Molecular Constants of the $A^1\Sigma_u^+$ and $B^1\Pi_u$ States of Na_2

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The $A^1\Sigma_u^+ - X^1\Sigma_g^+$ and $B^1\Pi_u - X^1\Sigma_g^+$ systems of Na_2 were excited by Ar^+ and Kr^+ lasers ranging from 4762 to 6471 Å. High-resolution Fourier transform spectroscopy has been used to analyze the observed spectrum. The study led to the calculation of the molecular constants of the upper $A^1\Sigma_u^+$ and $B^1\Pi_u$ states.

Key words: Molecular Spectroscopy; Spectroscopic Constants; Potential Curves.

1. Introduction

Laser-induced fluorescence spectra of the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ and $B^1\Pi_u - X^1\Sigma_g^+$ systems of Na_2 were excited in the gas phase by Ar^+ laser lines at 4880 and 4765 Å and Kr^+ laser lines at 6471 and 4762 Å. The resulting spectra have been studied in [1 - 5] using high-resolution Fourier transform spectroscopy. In that study, 28 series of fluorescence have been analyzed and identified. The strongest series contain, in addition to the main $P(J+1)$ and $R(J-1)$ doublets, rotational relaxation lines covering a wide range. The observation of these lines provides important information about the upper states and also increases the data of the lower state.

This analysis led to the determination of the molecular constants of the ground state $X^1\Sigma_g^+$ with high precision comparable to that already available in [6]. From these constants, the Rydberg-Klein-Rees (RKR) potential curve of the $X^1\Sigma_u^+$ state was obtained for vibrational levels v up to the dissociation limit $(v = 62)$ [1, 2].

In the present paper, the molecular constants of the upper $A^1\Sigma_u^+$ and $B^1\Pi_u$ states are reported. This calculation completes the work by O. Babaky and K. Hussein [1]. Figure 1 shows the states involved in this work.

2. Calculation and Results

The experimental arrangement and the method of attribution of the analyzed series of fluorescence are as reported in [1, 7 – 9].

The molecular constants of the ground state $X^1\Sigma_g^+$ and the upper states $A^1\Sigma_u^+$ and $B^1\Pi_u$ have been determined by simultaneous least-squares fits applied to all measured lines of the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ and $B^1\Pi_u - X^1\Sigma_g^+$ systems, in which the ground state $X^1\Sigma_g^+$ term-values were represented by the polynomial

$$T_{vJ} = T_e + \omega\,(v + 1/2) - \omega_e\chi\,(v + 1/2)^2 + \ldots + [\beta_e - \alpha_e\,(v + 1/2) + \ldots]\,J(J+1). \tag{1}$$

This representation is well suited for the ground state $X^1\Sigma_g^+$ [1], since this state is not perturbed, and it gives a great deal of information covering the range for vibrational levels v up to $v = 45$. This corresponds to 1410 lines involving the transitions A – X and B – X. Figures 2 and 3 are parts of the spectra of the transitions $A^1\Sigma_u^+ - X^1\Sigma_g^+$ and $B^1\Pi_u - X^1\Sigma_g^+$, respectively.

For the upper states $A^1\Sigma_u^+$ and $B^1\Pi_u$ there were relatively few vibrational levels involved in the transitions. For this reason, these states were represented by a model level by level. In this model, the term-value of each vibrational level v of these states was represented by

