because of a nonselective excitation by the electron beam.

It is also indicated that the emission beyond 440 nm is not due to the triplet $2^3\Pi_g \rightarrow a^3\Sigma_u^+$ transition. In fact, in our experiments it was indicated that the ranges of 436 and 452 nm have different pressure dependence. We believe that the emission in the 452 nm region belong to Na_2 $2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ bound-bound transitions³⁸⁾, according to our calculation of the FCF's for the $2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition. The $2^1\Sigma_u^+$ has two minima in the potential curve. A transition from the outside minimum (at 12.7 Bohr³³⁾) of the $2^1\Sigma_u^+$ state will hit at the long-range region of the ground $X^1\Sigma_g^+$ state. For this kind of potential curves a very narrow Franck-Condon vibrational envelopes for the transitions is

expected, even the quasi-continuous emission is also possible³⁹⁾. The calculation indicates that the transitions from the lower v' vibrational levels of the $2^1\Sigma_u^+$ states to the high v'' levels (about $v'' = 50$), where near to the dissociation limits of the $X^1\Sigma_g^+$ state, have the largest transition probabilities and centered transition wavelengths close to the 452 nm. In fact, a calculated spectrum for the $2^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition has a similar spectrum distribution with the experimental result given in Fig. 7(b).

The violet band signal in 436 nm was monitored as a function of the cell temperature from 400 to 600 °C (corresponding to sodium vapor pressure of 0.5-25 Torr) and argon buffer gas pressure from 100 to 1200 Torr. The maximum violet band signal was observed at a temperature of 520 °C, which corresponds to a sodium vapor pressure of 6.5 Torr, and an argon pressure of 200 Torr. The violet band emission feature is also present when the electron beam is used to excite helium/sodium-vapor mixtures.

Fig. 9 The emission spectra for electron-beam-excited Ar/Na/Na₂ mixtures showing the spontaneous emission (trace a) and the amplified spontaneous emission (trace b). The excitation energy densities are about 3.5 and 6 mJ/cm³, respectively. The base line for the ASE spectrum is vertically displaced.

Fig. 10 Observed excitation energy dependence of the bound-free 436 nm emission.

The behavior of the main transition was investigated as a function of the excitation energy density by varying the input electron particle energy. The apparent feature of the amplified spontaneous emission (ASE) was observed without mirrors, when the excitation energy density exceeded 5 mJ/cm^3 . Figure 9 shows a comparison of the spectrum including the ASE (upper trace) and the fluorescence (lower trace) in the region of 400–460 nm. The amplified emission in the 436 nm was obtained in Ar/Na/Na₂ mixtures at argon pressure ≥ 100 Torr and sodium vapor pressure between 1–10 Torr. The indication of the amplified phenomenon in 452 nm region was not present at the same experiment conditions, although a largest gain of the violet band was observed at 452 nm²³⁾.

Observed excitation energy dependence of the bound-free 436 nm emission was given in Fig. 10. In the lower pumping energies, the intensity of the fluorescence of the violet bands linearly increases with the increasing of the pumping energy. A strong enhancement of the 436 nm emission and a narrowing of the spectrum width

were observed at the higher pumping energies. Taking into account the change in sensitivity of the detector, a rough intensity calibration for the 436 nm wavelength region was obtained. For the pumping intensity of 5 mJ/cm^3 and Na vapor density of $10^{16}/\text{cm}^3$, approximately a low limit of the gain of 0.02 cm^{-1} is estimated, which correspond a population density of $10^{14}/\text{cm}^3$ occurred in the observable volume.

Helium/sodium-vapor mixtures did not exhibit the phenomenon of the stimulated-emission in the violet bands region in the present pressure range investigated.

4. Discussions

4.1 The Formation Mechanism of Na₂ $c^3\Sigma_g^+$ State

In a previous work⁷⁾, collisional energy transfer from the excited atomic levels was proposed and used to achieve inversion population on a number of bound-bound transitions in the singlet Na₂ $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ system. Making use of this mechanism we were able to transfer population effectively also to the triplet system.

