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**THEORETICAL STUDIES OF SOLAR-PUMPED LASERS**

By

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# THEORETICAL STUDIES OF SOLAR PUMPED LASERS

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Wynford L. Harries\*

## SUMMARY

The investigation of stimulated emission causing transitions from the  $B^1\Pi_u$  electronic state of sodium to the overlapping  $2^1\Sigma_g^+$  electronic state has been continued. A new method of estimating the Franck-Condon factors has been developed which instead of fitting the molecular potential curves with Morse functions, estimates the  $V(r)$  dependence by interpolation from given potential curves. The results for the sum of the rates from one vibrational level in the upper state to all the levels in the lower state show good agreement with the previous method implying that "curve crossing" by stimulated emission due to photons from the oven is an important mechanism in sodium.

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## 1. INTRODUCTION AND PURPOSE

The experimental results at NASA Langley indicate that absorption of the 488 nm Argon ion laser light in sodium occurred from the transition  $X(v=0) \rightarrow B(v=6)$  (path #1, Fig. 1). The increased fluorescence occurred at wavelengths of 730 nm or greater, and the emission could only have come from the transition  $A \rightarrow X$  (path #4, Fig. 1). The dotted path #5 from  $B^1\Pi_u$  to  $A^1\Sigma_u^+$  is forbidden ( $u \rightarrow u$ ). However, the pathways  $B^1\Pi_u \rightarrow 2^1\Sigma_g^+$ , and subsequent path  $2^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$  are allowed. The question arises of the mechanism and rate of transfer for these last two transitions, especially the transition for "curve-crossing",  $B^1\Pi_u \rightarrow 2^1\Sigma_g^+$ .

The effect of particle collisions on the transfer rates is first considered. No buffer gas was used in the experiments with sodium.

At 450°C (723k) the total vapor pressure was estimated at about 1.31 torr, with the pressure of atomic Na about 1.24 torr, and of molecular  $Na_2$  about 0.073 torr; thus  $Na_2/Na = 0.06$ . The calculated collision time of Na,  $Na_2$  with an excited  $Na_2^*$  was  $4 \times 10^{-8}$ s, and the collision time of excited  $Na_2^*$  with  $Na_2^*$  was about  $7 \times 10^{-7}$ s. Both times are longer than the spontaneous emission time from the B level of  $7 \times 10^{-9}$  sec, to the ground X state and therefore collisions can be neglected.

It is suggested that the transition between the two overlapping states  $B^1\Pi_u$  and  $2^1\Sigma_g^+$ , and the transition  $2^1\Sigma_g^+ \rightarrow A^1\Pi_u$  are due to stimulated emission from radiation due to the oven at 450°C (723k). The energy differences between the levels  $v_1 = 6$  in the B state, and  $v_2 = 0$  to 20 in the  $2^1\Sigma_g^+$  state correspond to  $\approx 0.3$ eV and require photons of wavelength  $\approx 4 \mu m$ . The Wien displacement law,  $\lambda_{max} T = 2898 (\mu m.K)$  indicates that the wavelength  $\lambda_{max}$  at

peak radiation intensity was indeed  $\approx 4\mu\text{m}$  at 723 k. The  $\Sigma \rightarrow A$  transition is around 0.5 eV corresponding to radiation  $\approx 2\mu$  where there is still ample energy.

The transitions  $B - 2^1\Sigma$ , and  $2^1\Sigma - A$  would predominate only if the stimulated emission rates were far higher than the spontaneous emission rates  $B - X$ , and  $2^1\Sigma - X$  respectively. We shall first estimate the ratio R of the stimulated emission rate  $W(B \rightarrow 2^1\Sigma)$  with the spontaneous emission rate  $(B \rightarrow X)$ .

## 2. TRANSITION RATES

As is well known, the rate of stimulated emission  $W = \rho B$ , where  $\rho$  is the energy density of the black body radiation and B is the Einstein coefficient. The value of  $\rho$  was obtained from Planck's radiation formula and depended on the wavelength  $\lambda_{v_1, v_2}$  determined by the transition from level  $v_1$  to level  $v_2$  and the absorption bandwidth. The latter was obtained by assuming absorption occurred over of order 100 rotational lines, so  $\Delta\lambda$  was 100 times the Doppler bandwidth of one line. Pressure broadening was negligible under the conditions here.

