

## On the non-Boltzmann $A$ - $X$ emission in $\text{Na}_2$ following laser excitation of the $B$ state

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**Abstract.**  $A^1\Sigma_u^+ - X^1\Sigma_g^+$  emission in  $\text{Na}_2$  is observed following excitation of  $B^1\pi_u$  by various lines of an argon ion laser. The excitation energy of  $B^1\pi_u$  is collisionally transferred to the  $(2)^1\Sigma_g^+$  which then radiatively populates the  $A^1\Sigma_u^+$  state. The Na vapour is contained in a stainless steel crossed heat pipe with Ar buffer gas and temperature around  $600^\circ\text{C}$ . For all laser lines except  $4579 \text{ \AA}$ , the coarse features of  $A$ - $X$  emission are independent of the laser wavelength. However, at high resolution the finer differences between different laser line excitation are explained. Various  $v$ - $v'$  transitions in this emission are identified. Computer simulation is presented to help explain some features of this emission.

**Keywords.**  $\text{Na}_2$ ; energy transfer; argon ion laser.

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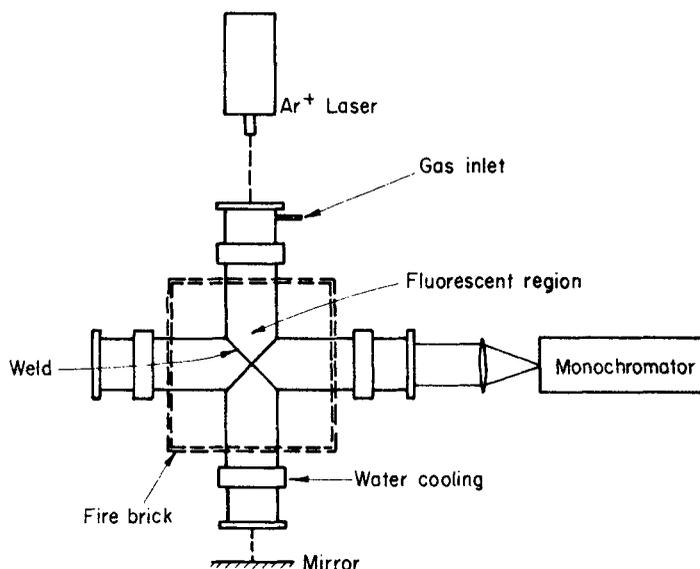
### 1. Introduction

Extensive studies have been made of the excitation energy transfer in alkali dimers induced by collisions with other atoms. The energy transfer could be within the rovibrational manifold of the same electronic state (Bergmann and Demtroeder 1974; Bruner *et al* 1979; Ottinger and Schroeder 1980) or to a neighbouring electronic state (Kraulinya *et al* 1976; Lam *et al* 1978; Ennen and Ottinger 1982; Arrowsmith *et al* 1983). If the excitation of molecules is close to the dissociation continuum, the colliding atom could very efficiently dissociate the molecule (Ennen and Ottinger 1979a, b). The cross-sections for all these processes could be quite significant. Ottinger and Schroeder (1980) found that only 5 torr of argon can cause extensive rotational mixing in the  $A^1\Sigma_u^+$  state of  $\text{Li}_2$ . Similar results were obtained for the  $B^1\pi_u$  state of  $\text{Na}_2$  wherein Bruner *et al* (1979) reported changes in rotational quantum number of the order of  $\Delta J \approx 30$  using 10 torr of Xe as the buffer gas. In the examples cited above rotational mixing occurs in the rovibrational levels of the electronic state which is directly pumped by the laser radiation. There are instances where alkali dimers after having been pumped to a given electronic state collisionally transfer their energy, and one observes a broad emission from an electronic state other than the pumped one. Among examples of this kind, is the work by Ennen and Ottinger (1982) who observed the broad  $B$ - $X$  and  $A$ - $X$  emissions in  $\text{Li}_2$  after exciting it to its  $C$  and  $B$  states respectively. Similarly Huennekens *et al* (1984) obtained the  $A$ - $X$  emission in  $\text{Na}_2$  and  $\text{K}_2$  after laser excitation to their respective  $B$  states. Their study has resulted in the observations of the lowest triplet transitions in  $\text{Na}_2$  and  $\text{K}_2$ . In a recent work on  $\text{Na}_2$ , Astill *et al* (1986)

observed a quasi-continuous emission in  $\text{Na}_2$  due to the  $A^1\Sigma_u^+ - X^1\Sigma_g^+$  transition following the laser excitation of the  $B^1\pi_u$  state. This process involves the  $B^1\pi_u \rightarrow (2)^1\Sigma_g^+$  excitation energy transfer as shown by Hussein *et al* (1985). In the present work we submit the results obtained from the reinvestigation of studies made by Astill *et al* (1986). Good signal-to-noise ratio in our experiments enabled us to uniquely identify the vibrational levels involved in the transitions which significantly differ from those reported by Astill *et al* (1986). We have simulated the observed spectrum in support of our identification.

