A Study of Perturbations of the $A^1\Sigma_u^+$ State of Na_2

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High resolution Fourier spectrometry techniques have been used to study the $A^1\Sigma_u^+$ state, which is perturbed by the $b^3\Pi_u$ state of the Na_2 molecule. This study was achieved by means of exciting the $B^1\Pi_u$ state from the $X^1\Sigma_g^+$ ground state by 4880 Å and 4965 Å lines of an Ar^+ laser. The excitation is followed by collisional transfer energy produced between $B^1\Pi_u$ and $(2)^1\Sigma_g^+$ states, which led to the population of the vibrational levels of the $(2)^1\Sigma_g^+$ state *v*. The analysis of the collision-induced system $(2)^1\Sigma_g^+ - A^1\Sigma_g^+$ enabled us to study, in detail, the perturbations of 11 vibrational levels from $v = 0$ to $v = 10$ of the $A^1\Sigma_u^+$ state.

Key words: Perturbations; Vibrational Levels; Molecular Constants; Excited State $A^1\Sigma_u^+$.

1. Introduction

The study of the first excited singlet state $A^1\Sigma_u^+$ of Na_2 can be used as a platform of departure towards multiphotons. But $A^1\Sigma_u^+$ is perturbed by the second excited triplet state $b^3\Pi_u$, and in spite of the many studies concerning the state $A^1\Sigma_u^+$, the fine analysis of the perturbation, caused by the triplet state $b^3\Pi_u$, remained without investigation.

In most of the previous work the molecular constants of the states $A^1\Sigma_u^+$ and $b^3\Pi_u$ are calculated, without dealing with their perturbation [1 – 3]. The only researchers who touched the problem of the perturbation of the $A^1\Sigma_u^+$ state were Kusch and Hessel [4]. They studied roughly the perturbation of the $v = 0$ and $v = 1$ vibrational levels.

In a previous work [5] we have calculated the perturbations of eleven vibrational levels from $v = 0$ to $v = 10$ of the $A^1\Sigma_u^+$ state by high resolution Fourier spectroscopy to study the transition $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$. The upper $(2)^1\Sigma_g^+$ state is populated by collisional transfer between $B^1\Pi_u$ and $(2)^1\Sigma_g^+$ states. The analysis led to the calculation of the perturbed constants of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states, and the interaction matrix elements are well determined, in addition to an unambiguous confirmation of the vibrational numbering of the $b^3\Pi_u$ state.

In this paper the perturbation of the $A^1\Sigma_u^+$ state is reported in detail, which completes the previous work [5 – 8].

2. Experimental

The experimental arrangement described in [5, 9], consisted of a heat pipe in which argon was introduced both as buffer gas and to produce the collisional phenomenon of relaxation. Sodium vapour in the heat pipe was maintained at 500 °C. The pressure of argon was about 10 Torr. A schematic diagram of the apparatus is shown in Figure 1. A series of experiments was carried out, using selective laser excitation techniques and recording the spectrum by high resolution Fourier transform spectrometry. The exciting lines are $\lambda = 4880$ Å and $\lambda = 4965$ Å of an Ar^+ laser.

2.1. Observed Spectra

In addition to the usual series of doublets or triplets [9], a system of bands, similar to that excited by classical sources of excitation, in the spectral range 5200 cm^{-1} – 6200 cm^{-1} was observed. The analysis of these spectra shows that it is the transition $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$. The upper state $(2)^1\Sigma_g^+$ of this transition can not be excited directly by any means from the ground state $X^1\Sigma_g^+$, because of the selection