The Einstein coefficient B is given by Ref. 1:

$$B = \pi |\mu_{1, v_1, v_2}|^2 / 3 \epsilon_0 \hbar^2 \quad (1)$$

where  $|\mu_{1, v_1, v_2}|$  is the matrix element for the electron dipole moment for the transition  $B \rightarrow 2^1\Sigma$ , from level  $v_1$  to level  $v_2$ ,  $\epsilon_0$  is the dielectric constant for free space, and  $\hbar$  is Planck's constant/2 $\pi$ .

The matrix elements are of the form  $|\mu| = e \int \psi_1 r \psi_2^* dr$  where  $\psi_1, \psi_2$  are the wavefunctions of the two respective states, e is electronic charge,

and  $r$  the length of the dipole. Assuming the transition is instantaneous, we take  $r$  as a constant and take it outside the integral. Then  $|\mu|$  can be expressed as

$$|\mu_{1,v_1,v_2}| = e r F_{1,v_1,v_2} \quad (2)$$

where  $F_{1,v_1,v_2}$  is the Franck-Condon factor for the transition  $v_1 v_2$ . In the experiments the Argon ion laser pumped the molecules from the ground (state) to the  $v_1 = 6$  level in the B electronic state.

The rate of transitions from the  $v_1 = 6$  to a level  $v_2$  in the  $2^1\Sigma_q^+$  state is then

$$W_{v_1 v_2} = \pi (er)^2 \rho(\lambda_{v_1 v_2}, T) F_{1,v_1,v_2}^2 / 3\epsilon_0 \hbar^2; \quad v_1 = 6 \quad (3)$$

and the total rate of all transitions from  $v_1 = 6$  to all the levels in the  $2^1\Sigma_g^+$  state below  $v_1$  in energy (corresponding to an upper value of  $v_2 = v_n$ ) is then

$$W = \sum_{v_2=0}^{v_n} W_{v_1,v_2}; \quad v_1 = 6 \quad (4)$$

The level corresponding to  $v_n$  in the  $2^1\Sigma$  state must lie below the  $v = 6$  level for the B state, for stimulated emission, and its value is

$$v_n = 24.$$

### 3. PRELIMINARY COMPARISON OF STIMULATED TO SPONTANEOUS RATES

Next, we consider spontaneous emission,  $B \rightarrow X$  with a rate coefficient  $A$  given by (Ref. 1):

$$A = \frac{8\pi^2}{3 h \epsilon_0} \left| \frac{\mu_{2, v_1, v_3}}{\lambda_a^3} \right|^2 ; v_1 = 6 \quad (5)$$

with the same nomenclature as Eq. (1);  $|\mu_2|$  is for the transition  $B \rightarrow X$  and  $\lambda_a$  the wavelength corresponding to the transition between the vibrational quantum states,  $B(v_1)$  to  $X(v_3)$ . However, the energy difference is about 2.6 eV, for  $v_1 = 6$  and  $\lambda_a \approx 0.5 \mu\text{m}$ , a value 10 times smaller than the peak wavelength for black body radiation. The spread in  $\lambda_a$  turns out to be small or of order  $\pm 0.03 \mu\text{m}$ , as transitions are only appreciable for  $0 < v_3 < 4$ , hence we neglect any spread in  $\lambda_a$  due to different values of  $v_3$  and take its value as  $0.5 \mu\text{m}$ .

Again, in the electronic transition,  $r$  is assumed constant, and is the same  $r$  as in Eq. (3). The total rate of spontaneous emission is then  
Ref. 1

$$A = \frac{8 \pi^2 (er)^2}{3 h \epsilon_0 \lambda_a^3} \sum_{v_3} F_{2, v_1, v_3}^2 ; v_1 = 6 - \quad (6)$$

where  $F_{2, v_1, v_3}$  is the Franck-Condon factor for the transition  $v_1, v_3$ .