## 2. Experimental

A schematic of the experimental set-up used is shown in figure 1. The sodium vapour is contained in a stainless steel crossed heat pipe oven. Each arm of the heat pipe is about 20 cm in length and 2 cm in diameter. The end of each arm is covered with a glass window for passing the laser beam and to observe the fluorescence. The heat pipe is heated in the middle with cartridge heaters and temperatures up to 1000 K can be easily obtained. The temperature was measured using a chromel-alumel thermocouple and was kept constant within  $\pm 2$  K. Argon buffer gas is used to prevent the sodium vapour from migrating to the glass windows. The ends of the arms of the heat pipe have water jackets to keep the glass windows cold. The pressure of the gas inside the heat pipe is measured with a Bourdon gauge that has been precalibrated with a mercury manometer. Argon pressure between 10 and 120 torr was used in the experiment. Various lines of an argon ion laser (Spectra Physics model 164) are used to excite  $\text{Na}_2$  molecules to the  $B^1\pi_u$  state. Fluorescence was monitored in a direction perpendicular to the laser beam using 0.5 meter monochromator (Mckee Pedersen Instruments Co.)

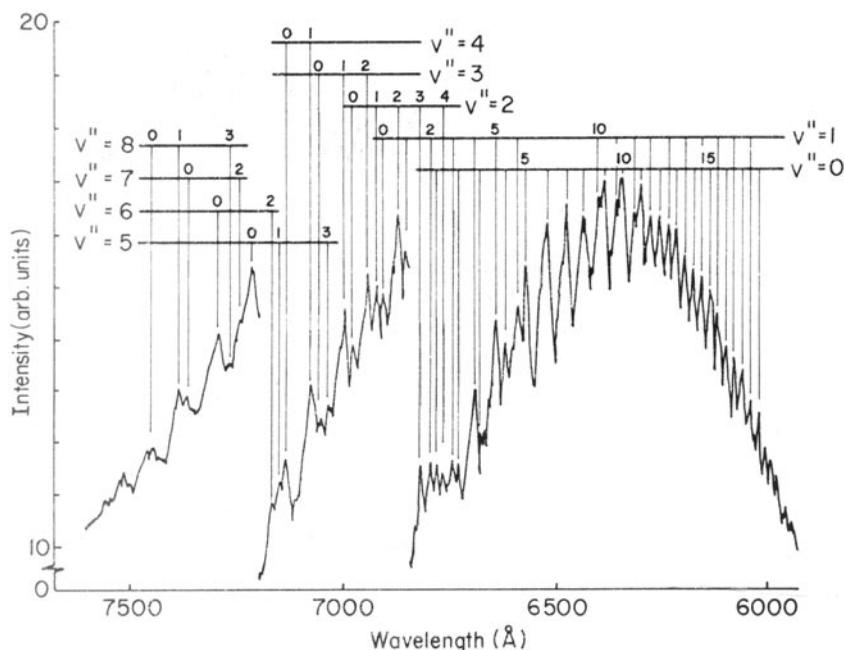


**Figure 1.** A schematic experimental set-up using a stainless steel heat pipe for containing the sodium vapour.

fitted with an uncooled photomultiplier tube (EMI 9558 QB). Neon lines from an electrodeless discharge tube were used for wavelength calibration.