The electronic excitation of Na (3P) was studied both theoretically⁴⁰⁾ and experimentally^{41,42)} in high-pressure sodium discharges. Those studies showed that almost all of the input electron energy was transferred to the Na (3P) state⁴⁰⁾ by this process. The similar discussion also has been made on Na-rare gas systems⁴³⁾. Therefore we suppose that high Na (3P) density is created in the case of electron beam excitation. Furthermore, if we take account of the self absorption^{31,32)} at high temperature the measured emission intensities are proportional to the square of the sodium density in every buffer gas. These make us to propose that the following three body collisional recombination process was a main channel for triplet $c^3\Sigma_g^+$ state production:

Because of the repulsive or shallow potential well of the higher lying states, the important states should be only the $c^3\Sigma^+_g$, $A^1\Sigma^+_u$, $B^1\Pi_u$ and $b^3\Pi_u$ for this recombination process. Assuming the high density excited atoms, the excited and unexcited sodium atoms collide with each other frequently as well as rare gas atoms. The population of the triplet states due to recombination is expected to be higher than that of the singlet states due to the statistical ratio. In addition, the radiative transition from the $b^3\Pi_u$ state to the $A^1\Sigma^+_u$ or $a^3\Sigma^+_u$ state is forbidden because of $\Delta S=0$ and u-u selection rules. Thus, most of the vibrational-rotational levels of the $b^3\Pi_u$ state have a long radiative lifetime ($\kappa \sim 10^5\text{--}10^6 \text{ s}^{-1}$)⁴⁴⁾. The long lifetime of the $b^3\Pi_u$ state favors the population of the $c^3\Sigma^+_g$ state through the $\text{Na}(3P) \leftarrow \rightarrow \text{Na}_2(b^3\Pi_u)$ forward and backward coupling and a predissociation⁴⁴⁾.

Another possibility is an excitation process of a ground state sodium dimer to the $c^3\Sigma^+_g$ state by collision of a sodium atom in 3P state:

This process should have the same temperature dependence, because the sodium dimer density is approximately proportional to the density of sodium atom at a given temperature under the present condition. In this energy transfer process, the excitation transfer to the higher lying molecular states can be neglected, because the energy defect is too large. The excitation transfer to the $A^1\Sigma^+_u$ and $b^3\Pi_u$ state, according to Lam et al⁴⁴⁾, has a large rate constant of $k \sim 3.4 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ corresponding to a cross

section of $\sigma \sim 300 \text{ \AA}^2$. The excitation transfer to the $c^3\Sigma^+_g$ state exhibits an energy defect of $\sim 1400 \text{ cm}^{-1}$, and the available data are insufficient to estimate the cross-section corresponding to this process.

In addition, the $A^1\Sigma^+_u$ state also can be populated by the electric-dipole allowed $A \leftarrow X$ transition. The $c^3\Sigma^+_g$ state may then obtain population by the perturbation^{45,46)} of the $b^3\Pi_u$ state with the $A^1\Sigma^+_u$ state and further excitation from the $b^3\Pi_u$ state. In the case of the electron beam excitation, the singlet-triplet transition may also have some probabilities because it is not strictly forbidden as that in the optical pumping. But the temperature dependence of these processes should not coincide with our experimental results (see Fig. 5). So we believe these processes are not main processes in the present experiments. Thus we are inclined to assume that the three body recombination process may be the main channel for the $c^3\Sigma^+_g$ state generation.

It is of great interest that the c-a transition intensity is drastically increased by the choice of the buffer gas in the present experiment. The molecular components of the spectra observed with helium buffer gas has a close resemblance to the spectrum observed on the argon seeded sodium vapor jet¹⁴⁾. However, such a strong c-a emission has never been reported before by the experiments of optical excitation. The most important differences in the experimental condition are the methods of excitation and the high electron density in our experiment.