Experimentally, the spontaneous lifetime of the B state is known to 7ns, so

$$A = 1.4 \times 10^8 \text{ s}^{-1}.$$

Equations (5) and (6) can be evaluated if  $r$  and the Franck-Condon

factors are known, but first it is instructive to take the ratio

$$R = W/A = \rho B/A:$$

$$R = \frac{\lambda_a^3}{4\pi} \frac{\sum \rho(\lambda_{v_1, v_2}, T) \cdot F_1^2 v_1 v_2}{\sum F_2^2 v_1 v_3} \quad (7)$$

Here, as both transitions started from the B state,  $r$  cancels. The Franck-Condon factors are finite for only specific values of  $\lambda_{v_1, v_2}$ . To get an order of magnitude for  $R$ , assume the contributions from the Franck-Condon factors in the numerator and denominator cancel, and define a quantity  $R' = \rho(\lambda_{v_1, v_2}, T) \lambda_a^3 / 4\pi$ . The quantity  $R'$  essentially reflects the contribution from the radiation density. Assuming  $\lambda_a = 0.5 \mu\text{m}$  and constant,  $R'$  is plotted as a continuous function of  $\lambda_{v_1, v_2}$ , for different temperatures in Fig. 2. It can be seen that for  $\lambda_{v_1, v_2} > 4 \mu\text{m}$  that  $R' \approx 10^6$ , but if  $\lambda_{v_1, v_2} \approx 0.5 \mu\text{m}$  then  $R' \ll 1$ , indicating that here  $R$  would be much less than 1. Hence stimulated emission should predominate at around  $5 \mu\text{m}$ , and not around  $0.5 \mu\text{m}$ .

#### 4. CALCULATION OF TRANSFER RATES

We next confirm this conclusion by evaluating the actual stimulated and spontaneous emission rates, based on estimations of the Franck-Condon factors. The basis of the method has been reported already (Ref. 2), but the detailed calculations were done in two different ways, the difference being

in how the initial constants were obtained from the given potential curves of Jeung (Ref. 3).

With the first method, Morse functions were fitted to the potential curves, and the values of  $\omega_e$ ,  $\omega_e x_e$  etc., taken from Ref. 4 for the  $B^1\Pi_u$  state and from Ref. 5 for the  $2^1\Sigma_g^+$  state except that the value of  $D_e$  was made larger (0.7 eV) to fit the curves of Jeung. With the second method, the potential curves were digitized using a computer interpolation technique, and all the required constants estimated from these numbers.

#### 4.1 Evaluating Franck-Condon Factors Using Morse Functions

Morse functions were fitted to the curves of Jeung (Ref. 3) at three points: the values were  $T_e$  at the equilibrium distance of  $r_i$  the internuclear distance, the value of  $V$  at  $r_i \rightarrow \infty$  which is  $T_e + D_e$ , where  $D_e$  is the dissociation energy, and the value of  $r_i$  corresponding to the level halfway between  $T_e$  and  $T_e + D_e$ . It can be seen the fit is approximate. The variations from the curves shown in Fig. 1 may predicate that the energy levels may be inaccurate by one or two vibrational levels, but nevertheless the overall results in calculating  $W$ , the sum of contributions from  $v = 6$  to all the levels below it were relatively insensitive ( $\pm 10\%$ ) to changes of 50% in  $D_e$  for example. The reason may be that an error in level  $v$  merely meant that the next  $v + 1$  level would give a compensatory contribution.

The wavefunctions were obtained from the one dimensional Schroedinger equation with potential  $V$  represented by a Morse function (Ref. 5). First asymptotic solutions were obtained for large values of  $r_i$ , the internuclear distance. The values of  $r_i$  were then reduced in small increments and iterative solutions of the wave functions obtained by Euler's method. The

value of  $\omega_e$  were taken from the literature but the anharmonicity constants  $\omega_e x_e$ , were calculated from  $\omega_e$  and  $D_e$ , the dissociation energy read from the curves:  $\omega_e x_e = \omega_e^2 / 4 D_e$  (Ref. 5). The second set of anharmonicity constants  $\omega_e y_e$  were taken as zero in all cases. Thus the calculations are approximate. The wave functions were well-behaved and crossed the axis the correct number of times up to the 50th level, although only 35 levels were used for each electronic state. The maximum values of the Franck-Condon factors occurred when the turn around points for the two electronic levels occurred at the same value of  $r_i$ . Checks on orthogonality showed that  $\int_0^{r_1} \psi_1 \psi_2^* dr$ ;  $r_1 = 8A^\circ$  were always within or less than a few tenths of a percent. The Franck-Condon factors  $\int_0^{r_1} \psi_n \psi_m dr$  (where  $\psi_n, \psi_m$  were normalized,) were then evaluated for all combinations of  $n, m$  from 0 to 35. The Franck-Condon factors ranged from  $\approx 0$  to  $\approx 0.2$  and agreed (for the B  $\rightarrow$  X transition) with Kusch and Hessel (Ref. 7). The vibrational sum rule, (Ref. 5) that the sum of the squares of the Franck-Condon factors summed over all values of the vibrational quantum numbers of both of the states should be equal to 1 showed values approaching 1 from the lower side, as expected when the quantum numbers for both levels were truncated at 35. Plots of the Franck-Condon factors plotted on a  $v_1 v_2$  plane, where  $v_1, v_2$  are the vibrational quantum numbers for both states, clearly showed a Condon parabola (Ref. 6).