### 3. Results and discussion

Fluorescence in sodium vapour is observed when excited by 5145 Å, 4965 Å, 4880 Å, 4765 Å and 4579 Å lines of an argon ion laser. All these lines excite  $\text{Na}_2$  molecules to the  $B^1\pi_u$  state (Kusch and Hessel 1978). In addition to the usual  $B$ - $X$  fluorescence of  $\text{Na}_2$ , a structured emission between 6000 Å and 7500 Å was observed. The rapidly deteriorating response of our photomultiplier tube prevented us from recording the spectrum on the longer wavelength side of 7500 Å. Figure 2 shows a typical chart recorder trace of  $A$ - $X$  emission using 4880 Å laser line. The coarse features of this emission are in complete agreement with the observation of Astill *et al* (1986) who identified it as the  $A^1\Sigma_u^+ - X^1\Sigma_g^+$  emission. However the better signal-to-noise ratio in our measurements has made it possible to identify each of the peaks in this highly structured emission. The identification is also shown in figure 2. On the basis of a computer simulation, Astill *et al* (1986) argued that the emission could be best explained by a very broad Gaussian population distribution function of the form  $(\alpha/\pi)^{1/2} \exp(-\alpha(v-v_0)^2)$  where  $v_0$  is the central vibrational level of the  $A$  state and  $\alpha = 1/750$ .  $v_0$  was assumed to be between 44 and 54 for the best fit with the experimentally observed  $A$ - $X$  emission. This does not agree with our observation. From individual identification of each of the  $A$ - $X$  bands we find that most of the observed emission could be explained by a few low-lying



**Figure 2.**  $A$ - $X$  emission in  $\text{Na}_2$  using 4880 Å laser line excitation. The running index on the horizontal lines represents the vibrational quantum in the  $A$  state.

vibrational levels in the  $A^1\Sigma_u^+$  as shown in figure 2. The spectrum in figure 2 was recorded for a cell temperature of 850 K, 60 torr buffer gas pressure and a low monochromator resolution of  $10\text{ cm}^{-1}$  HWHM. Under identical experimental conditions 5145 Å, 4765 Å and 4965 Å give the same  $A$ - $X$  emission. The envelope of the emission varies somewhat for different laser lines but every peak in the structure of this emission is identically reproduced. In contrast to the observation made by Astill *et al* (1986), the 4579 Å incident light does not produce the above mentioned  $A$ - $X$  emission. Figure 3 shows the emission obtained by using 5145 Å and 4579 Å laser lines. While the emission produced by 5145 Å laser line is identical in structure to that produced by 4880 Å line (figure 2), that produced by 4579 Å is completely different. In fact the emission due to 4579 Å laser line is just the pressure broadened wing of the Na D line. This has been shown to be due to the formation of NaAr Van der Waals molecule (York *et al* 1975).

As discussed by Astill *et al* (1986), the most likely mechanism for populating the  $A^1\Sigma_u^+$  is by collisional transfer of  $B^1\pi_u$  state population to the  $(2)^1\Sigma_g^+$  followed by radiative decay to the  $A^1\Sigma_u^+$  state. Hussein *et al* (1985) studied the  $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$  fluorescence following a very efficient  $B^1\pi_u \rightarrow (2)^1\Sigma_g^+$  collisional transfer. The mechanism for this excitation transfer could be represented by the equation

