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DEPARTMENT OF PHYSICS
COLLEGE OF SCIENCES
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA 23529

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THEORETICAL STUDIES OF SOLAR-PUMPED LASERS

By

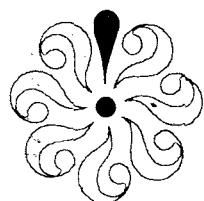
Wynford L. Harries, Principal Investigator

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Norfolk, Virginia 23508

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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.

*Eminent Professor, Department of Physics, Old Dominion University, Norfolk, Virginia 23529

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 4×10^{-8} s, and the collision time of excited Na_2^* with Na_2^* was about 7×10^{-7} s. Both times are longer than the spontaneous emission time from the B level of 7×10^{-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 ≈ 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 λ_{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 ρ is the energy density of the black body radiation and B is the Einstein coefficient. The value of ρ was obtained from Planck's radiation formula and depended on the wavelength λ_{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 , ϵ_0 is the dielectric constant for free space, and \hbar is Planck's constant/2 π .

The matrix elements are of the form $|\mu| = e \int \psi_1 r \psi_2^* dr$ where ψ_1, ψ_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 λ_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 λ_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 λ_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 λ_{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 λ_{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 ω_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 ω_e were taken from the literature but the anharmonicity constants $\omega_e x_e$, were calculated from ω_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 ψ_n, ψ_m were normalized,) were then evaluated for all combinations of n, m from 0 to 35. The Franck-Condon factors ranged from ≈ 0 to ≈ 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 ω_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 ω_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 ω_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 $\sqrt{V - T_e}$ 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 ω_e , obtained knowing the effective mass for Na_2 , showed differences of about 5% with those in Ref. 4. The values of $\omega_e x_e$ were then calculated from $\omega_e x_e = \omega_e^2 / 40e$ 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 μ_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 μ 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 ρ 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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TABLE 1

Transitions rates in Na₂ with initial and final vibrational levels, average energy difference Δ (eV) and average wavelength of transition $\bar{\lambda}$.