#### 4.2 Evaluation of Franck-Condon Factors Using Interpolation

In an attempt to get values which fitted the potential curves more accurately, the second technique included digitizing eleven points on the curves and entering the values into a computer. An interpolation sequence then fitted a 10th order Lagrange polynomial to the curves. The fit could

be accomplished to approximately within the breadth of the line and thus  $V$  as a function of  $r$  was known. Also digitized were  $T_e$ ,  $D_e$  and the value of  $r_i$  at the minimum of the curve. The values of  $\omega_e$ ,  $\omega_e x_e$  and  $\omega_e y_e$  were first taken from Refs. 4 and 5, but the wavefunctions were not well behaved. Even for  $v = 6$  for the  $B^1\Pi_u$  curve the number of crossings of the wavefunction was incorrect, being only 5. The functions were also unstable for values of  $r_i$  to the left of the intersection of  $V$  and the vibration energy corresponding to  $v = 5$ .

Considerable improvement was obtained by not using the values of  $\omega_e$ ,  $\omega_e x_e$  and  $\omega_e y_e$  from Refs. 4 and 5, but instead estimating them from our digitized curves. The value of  $\omega_e$  corresponds to the frequency of a harmonic oscillator, whose potential curve would coincide with the anharmonic curves near the potential minimum. Hence if  $r_e$  is the radius for the potential minimum, then near  $r_e$  a parabolic relation would be obeyed.

$$V - T_e = \frac{1}{2} k (r_i - r_e)^2 \quad (8)$$

where  $k$  is the spring constant. So a plot of  $\pm\sqrt{V - T_e}$  vs  $(r - r_e)$  should be a straight line of slope  $\sqrt{k/2}$  near  $r_e$ . Such plots showed constant slope for a region  $\pm 1\text{\AA}$  from  $r_e$ , hence yielding  $k$ . The value of  $\omega_e$ , obtained knowing the effective mass for  $\text{Na}_2$ , showed differences of about 5% with those in Ref. 4. The values of  $\omega_e x_e$  were then calculated from  $\omega_e x_e = \omega_e^2/4De$  and differed at worse by a factor of about 2 for the  $2^1\Sigma_g^+$  level, from Ref. 5, and as before  $\omega_e y_e$  was assumed to be zero. In this case the wavefunctions crossed the zero line the correct number of times up to the 20th level, but the functions were still unstable to the left of the  $V$

curves at higher value of  $v$ . As soon as instability set in the computer clamped the value of the wavefunction to zero.

The Franck-Condon factors obtained from the two methods differed by large factors when comparing the transitions from  $v_1 = 6$  in the upper level to individual levels in the lower state. For some values of  $v_2$  the Morse curve results were larger, for others it was the reverse. The two sets of Franck-Condon factors were then used to calculate the stimulated emission rates, where again the answers were different for individual levels. However, when the rates were added for 21 lower levels, the differences averaged out and gave total transition rates, in good agreement as shown below.

### 4.3 Stimulated Emission Rates

The value of  $W$  was obtained using the value of  $B$  from Eq. (1) where  $\mu_1$  was taken as  $(er) F_{1, v_1, v_2}$  with  $F_1$  the value for  $B \rightarrow 2\frac{1}{g}$ :

$$W_{v_1 v_2} = \rho \frac{\pi e^2 r^2 F_{1, v_1, v_2}^2}{3 \epsilon_0 h^2} \quad (9)$$

The value of  $r$  was obtained from the known value of  $A$ , Eq. (5), where  $|\mu_2| = er F_2$ , and  $\lambda_a = 0.5\mu$ ; then  $r = 1.5A$ , a reasonable value, half the equilibrium internuclear distance.