We consider the high density secondary electron in the medium excited by the electron beam together with a high collision frequency causes such a difference. This idea is supported by the fact that the I_{c-a}/I_{A-X} ratio increases with the ionization cross section of the buffer gas⁴⁷⁾. In the present experiment, the variation in the stop-

ping power causes a drastic change in the energy deposition for different buffer gases. For the krypton buffer gas, the energy deposition is rather localized in the axial direction, and for helium buffer gas the electron beam energy is deposited uniformly along the axial direction. Thus the energy deposition rate and the electron density are much higher in krypton buffer gas than they are in helium buffer gas. The Stark effect due to the strong local field produced by high density secondary electrons should increase the energy transfer rates between the $b^3\Pi_u$, the $A^1\Sigma^+_u$ and the $c^3\Sigma^+_g$ states. Such effect together with a high collision frequency may be playing an important role causing such a drastic increase in the $c^3\Sigma^+_g$ state population in krypton buffer gas. The energy transfer from the $b^3\Pi_u$ state should be much effective in increasing the $c^3\Sigma^+_g$ state population, because the relaxation from the $b^3\Pi_u$ state is a bottle-neck in sodium dimer system.

This triplet-triplet transition is of interest as an excimer type laser transition, and the feasibility of an electron beam pumped sodium dimer laser on this transition is one of our main motivations, because a synthesized band-shapes of the emission spectrum agrees with the present observation quite well in the krypton buffer gas medium if we assume that the $c^3\Sigma^+_g$ state density is three times of that of the $A^1\Sigma^+_u$ state, on which the laser action was observed⁷⁾. As mentioned in the early part of this paper the population density produced in the krypton buffer gas medium should be much higher in the present experiment. The maximum population density realized in the experiment was not determined in the present work. However, the theoretical value of the stimulated emission cross section of the c-a transition was given to have an extremely large value of $1.8 \times 10^{-15} \text{ cm}^2$, which is larger than the cross section of B-X transition of KrF

lasers⁴⁸⁾. Such a large cross section allows one to have a gain coefficient of 0.03 cm^{-1} by having a population density of only $5 \times 10^{13} \text{ cm}^{-3}$. Assuming the simple kinetic model without quenching processes, the preliminary results suggest a Na 3P state population of $8 \times 10^{14} \text{ cm}^{-3}$ for a mixture consisting of 400 Torr krypton and 30 Torr sodium. It seems to be not too difficult to realize the population density of the $c^3\Sigma^+_g$ state enough for the laser action by using electron beam excitation in a krypton buffer gas medium.

4.2 The Formation Mechanism of Na₂ 2³Π_g State

The formation of upper state of the violet band may probably be due to a rapid dissociative recombination of Na₃⁺²³⁾.

First of all, the atom-molecule associative ionization by excited states to directly form Na₃⁺ is possible⁴⁹⁾. The electronic excitation of Na (3p) has a very large formation cross section (approximate $4 \times 10^{-15} \text{ cm}^2$)⁴⁰⁾. This was observed in high-pressure sodium discharges^{50,51)}. In addition, the radiative transition from the $b^3\Pi_u$ state to the $X^1\Sigma^+_g$ or $a^3\Sigma^+_u$ state is forbidden (see above discussion). So the associative ionization by Na (3p) + Na₂ ($A^1\Sigma^+_u$ or $b^3\Pi_u$) may play an important role in the present electron beam excitation.