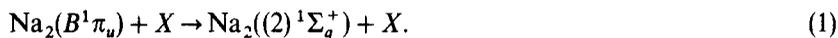
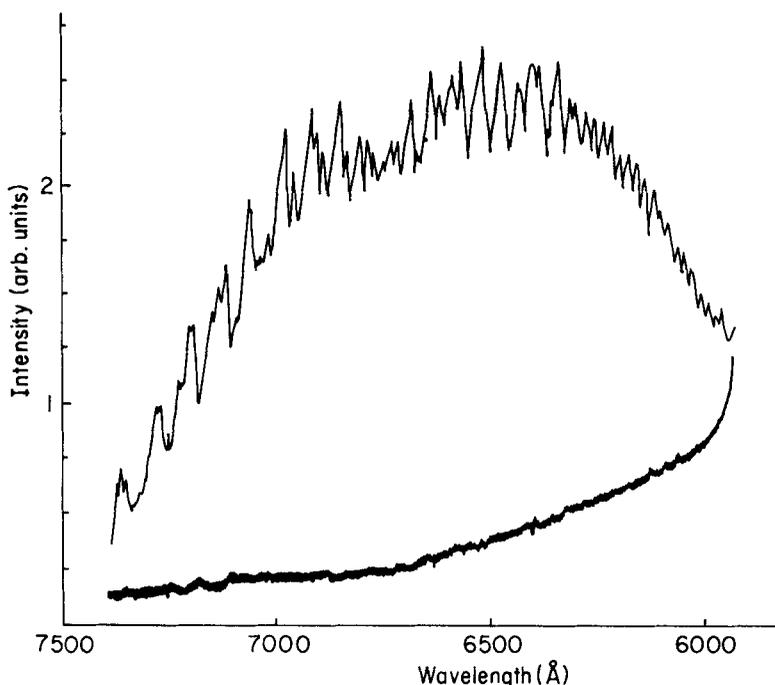
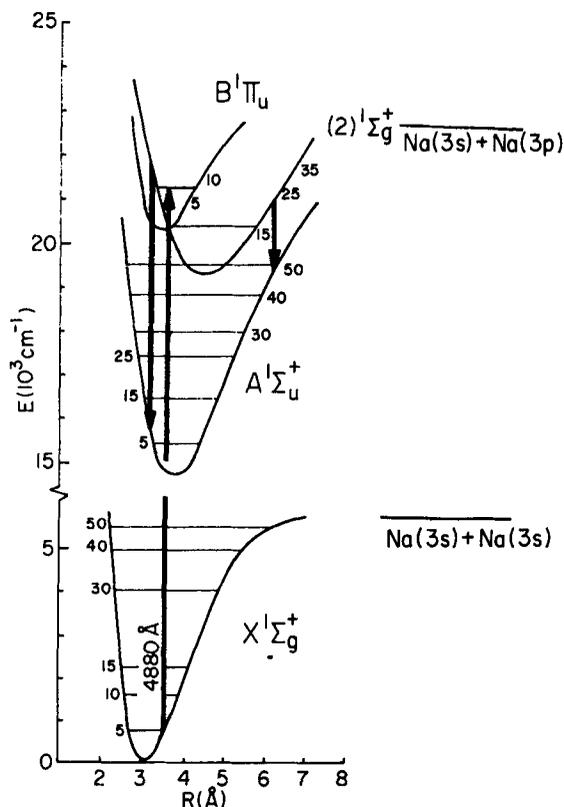


Figure 4 shows the relevant potential energy curves of  $\text{Na}_2$  to understand this.

In an earlier work, Astill *et al* (1986) had argued  $X$  to be Na atom in 3S state. Hussein *et al* (1985) in their theoretical treatment of  $B^1\pi_u \rightarrow (2)^1\Sigma_g^+$  collisional transfer assumed



**Figure 3.**  $A$ - $X$  emission in  $\text{Na}_2$  using 5145 Å (upper trace) and 4579 Å (lower trace) laser line excitations.



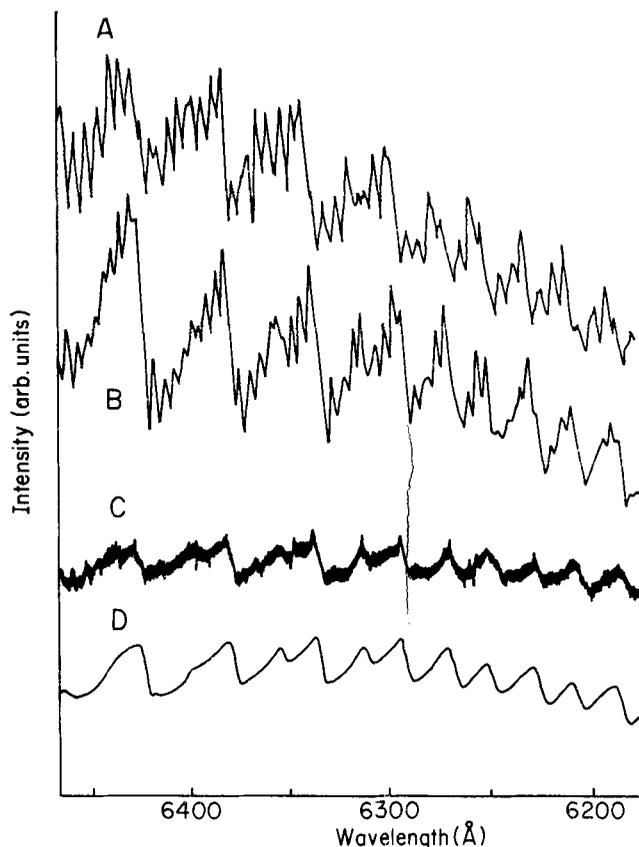
**Figure 4.** Some low lying potential energy curves of Na<sub>2</sub> molecule, used for explaining the collision induced A-X emission.

X to be an Na atom in the 3P state. However, no experimental justification for this was given. In our recently concluded experimental study we have shown that X is to be identified with Ar atom. These results will be published elsewhere. In this paper we confine ourselves to some hitherto unexplained characteristics of the collisionally induced A-X emission as mentioned earlier in the introduction.