A plot of  $W$  vs  $\lambda_{v_1 v_2}$ , the wavelength of the oven black-body radiation, is shown in Fig. 3, for values of  $v_1 = 5, 6, 7$ , using the Morse curve numbers and shows a series of "lines" occurring near  $\lambda = 5 \mu\text{m}$  with values  $\approx 10^{12} \text{ s}^{-1}$ . The addition of all the lines between 0 and 20  $\mu$  gave a total

rate of several times  $10^{12}$  for the stimulated emission rate  $B \rightarrow 1\gamma_g^+$ . The interpolation method gave individual values of  $W$ , ( $v_1 = 6$ ) for different  $v_2$  in qualitative agreement with Fig. 3, but, with individual values which showed differences of up to 5. However, when the rates for all the lines were added the net rates calculated by the two methods agreed within 20 percent. The spontaneous emission rate from  $B \rightarrow X$  is of order  $10^8$ , so the ratio  $R$  again approaches  $10^5$ .

Stimulated emission does not occur from  $B \rightarrow X$ . The 2 eV difference in the electronic levels calls for wavelengths of  $0.5 \mu\text{m}$  where the value of  $\rho$  is about six orders of magnitude smaller at  $T = 450^\circ\text{C}$ .

In a similar manner the stimulated and spontaneous emission rates were calculated for the various pathways shown in Fig. 1 and are shown in Table 1. It is evident that the stimulated emission rate  $B \rightarrow X$  far exceeds any stimulated or spontaneous rate  $B \rightarrow X$ . Likewise the stimulated emission rate  $2\gamma_g^+ \rightarrow A$  exceeds the spontaneous rate and also both stimulated and spontaneous  $2\gamma_q^+ \rightarrow X$ . For the  $A \rightarrow X$  transition the stimulated and spontaneous rates are comparable.

## 5. CONCLUSIONS

The model we have assumed in the calculations is approximate only. It may have inaccuracies in the value of  $r$  and also in the estimates of the energy levels and hence the actual values of the wavefunctions and Franck-Condon factors. Nevertheless, the insensitivity of our estimated total rates to variations in parameters such as  $D_e$ , and the differences of 5 orders of magnitude between the estimated stimulated and spontaneous emission rates (Table 1) suggest the pathways in Fig. 1 are valid. Moreover the suggested mechanism of stimulated emission due to the oven black body

radiation seems valid for transfer from electronic energy states which overlap, and for transfer in "curve crossing" in sodium.

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## REFERENCES

1. Svelto, O. "Principles of Lasers" 2nd Ed. Plenum Press N.Y. p43, etc.
2. Harries, W. L. "Theoretical Studies of Solar Pumped Lasers. Technical report PTR-81-9 for the period 15 Jan - 15 July 1981, under Research Grant NSG 1568.
3. Jeung, C. J. Phys. B: At Mol Phys V. 16 (1983) 4289-4297.
4. Huber, K. P. & Herzberg G. "Constants of Diatomic Molecules" Van Nostrand 1979, p. 432.
5. Effantin, C., d'Incan J., Ross A. J., Barrow R. F. and Verges J., J. Phys B: At Mol Phys V. 17 1515 (1984).
6. Herzberg, G. "Molecular Spectra and Molecular Structure I Spectra of Diatomic Molecules, Van Nostrand Reinhold (N.Y.) 1950.
7. Kusch P. and Hessel, M. M. J. Chem. Phys. 68(6), 2591 15 Mar. 1978.

TABLE 1

Transitions rates in Na<sub>2</sub> with initial and final vibrational levels, average energy difference  $\Delta$ (eV) and average wavelength of transition  $\bar{\lambda}$ .