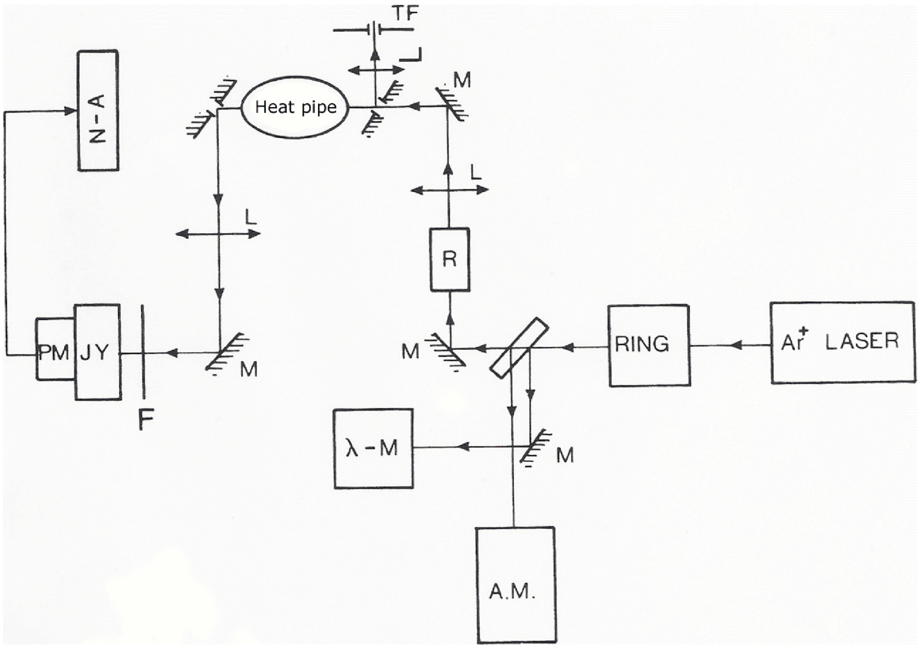

Fig. 1. Experimental arrangement: F, optical filter; M, mirror; L, lens; JY, system monochromator (H 20 Jobin Yvon, $F = 20$ cm, opening F / 3, 5, 1200 tr/mm); PM, photo-multiplicator; R, polarization rotator ($\pi/2$); $\lambda-$M, lambda-meter; N–A, nano-ammeter; A. M., mode analyzer; TF, Fourier transform spectrometer.

rules. On the other hand, the $B^1\prod_u$ state, which crosses the $(2)^1\Sigma_g^+$ state, can be populated directly from the ground state $X^1\Sigma_g^+$. The excitation of the upper state $(2)^1\Sigma_g^+$, of the transition $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$, is then obtained in an unusual manner, that is by collisional energy transfer from a level (v_i, J_i) of the $B^1\prod_u$ state. This level is itself pumped directly from the ground state $X^1\Sigma_g^+$. The excitation can be expressed according to the scheme

$$X^1\Sigma_g^+ \xrightarrow{v_L} B^1\prod_u(v_i, J_i) \xrightarrow{\text{Collision}} (2)^1\Sigma_g^+(v', J') \rightarrow A^1\Sigma_u^+ + h\nu.$$

Only one rotational level of the $B^1\prod_u$ state is excited by the pumping line. It can be antisymmetric (a), as the excitation by the pumping line $\lambda = 4880$ Å, Fig. 2, or symmetric (s), as the excitation by the pumping line $\lambda = 4965$ Å. By supposing that the nuclear symmetry must be conserved during the collision (collision at long range), only the levels with the same symmetry in the $(2)^1\Sigma_g^+$ state will be populated. From this state an emission takes place towards the $A^1\Sigma_u^+$ state obeying the selection rules a–a, s–s, and $+--$. In the first case (pumping line is antisymmetris) lines were obtained having even J'' and in the second case (pumping line is symmetris) lines were obtained having odd J''.