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

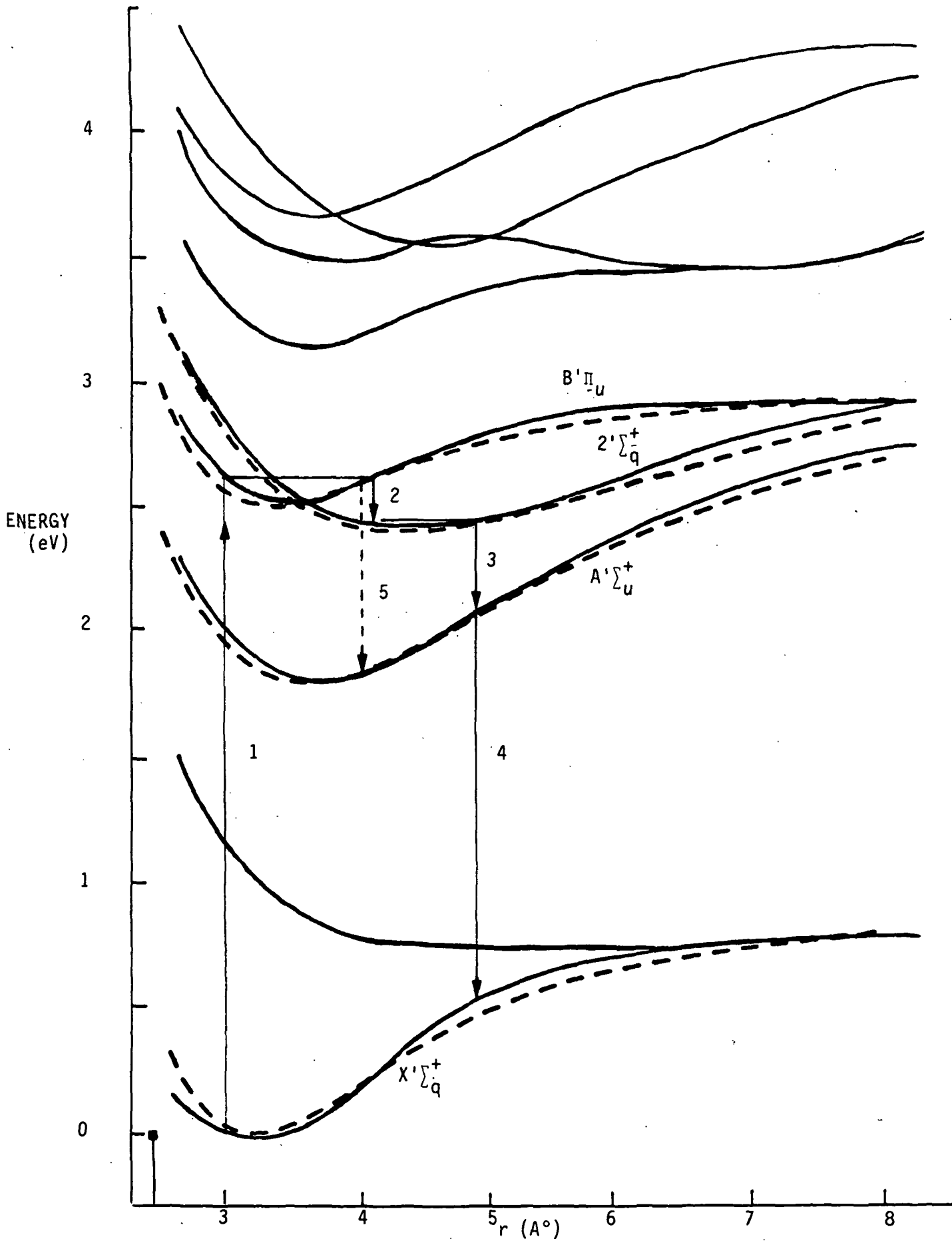


Figure 1. Energy level diagram for Na₂ according to Jeung (Ref. 3), with the transition pathways shown. The dotted curves are best fitted Morse functions.

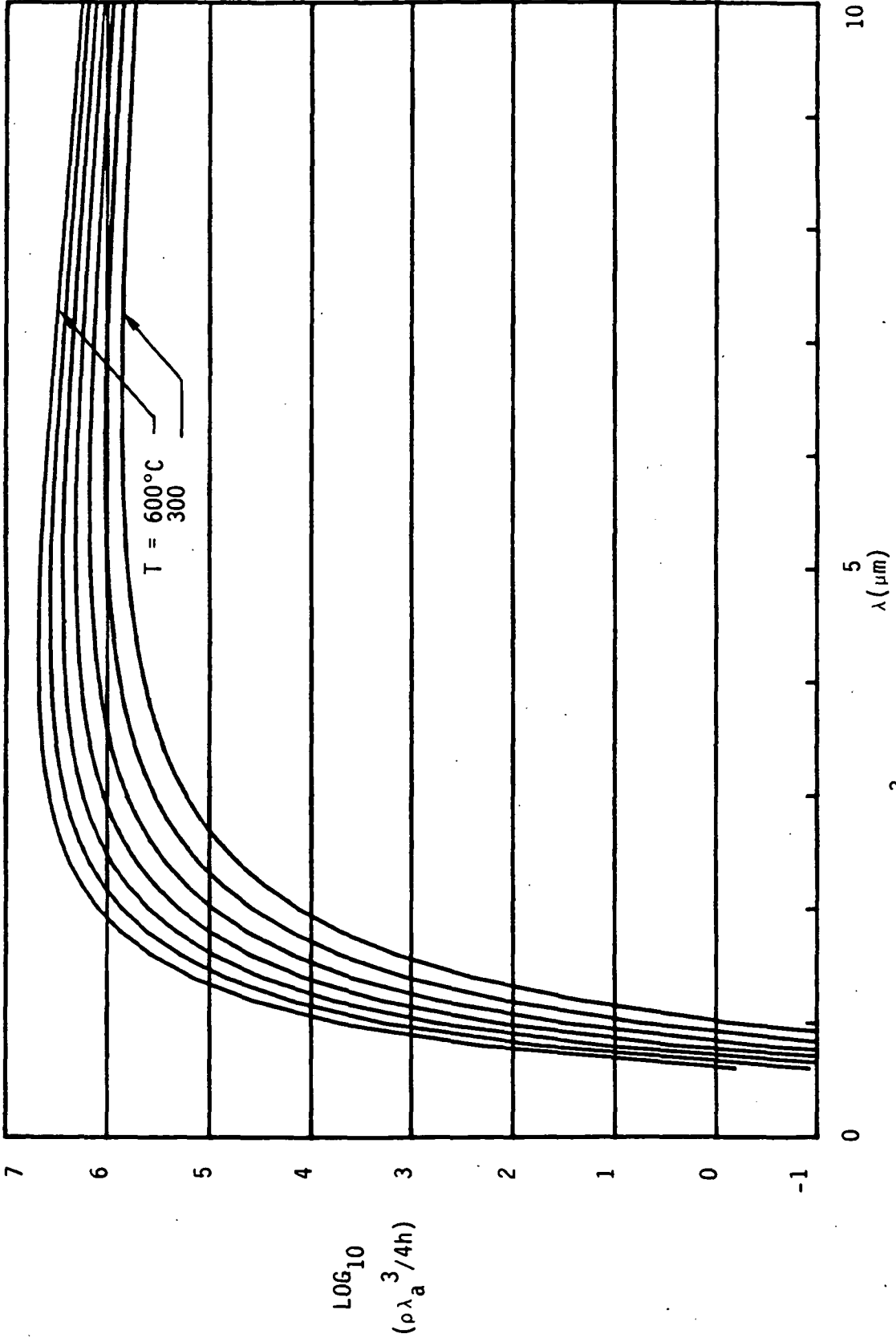


Figure 2. Plots of $R' = \rho \lambda_a^3 / 4h$ vs λ_v, v_1, v_2 for different oven temperatures $T(^{\circ}\text{C})$. The experiment was carried out at 450°C (723k).