Initial State	Transition	Upper vb level $v_1$	Final vb level $v_2$	$\Delta$ (eV)	$\bar{\lambda}$ ( $\mu\text{m}$ )	Max $W(\text{s}^{-1})$	Spont. $A(\text{s})^{-1}$
B	$B \rightarrow 2'\Sigma$	6	0-20	0.3	4	$8 \times 10^{12}$	$2 \times 10^5$
	$B \rightarrow A$	6	0-35		Forbidden		
	$B \rightarrow X$	6	0-35	2.5	0.5	$\approx 7 \times 10^2$	$1.4 \times 10^8$
$2'\Sigma_q^+$	$\Sigma \rightarrow A$	0-20	0-35	0.6	2	$2 \times 10^{13}$	$1.6 \times 10^6$
	$\Sigma \rightarrow X$	0-20	0-35	2.0	0.6	$\approx 1 \times 10^5$	$6 \times 10^7$
A	$A \rightarrow X$	0-35	0-35	1.7	0.7	$\approx 4 \times 10^7$	$3.7 \times 10^7$

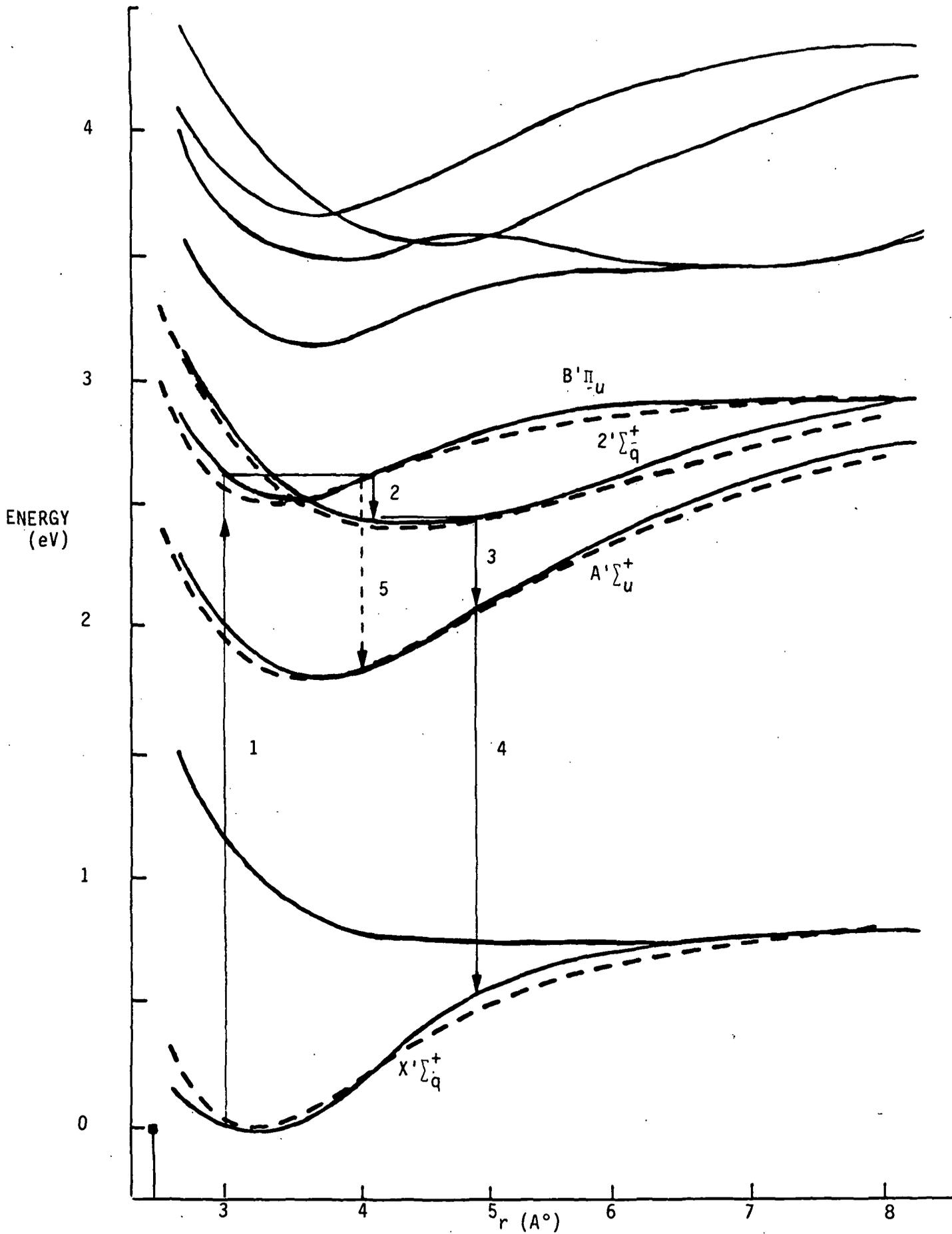


Figure 1. Energy level diagram for Na<sub>2</sub> according to Jeung (Ref. 3), with the transition pathways shown. The dotted curves are best fitted Morse functions.