2.2. Analysis

The general characteristic of the spectra induced by collisional transfer is the complexity relative to the spectra of fluorescence induced by laser, even at high resolution. That is due to the mode of excitation (collisional transfer) and to the presence of numerous perturbations in the rotational structure of the $A^1\Sigma_u^+$ state. But the analysis of the spectra becomes easier because of the mechanism of population, which is such that according to the exciting line only rotational levels having J'' even or odd. Next to the upper state $(2)^1\Sigma_g^+$ of the transition $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$ the transitions have been studied with greater precision than those used in this work [10], and no perturbations have been detected in the levels of this state, and it was found that its values are well represented by the constants already published [10].

Not all the vibrational levels of the perturbed $A^1\Sigma_u^+$ state can be represented by simple polynomials, within the perturbed zone. These levels are perturbed by, at least, one level of the $b^3\prod_u$, often by two and sometimes, within the range of observed values of J, by three levels. Each such region of interaction consists of three crossing points, with $b^3\prod_{u,0}$, $b^3\prod_{u,1}$ and $b^3\prod_{u,2}$ sub-states as shown in Figs. 3 and 4, for the levels $v'' = 0$ and $v'' = 1$, respectively.

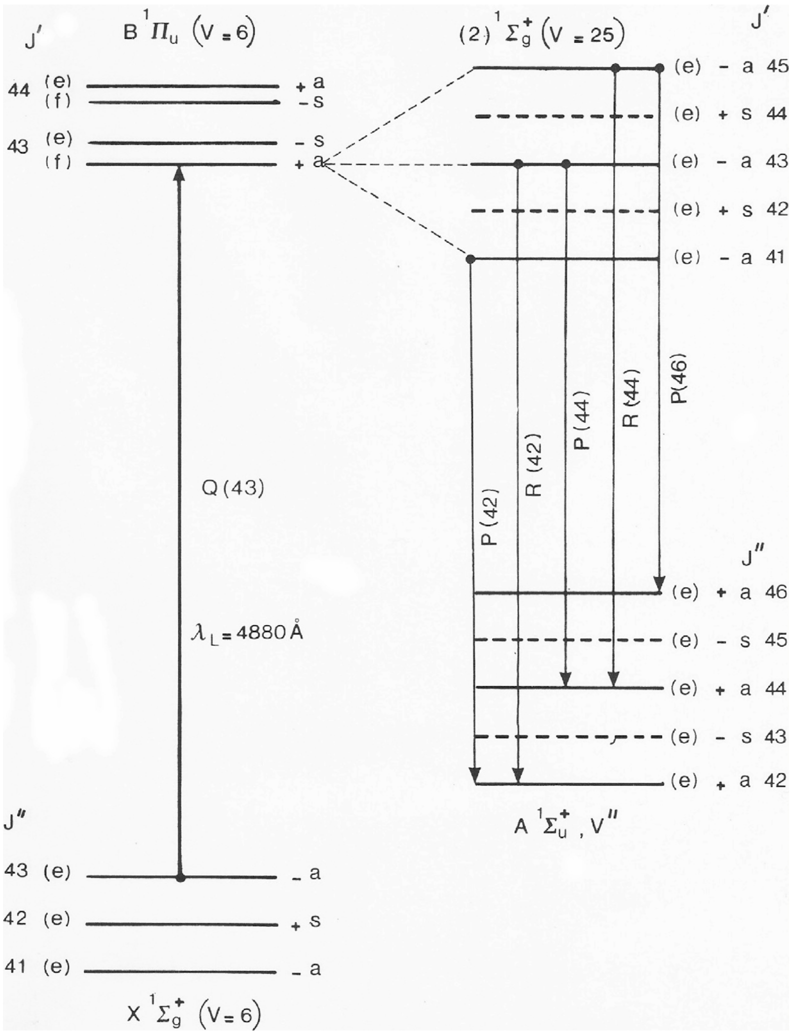

Fig. 2. Diagram of the indirect population of the $(2)^1\Sigma_g^+$ state of the molecule Na_2 excited by the Ar^+ line at 4880 Å.