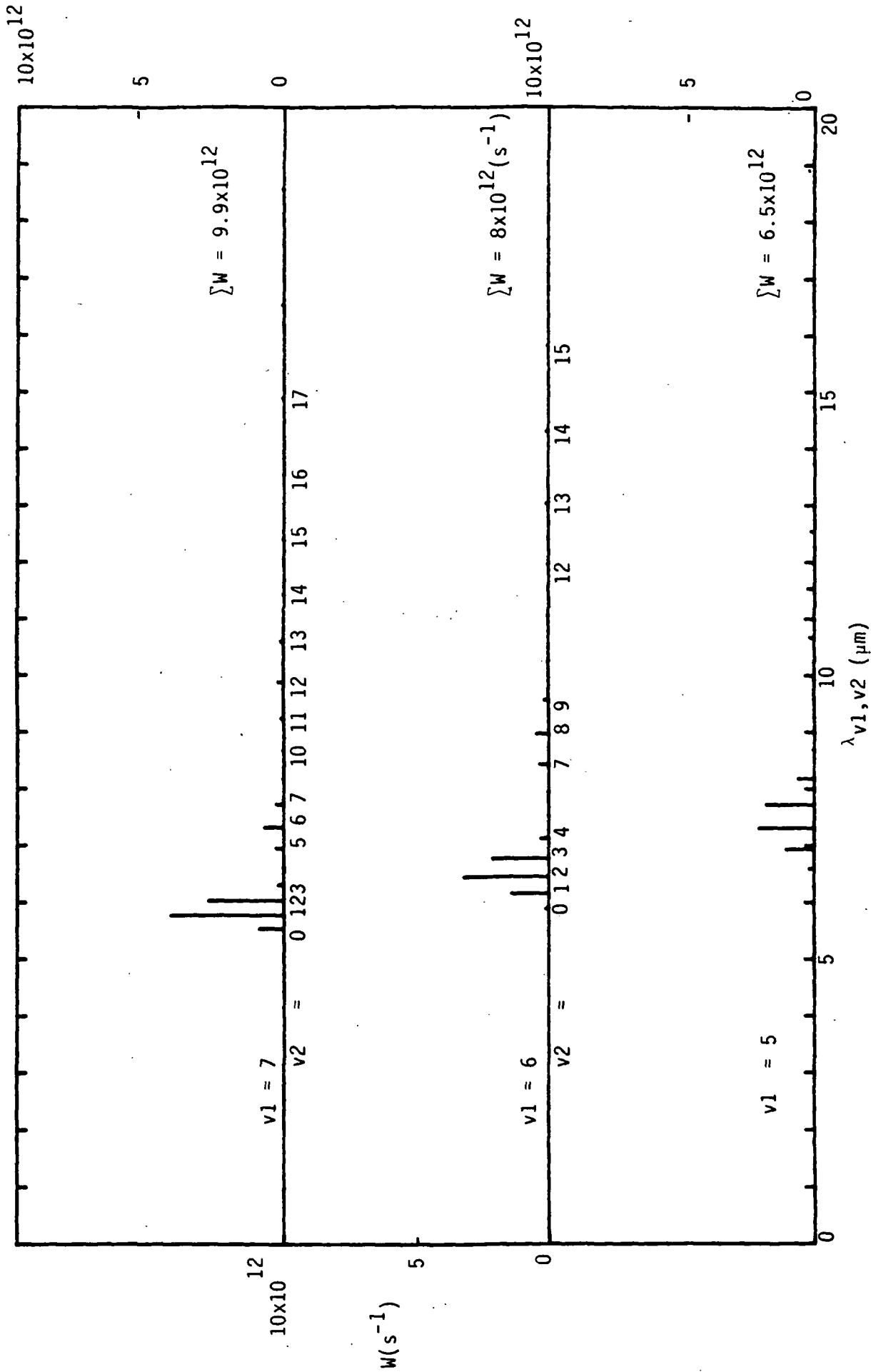


Figure 3. Plot of transition rates W from vibrational energy level v_1 (5,6,7) in $B^1\Pi_u$ state of Na_2 to vibrational level v_2 in the $2^1\Sigma^+_g$ vs λ_{v_1, v_2} . The bandwidths ($\approx 1.4 \times 10^{-3} \mu m$) are too narrow to be evident. Oven temperature 723k.