$$T_v = T_e + B_v(J+1)J - D_v(J+1)^2J^2 + H_v(J+1)^3J^3 + \ldots. \tag{2}$$

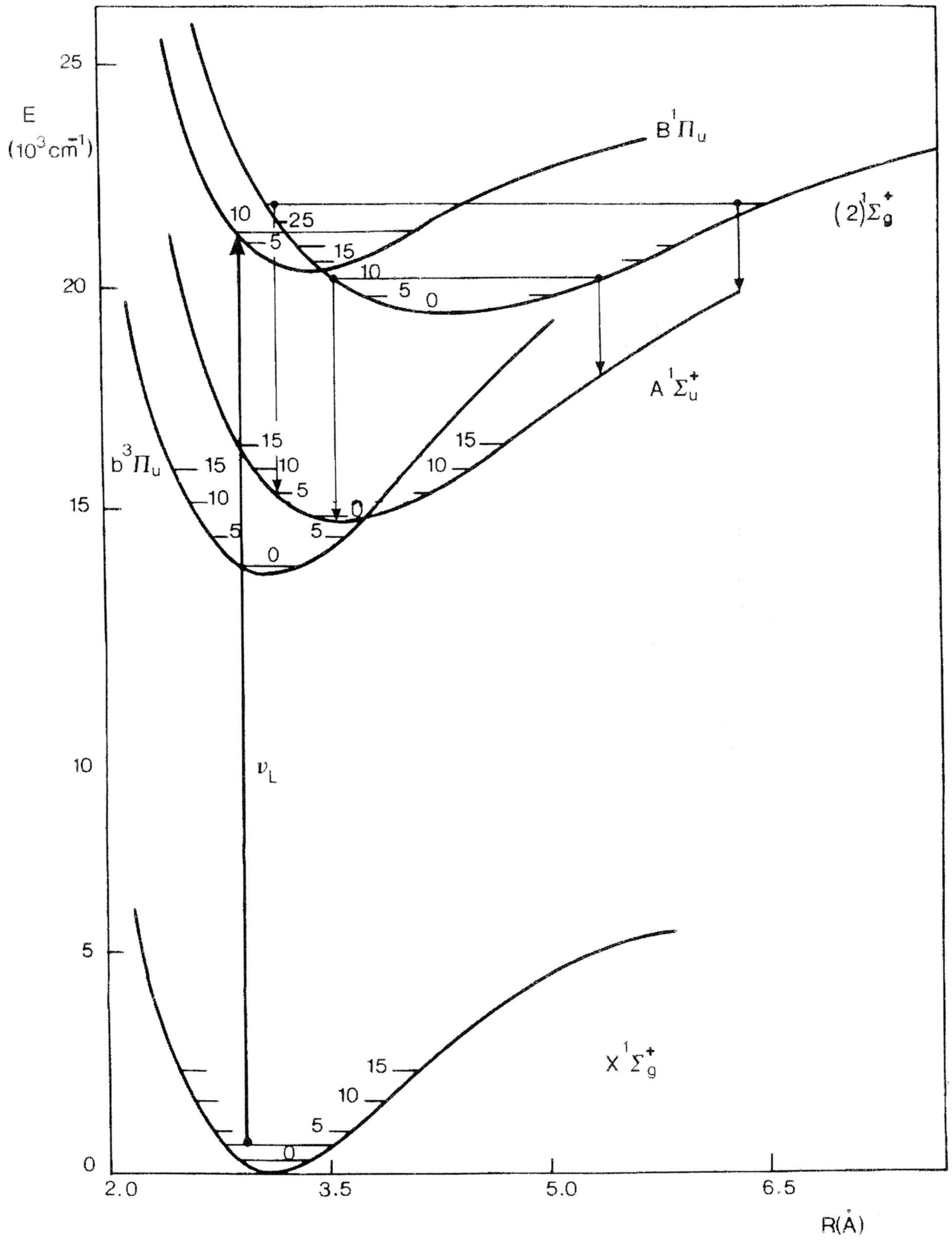

Fig. 1. Potential curves of the states involved in this work.

The parameters T_v, B_v, D_v, and H_v were obtained for each vibrational level v.

These constants can be obtained if there are rotational relaxation lines and the level is not perturbed, while in the case of the absence of the rotational relaxation lines our calculation is restricted to determining the term-values T_{vJ} of the rotational levels $(v,\ J)$. The molecular constants of the $A^1\Sigma_u^+$ and $B^1\Pi_u$ states deduced from this study are limited in number.

The determined constants for the $A^1\Sigma_u^+$ state are given in Table 1. However, for this state more extensive results were derived from the perturbation study of this state [10]. The results concerning the $B^1\Pi_u$ state are associated on one hand with a small amount of information obtained for this state, and on the other hand