In order to get an unambiguous analysis, it was necessary to study several bands of the transition $\big((2)^1\Sigma_u^+, v\big) - (A^1\Sigma_u^+, v'')$ for each perturbed level. For example, for the study of the perturbation in the level $v'' = 4$, six $(v' - v'')$ bands were studied; they are (21–4), (22–4), (23–4), (24–4), (25–4), and (26–4) arising from different levels of the upper $(2)\,^1\Sigma_g^+$ state and transmitting towards the same lower level $v = 4$ of the $A^1\Sigma_u^+$ state. The values of four $(v' - v'')$ bands (23–4), (24–4), (25–4) and (26–4) are listed in Table 1. the differences between the $\Delta_2 F''(J)$ values of the same type does not exceed a few thousandth of reciprocal centimeter, except for the particular cases of superposed lines, where a difference of up to $15 \cdot 10^{-3}$ cm^{-1} exists. A list of sixty bands analyzed is given in Table 2. For the levels with $v'' = 1$ to 6, lines of both even and odd J'' have been observed, but for $v'' = 0$ and 7 to 10, only the even J'' lines have been observed.

For each v'' level, the variation of the effective values of B''_v with J was determined, either from

$$B'' = \frac{R(J-1) - P(J+1)}{4(J+0.5)} + 2D''(J+0.5)^2 \ldots \quad (1)$$

for levels $v'' = 0$, 7–10 (these bands possess only even J'' lines) or from

$$B' - B'' = \frac{P(J-1) - P(J) + R(J-1) - R(J)}{4J} + 6D' + 2(D' - D'')J^2 + \ldots \quad (2)$$