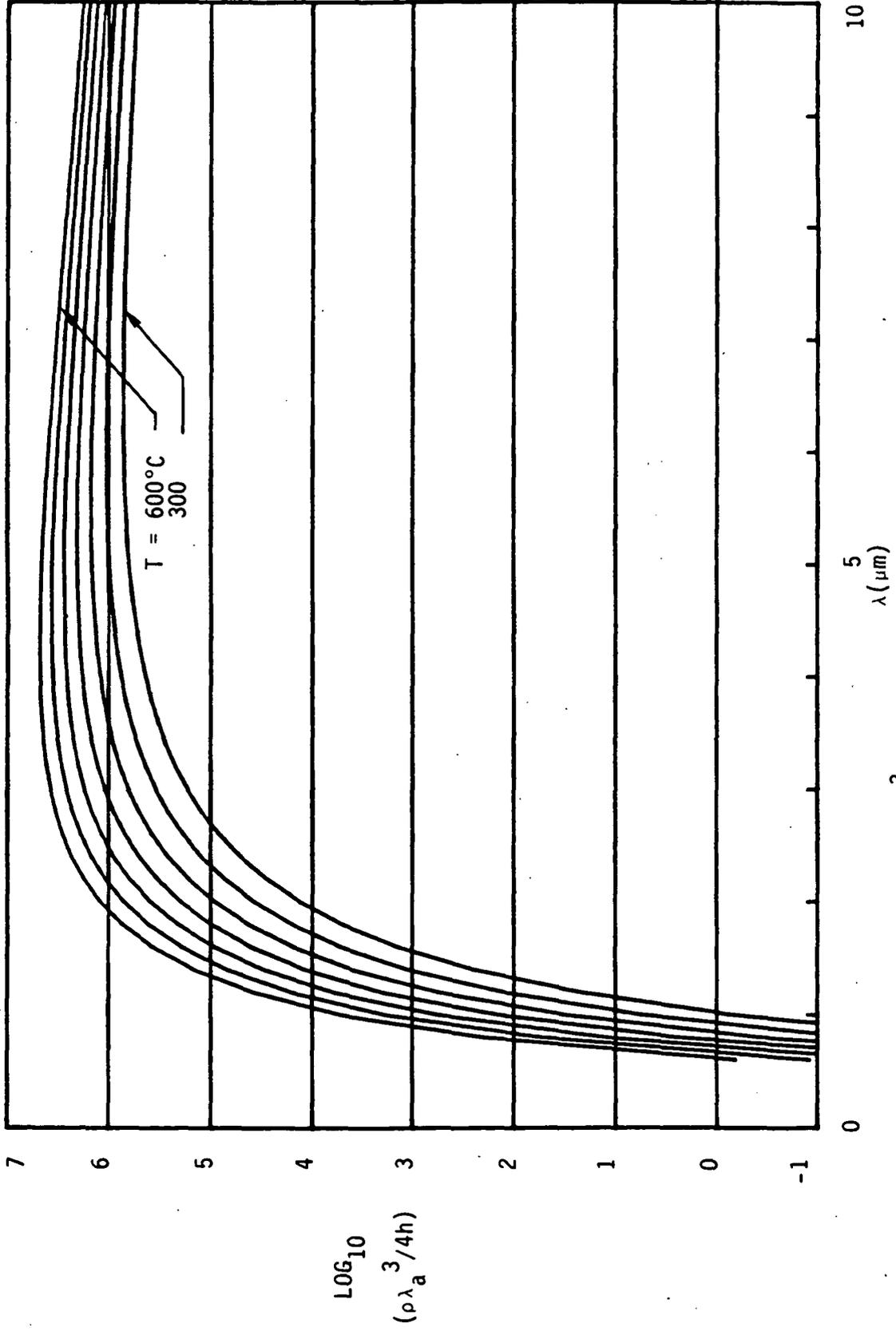


Figure 2. Plots of  $R' = \rho \lambda_a^3 / 4h$  vs  $\lambda_v, v_1, v_2$  for different oven temperatures  $T(^{\circ}\text{C})$ . The experiment was carried out at  $450^\circ\text{C}$  (723k).