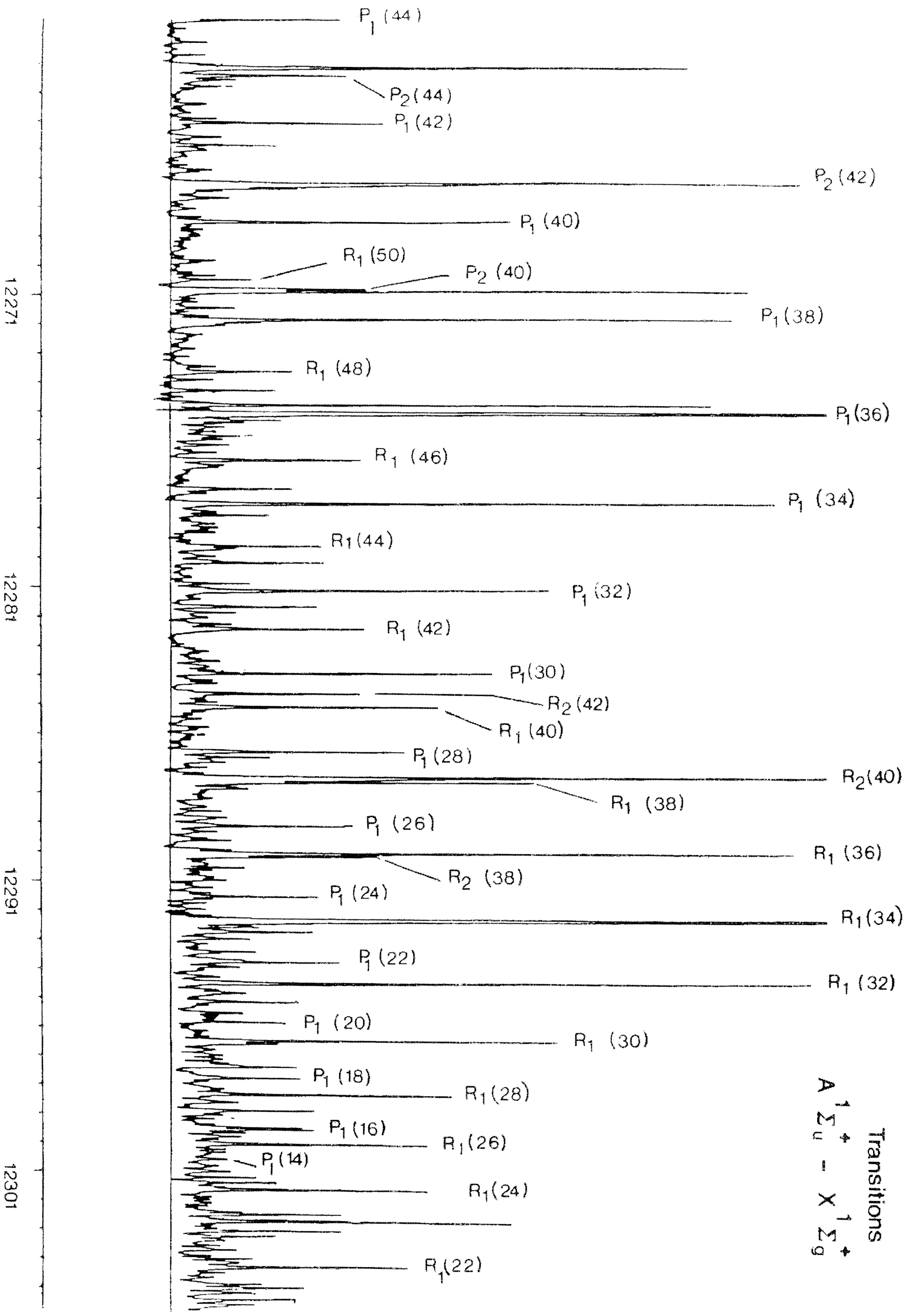

Fig. 2. Part of the spectrum of the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ transition of Na_2, excited by the Kr^+ line $\lambda = 6471$ Å. The indices 1 and 2 show the series of $P(J+1)$ and $R(J-1)$ lines.