It is observed that under low resolution (HWHM = 10 cm<sup>-1</sup>) the structure in A-X emission is identical for 5145 Å, 4965 Å, 4880 Å and 4765 Å laser line excitation. To explain this we observe that all these laser lines populate the same energy region in the B<sup>1</sup>π<sub>u</sub> state (1000–2000 cm<sup>-1</sup> above v = 0) (Kusch and Hessel 1978). The B<sup>1</sup>π<sub>u</sub> state population induced by these four laser lines is further equalized because of extensive rotational mixing induced by collisions with argon atoms. As mentioned earlier (Bruner *et al* 1979) a buffer gas pressure of only 10 torr causes ΔJ to change by as much as 30. In our experiments we have used an argon pressure of around 60 torr for most runs. The 4579 Å laser line behaves differently in that it populates B<sup>1</sup>π<sub>u</sub> within 200 cm<sup>-1</sup> of the dissociation limit (Kusch and Hessel 1978). The presence of argon at a pressure of 10–80 torr can very efficiently dissociate these molecules excited by 4579 Å line (Ennen and Ottinger 1979a, b).

Collisionally-induced dissociation cross-section varies as exp(-ΔE/kT), ΔE being the energy difference of a given rovibrational level as measured from the dissociation

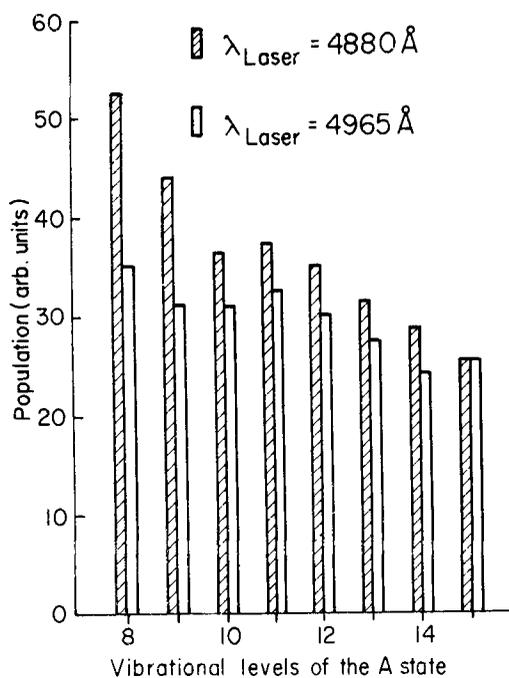
limit.  $\Delta E$  is about  $200 \text{ cm}^{-1}$  for  $4579 \text{ \AA}$  laser line induced  $B^1\pi_u$  state population as compared to  $\sim 1500 \text{ cm}^{-1}$  for  $B^1\pi_u$  levels populated by other four laser lines used. Under somewhat higher resolution ( $\text{HWHM} = 5 \text{ cm}^{-1}$ ), the  $A-X$  emission induced by  $4965 \text{ \AA}$  and  $4765 \text{ \AA}$  remains almost the same as at lower resolution. However,  $A-X$  emission induced by  $4880 \text{ \AA}$  or  $5145 \text{ \AA}$  laser lines shows further rotational structure within each of the assigned bands. This can be seen in runs *A* and *C* in figure 5 in which the  $A-X$  emission due to  $4880 \text{ \AA}$  line shows up the structure whereas that due to  $4965 \text{ \AA}$  line does not. This can be explained with the help of table 1. As can be seen both  $4880 \text{ \AA}$  and  $5145 \text{ \AA}$  laser lines excite mainly those levels that have odd values for the rotational quantum number  $J$  in the ground state  $X^1\Sigma_g^+$ . These correspond to the electronic wavefunction which is antisymmetric with respect to the exchange of the two Na nuclei. Collisions do not change this symmetry (Herzberg 1950) and so the  $\text{Na}_2$  molecules end up with odd  $J$  in  $(2)^1\Sigma_g^+$  state after  $B^1\pi_u \rightarrow (2)^1\Sigma_g^+$  collisional transfer. Only  $P$  and  $R$  radiative transitions are allowed in the  $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$  decay. Thus only even  $J$  levels are populated in the  $A^1\Sigma_u^+$  state. Experimentally, we find that excitation by either  $5145 \text{ \AA}$  or  $4880 \text{ \AA}$  laser line produces precisely the same structure in the  $A-X$  as shown in figure 5a. In their analysis of  $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$  transition Hussein *et al* (1985) also



**Figure 5.**  $A-X$  emission in  $\text{Na}_2$  using  $4880 \text{ \AA}$  (trace A) and  $4965 \text{ \AA}$  (trace C) laser line excitation. Traces B and D represent the computer simulations for A and C respectively.