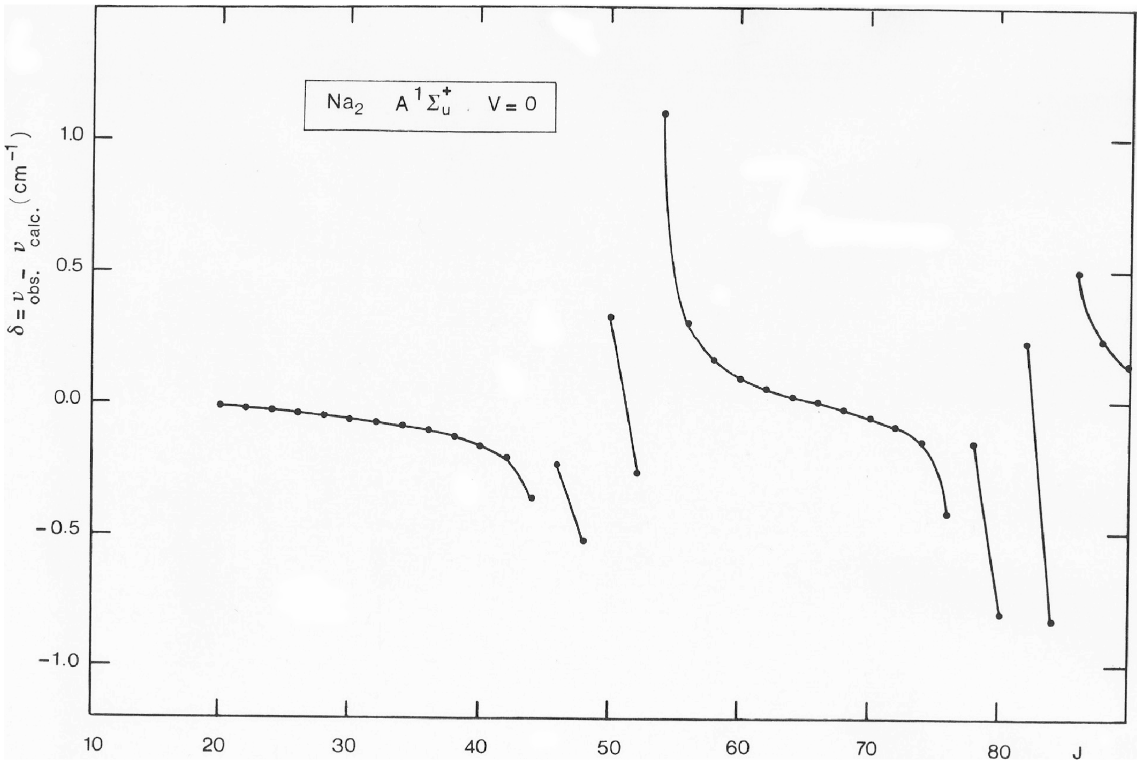

Fig. 3. Variation of the difference $\delta = \nu_{obs} - \nu_{unpert}$ between the observed (obs) and the unperturbed (unpert) wave numbers as a function of J for $v'' = 0$ in the $A^1\Sigma_u^+$ state perturbed by ($v = 7$, $J = 35-62$) and ($v = 6$, $J = 78-95$) in $b^3\Pi_u$.

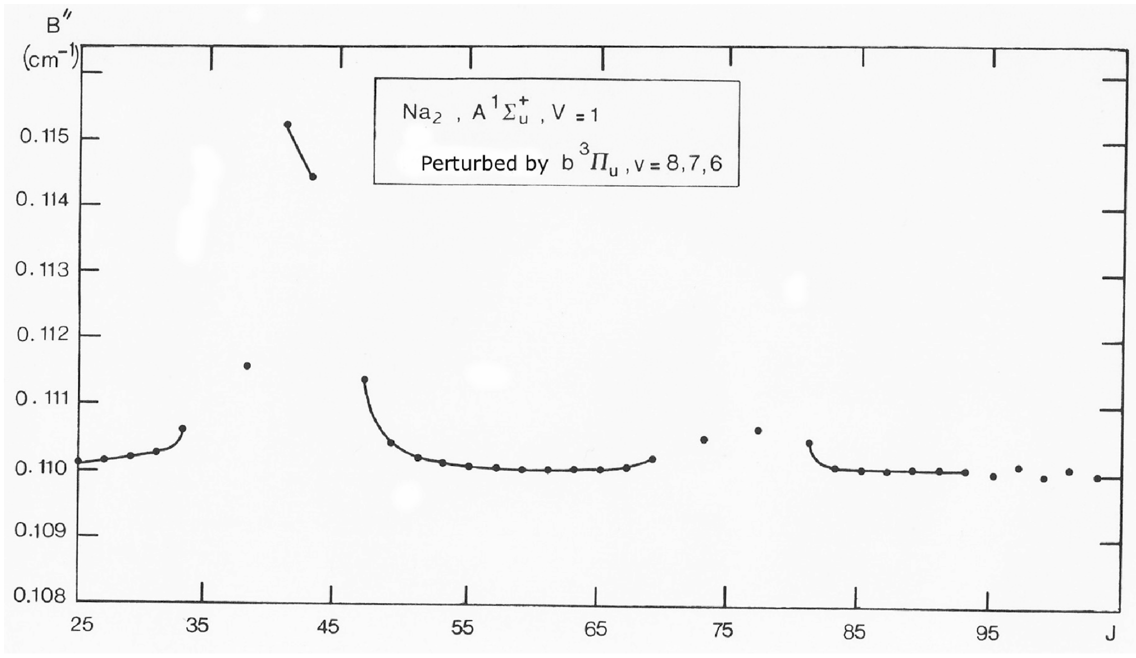

Fig. 4. Values of B_v'' plotted against J to illustrate the perturbation in the $b^3\Pi_u$ ($v = 1$) level caused by $b^3\Pi_u^+$ ($v = 8$, $J = 33-49$), $b^3\Pi_u$ ($v = 7$, $J = 67-83$) and $b^3\Pi_u$ ($v = 6$, $J = 95-110$) levels.