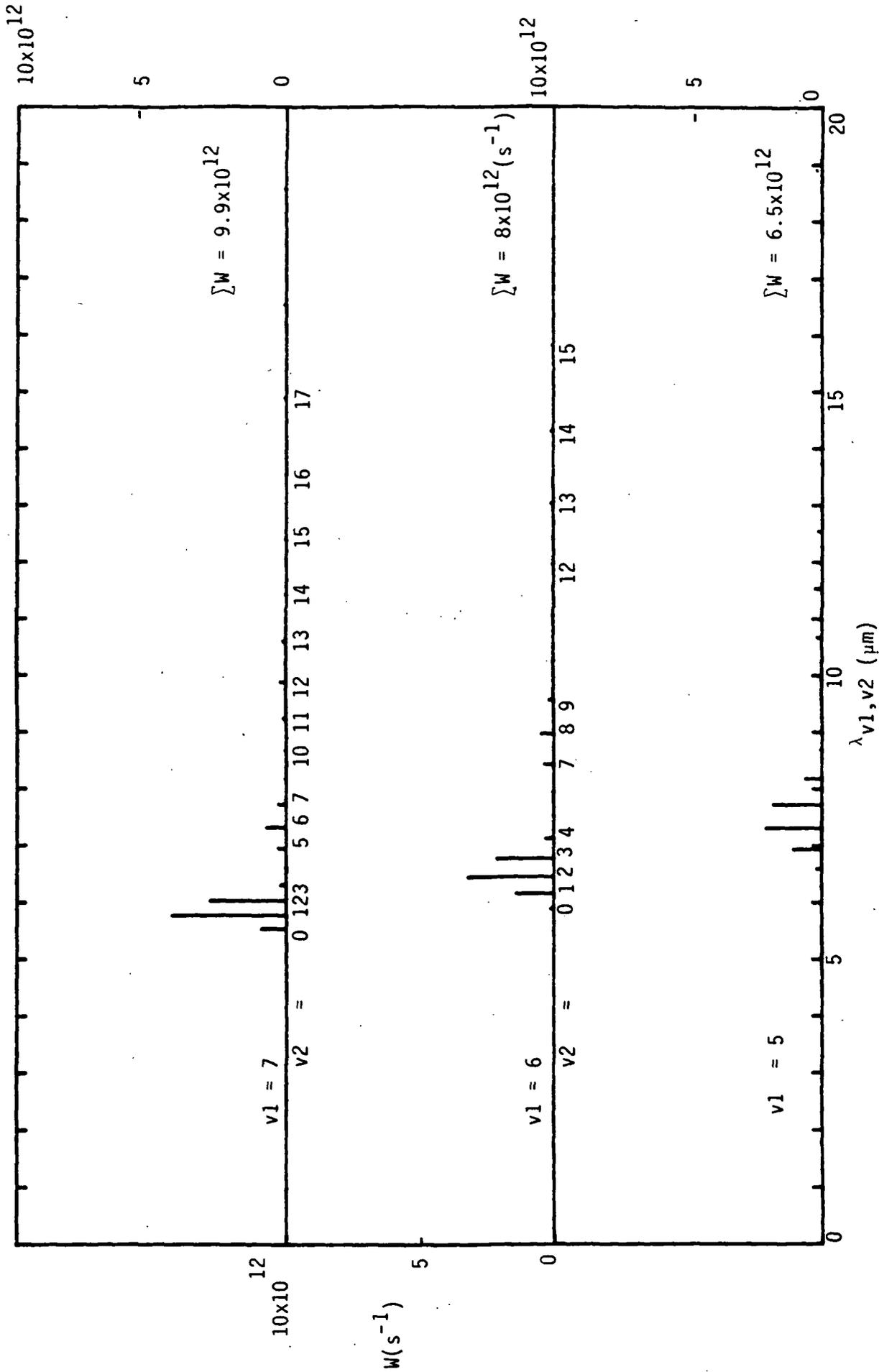


Figure 3. Plot of transition rates  $W$  from vibrational energy level  $v_1$  (5,6,7) in  $B^1\Pi_u$  state of  $Na_2$  to vibrational level  $v_2$  in the  $2^1\Sigma^+_g$  vs  $\lambda_{v_1, v_2}$ . The bandwidths ( $\approx 1.4 \times 10^{-3} \mu m$ ) are too narrow to be evident. Oven temperature 723k.