**Table 1.** Some of the strongest transitions induced by various lines of an argon ion laser (Kusch and Hessel 1978).

Exciting line (Å)	Excited transition			
	<i>v'</i>	<i>v''</i>	<i>J'</i>	<i>J''</i>
5145	9	12	64	65
	11	14	49	49
	0	2	152	151
	13	15	74	73
4965	7	6	43	44
	8	7	28	29
4880	6	3	43	43
	10	6	42	41
	9	5	56	55
	3	0	75	75
4765	6	0	27	28
	10	3	12	13
4579	27	7	31	31
	28	7	43	43
	29	8	25	24



**Figure 6.** Assumed population distribution in A state vibrational levels for simulation of A-X emission excited by 4880 Å and 4965 Å laser lines.

noticed that excitation by 4880 Å populates only odd  $J$  levels in the  $(2)^1\Sigma_g^+$  state. Figure 5b is a simulation of a small part of the  $A$ - $X$  emission excited by 4880 Å laser line. For this, we have used the equation of Herzberg (1950) for the intensity,

$$I_{v'v''} = \frac{64}{3} \pi^4 c v^4 \omega_{J'} S_{J'J''} R^2 N_v |\langle v'|v'' \rangle|^2, \quad (2)$$

where  $N_v$  is the population of the  $v'$  level of the excited state,  $\langle v'|v'' \rangle$  is the Frank-Condon (FC) overlap integral,  $\omega_{J'}$  accounts for the nuclear spin statistics and  $S_{J'J''}$  is the Honl-London factor. The assumed population distribution of the  $A$  state vibrational levels which contributes to this part of  $A$ - $X$  emission is shown in figure 6. Only even  $J$  values ( $J = 0, 2, 4, \dots, 70$ ) in  $A^1\Sigma_u^+$  have been considered and a Boltzmann distribution assumed over them. In simulation the FC factors were calculated using a computer program and were assumed to be rotationally independent. These factors were checked against those of Zemke *et al* (1981) and were found to be in good agreement. The Honl-London factors were obtained from the usual formulae (Herzberg 1950). It was seen that increasing the range of  $J$  does not drastically change the simulated spectrum. The range of  $J$  assumed is reasonable because under Boltzmann distribution in the  $A^1\Sigma_u^+$  state, the maximum population at 800 K corresponds to  $J \approx 45$ . This assumption has obvious limitations. It is questionable if within the relatively short lifetimes of all the electronic states involved, the molecules have time to reach a distribution which is truly Boltzmann. Nevertheless the simulated spectrum (figure 5b) shows close resemblance to the observed one (figure 5a) even in finer details. Figure 5c shows a small part of the observed  $A$ - $X$  emission obtained with 4965 Å incident light. As seen in table 1 both even as well as odd  $J$  levels in  $X^1\Sigma_g^+$  are involved in pumping the  $X$ - $B$  laser induced transition. Invoking earlier arguments it is clear that both even and odd  $J$  levels are populated in the  $A^1\Sigma_u^+$  state. Thus to simulate the spectrum in figure 5c we assume a Boltzmann distribution in all  $J$  between 0 and 70. Figure 6 shows the assumed population distribution in those vibrational levels of the  $A^1\Sigma_u^+$  which contribute most to this part of  $A$ - $X$  emission. Clearly, the agreement between observed emission (figure 5c) and the simulated emission (figure 5d) is very good.

In conclusion, we have been able to clearly identify the various  $v'$ - $v''$  transitions involved in the  $A$ - $X$  emission of  $\text{Na}_2$  resulting under high argon pressure when excited by various argon ion laser lines. We have been able to explain the shape of this emission under high resolution when excited by 4880 Å and 5145 Å lines and how it differs from the emission obtained by either 4765 Å or 4965 Å laser lines. Finally, we have also explained why the 4579 Å laser line does not produce the highly structured  $A$ - $X$  emission as for other laser lines. Further work is being carried out towards identifying similar excitation transfer processes in other alkali systems.

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