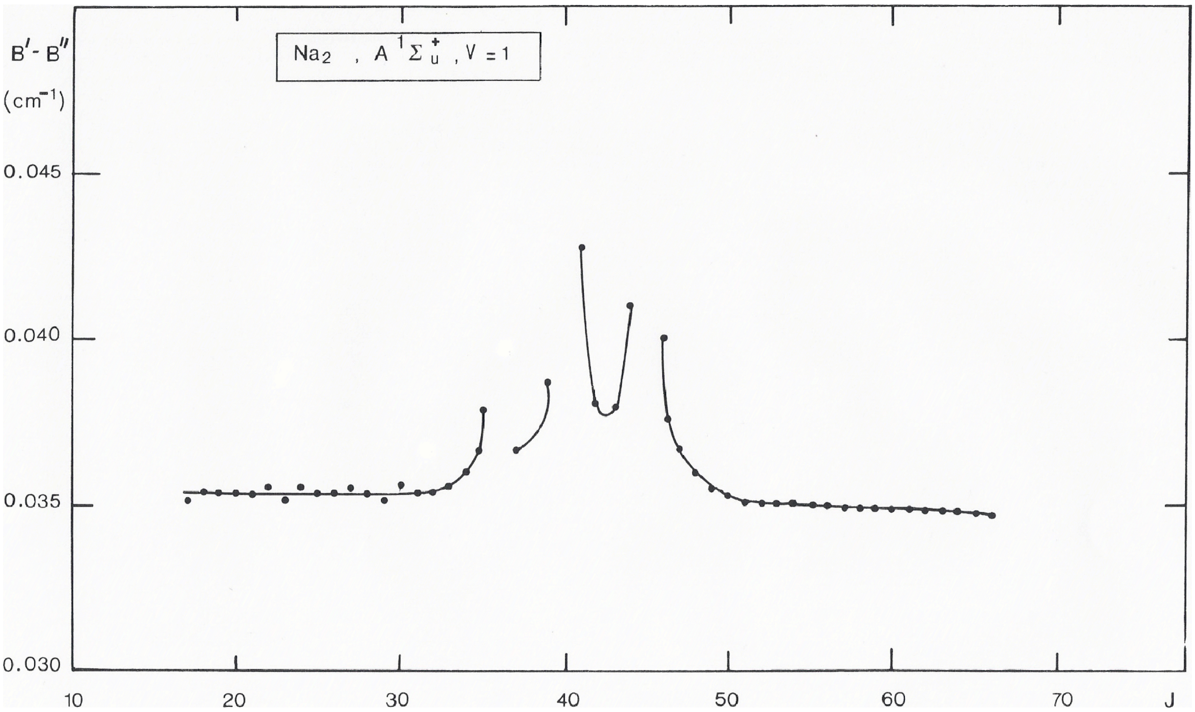

Fig. 5. Values of $B''_v - B'_v$ plotted against J to illustrate the perturbations between the $A^1\Sigma_u^+$ ($v = 1$) level and the level $b^3\Pi_u$ ($v = 8$, $J = 33-49$).

Table 1. Comparison of different $\Delta^2 F(J)$ values obtained experimentally for bands of the system $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$ transmitting towards the level $v'' = 4$.