On the other hand, the associative ionization from two Na (3p) atoms to form Na₂⁺ also has a large rate coefficient ($\kappa \sim 5.6 \times 10^{-12} \text{ cm}^3/\text{s}$)⁵²⁾. In addition, as well known, Na⁺ can be generated by high energy electron impact and by penning ionization. Although Na₂⁺ or Na⁺ is initially formed, still Na₃⁺ having low energy compared to Na⁺ and Na₂⁺ should constitute a 'sink' for ionization, which is supported by the recent ab initio calculation⁵³⁾ for the electronic state of Na₃⁺. The ab initio result indicates that the lowest three electronic states of Na₃⁺ all are

stable with respect to dissociations into $\text{Na}_2^+ (X^2 \Sigma_g^+) + \text{Na} (3s)$ and $\text{Na}_2 (X^1 \Sigma_g^+) + \text{Na}^+$. The bonding energy of the ground state of Na_3^+ (1.136 eV) is much larger than the bonding energy of the ground state of Na_3 (0.289 eV)⁵³, which may be compared to the sodium dimer values: $D_e(\text{Na}_2) = 0.747 \text{ eV}$ ⁵⁴ and $D_e(\text{Na}_2^+) = 0.986 \text{ eV}$ ⁵⁵. This differential effect is the origin of the abrupt change in the ionization potential of Na_n (for small n). For this reason, the formation of Na_3^+ should be having a larger probability under the typical heat pipe conditions. Therefore we predict that high Na_3^+ density is created in the present experiment. This may also explain the relative weakness of the Na^+ radiative recombination continuum versus the violet band continuum.

Finally, for the formation mechanism of the violet bands, one important reaction is dissociative recombination, e.g. $\text{Na}_3^+ + e^- \rightarrow \text{Na}_2^* + \text{Na}$. This allows a mechanism for selective production of a variety of highly excited atomic and diatomic states⁴⁹. Of particular significance is the selective production of the violet emitting states of $\text{Na}_2 (2^3 \Pi_g, 2^1 \Sigma_u^+)$ via dissociative recombination of Na_3^+ . Keeping in mind the high electron density in the present experiment, the following dissociative recombination processes are proposed as a main channel for the $2^3 \Pi_g$ and $2^1 \Sigma_u^+$ state productions:

The reaction process (3) is resonant in energy. The intermediate state Na_3^* is expected to be unstable because the reaction energy is over the dissociation limit of the Na_3^* bound states thus

resulting in a rapid dissociation to $\text{Na}_2^* + \text{Na}$. The processes (4) and (5) are predicted having the larger cross sections^{23,49}, because they are near resonant in reaction energies especially for the reaction (4) which form the upper state of the 436 nm diffuse emission.

Thus, the upper state of a specific excimer transition may be produced selectively by such dissociative recombination process following a very non-selective ionization. For this reason, the potential Na_2 violet band laser might be very suited for electrically pumping.

Of course, it is quite conceivable that such dissociative recombination-based excimer lasers might also be presented in the other alkali metals.

5. Conclusion

In this work, we report a near infrared broad-band excimer emission and an ASE of the Na_2 violet diffuse band for the first time by electron beam pumping of sodium vapor. The continuum from 820 to 900 nm is attributed to the Na_2 first bound-free transition band $c^3 \Sigma_g^+ \rightarrow a^3 \Sigma_u^+$ and the violet excimer band centered at 436 nm is attributed to the $\text{Na}_2 2^3 \Pi_g \rightarrow a^3 \Sigma_u^+$ bound-free emission. The unfavorable selection rules for exciting the optically forbidden upper $c^3 \Sigma_g^+$ state were overcome by collisional energy transfer from $\text{Na} 3P$ level which was efficiently excited by the electron beam. The characteristics of the triplet c-a emission such as the temperature dependence, pressure dependence, and the buffer gas effects has been studied. The cause of a very high population density of the $c^3 \Sigma_g^+$ state was proposed to be due to the three body collisional recombination assisted by high electron density. The formation of the $2^3 \Pi_g$ state is proposed by a dissociative recombination of Na_3^+ which is efficiently yielded by electron beam. Hopefully tunable near infrared and violet excim-

er lasers may be realized by the use of such a high current electron excitation.

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