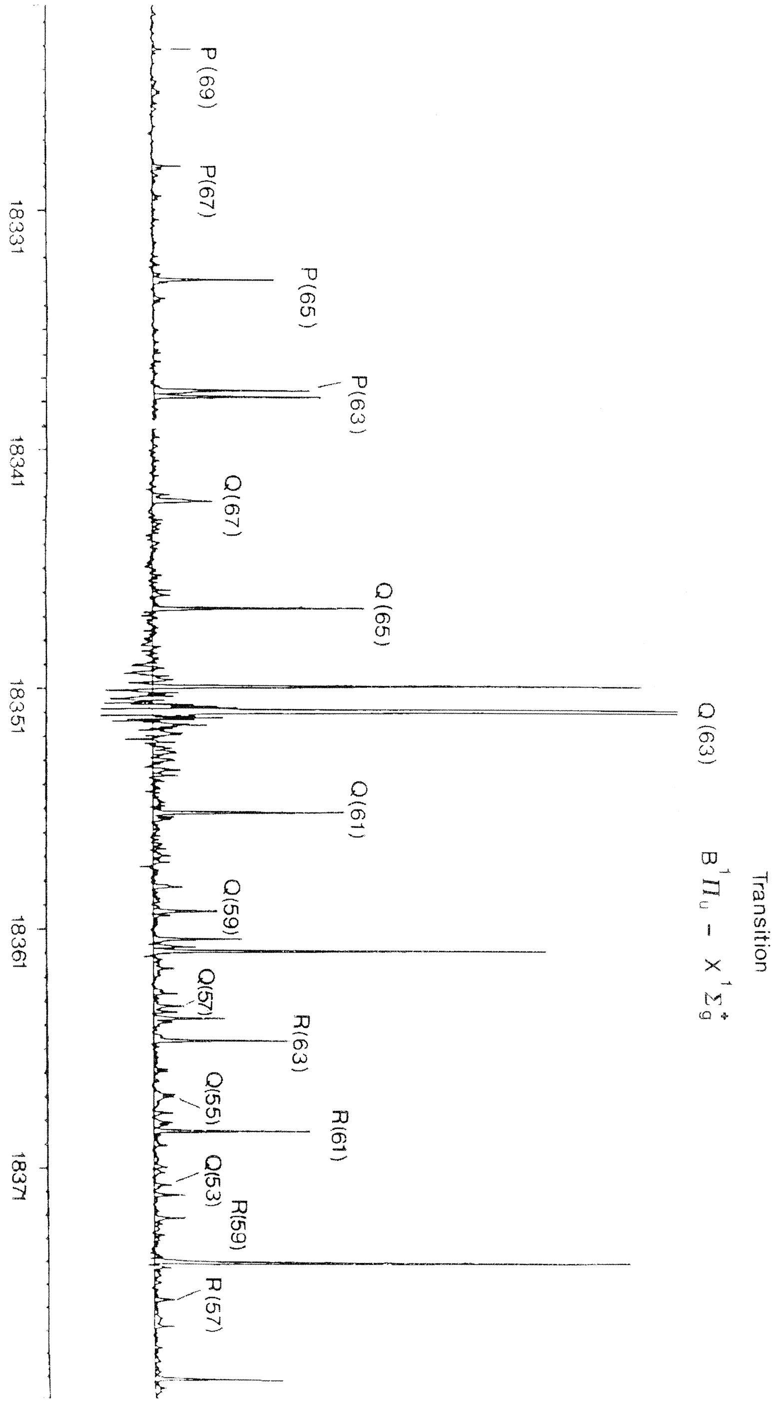

Fig. 3. Part of the spectrum of the $B^1\Pi_u - X^1\Sigma_g^+$ $(v = 13 - v = 4)$ Q(63) transition of Na_2 excited by the Kr^+ line $\lambda = 4762$ Å.

to the fitting which was done in two distinct sub-levels (e and f). For these reasons, no better results were obtained than those already available in the literature [3]. The obtained results are summarized in Table 2.

Table 1. Term-values and rotational constants of vibration level of the $A^1\Sigma_u^+$ state of Na_2 (rms = 0.0069cm^{-1}).

v	T_v	B_v	$D_v \cdot 10^{-6}$	$H_v \cdot 10^{-11}$
7	15540.47 (01)	0.106581 (62)	0.0900 (14)	
10	15872.40 (08)	0.105332 (44)	0.4160 (60)	
12	16091.34 (04)	0.103896 (48)	0.3400 (20)	
13	16199.53 (01)	0.103294 (18)	0.3409 (74)	−0.289 (76)
30	17927.55 (19)	0.096950 (18)		
31	18025.90 (02)	0.093728 (14)	0.3905 (32)	

v	J	T_{vJ}
20	53	17047.817
29	50	18073.353
34	14	18327.689
39	32	18858.799
40	55	19104.923

Table 2. Term-values and rotational constants of the $B^1\Pi_u$ state of Na_2 (rms = 0.0069cm^{-1}).

Sub-state $B^1\Pi_{ue}$

v	T_v	B_v
12	21749.99 (03)	0.112302 (18)
13	21852.35 (01)	0.111266 (03)

v	J	T_{vJ}
6	27	21095.23 (01)
10	12	21538.72 (00)
14	48	21952.90 (01)
28	39	23107.71 (01)

Sub-state $B^1\Pi_{uf}$

v	T_v	B_v
12	21749.64 (02)	0.112537 (12)
13	21852.32 (01)	0.111264 (03)

v	J	T_{vJ}
6	43	21095.17 (01)
15	37	22051.54 (01)
16	60	22148.01 (01)

3. Conclusion

The value of the constants of the $A^1\Sigma_u^+$ and $B^1\Pi_u$ states, obtained in the present work, agree with those derived by C. Effantin et al. [10] and Kusch and Hessel [6], but these results are restricted to few numbers of vibrational levels. It appears that a study of laser-induced fluorescence provides precise and extensive results for the lower states [1] and limited results for the upper states, since this technique is very selective for the excited states. Only a limited number of vibrational levels of the upper states can be populated.

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