J''	23–4 $\Delta_2 F''(J)$	24–4 $\Delta_2 F''(J)$	25–4 $\Delta_2 F''(J)$	26–4 $\Delta_2 F''(J)$	J''	23–4 $\Delta_2 F''(J)$	24–4 $\Delta_2 F''(J)$	25–4 $\Delta_2 F''(J)$	26–4 $\Delta_2 F''(J)$
5		2.3961	2.3839		51	21.8089	21.8087	21.8088	21.8092
7	3.2527	3.2493	3.2530	3.2426	53	22.8403	22.8529	22.8482	22.8475
9	4.1158	4.1181	4.1157	4.1252	55	22.9769	22.9775	22.9766	22.9682
11	4.9772	4.9760	4.9789	4.9859	57	24.7355	24.7370	24.7325	24.7291
13	5.8569	5.8419	5.8469	5.8468	59	24.1096	24.1216	24.1177	24.1192
15	6.7090	6.7073	6.7098	6.7098	63	26.7953	26.7925	26.7948	26.7942
17	7.5711	7.5724	7.5697	7.5673	65	27.5442	27.5450	27.5461	27.5445
19	8.4417	8.4309	8.4334	8.4252	67	28.3203	28.3198	28.3216	28.3212
21	9.2922	9.2937	9.2903	9.2895	69	29.0998	29.0993	29.0970	29.0993
23	10.1421	10.1456	10.1396	10.1452	71	29.8729	29.8765	29.8701	29.8735
25	11.0021	11.0072	11.0007	11.0010	73	30.6448	30.6448	30.6371	30.6430
27	11.8517	11.8554	11.8546	11.8563	75	31.4112	31.4120	31.4021	31.4109
29	12.7064	12.7069	12.7060	12.7117	77	32.1720	32.1741	32.1743	32.1738
31	13.5556	13.5513	13.5555	13.5465	79	32.9620	32.9619	32.9540	32.9630
33	14.4095	14.4066	14.4023	14.4016	81	33.6468	33.6499	33.6480	33.6493
35	15.2471	15.2471	15.2467	15.2474	83	34.4983	34.4975	34.4981	34.5030
37	16.0901	16.0900	16.0889	16.0888	85	35.0871	35.0867	35.0870	35.0876
39	16.9285	16.9292	16.9284	16.9314	87	35.9263	35.9283	35.9306	35.9161
41	17.7669	17.7659	17.7651	17.7651	89	36.6012	36.6037	36.6040	
43	18.6013	18.5997	18.5995	18.5996	91	37.3608	37.3577	37.3632	
45	19.4321	19.4316	19.4321	19.4318	93	38.0742	38.0899	38.0803	
47	20.2640	20.2640	20.2651	20.2685	95	38.7920	38.7916	38.7937	
49	21.1057	21.1075	21.1072	21.0978	97	39.5020	39.5015	39.5061	

Table 2. List of the analyzed bands of the system $X^1\Sigma_g^+$ and their intensities.

$v'-v''$	Excitation by Ar^+ $\lambda = 4880$ Å J''	Intensity[a]	Excitation by Ar^+ $\lambda = 4965$ Å J''	Intensity[a]
$9-0$	$22 \le J'' \le 66$	w		
$10-0$	$18 \le J'' \le 78$	w		
$11-0$	$18 \le J'' \le 90$	w		
$12-0$	$18 \le J'' \le 96$	w		
$13-0$	$18 \le J'' \le 96$	w		
$13-1$	$14 \le J'' \le 86$	w		
$14-1$	$12 \le J'' \le 104$	w		
$15-1$	$12 \le J'' \le 104$	w	$17 \le J'' \le 77$	w
$16-1$	$12 \le J'' \le 104$	w	$17 \le J'' \le 91$	w
$17-1$	$14 \le J'' \le 104$	w	$17 \le J'' \le 77$	w
$18-1$	$18 \le J'' \le 104$	w	$17 \le J'' \le 79$	w
$17-2$			$15 \le J'' \le 61$	w
$18-2$	$10 \le J'' \le 88$	w	$15 \le J'' \le 61$	w
$19-2$	$18 \le J'' \le 88$	w	$15 \le J'' \le 61$	w
$20-2$	$16 \le J'' \le 88$	w	$15 \le J'' \le 61$	w
$19-3$	$16 \le J'' \le 84$	m		
$20-3$	$16 \le J'' \le 86$	m	$19 \le J'' \le 83$	w
$21-3$	$14 \le J'' \le 86$	m	$21 \le J'' \le 83$	w
$22-3$	$16 \le J'' \le 86$	m	$21 \le J'' \le 75$	w
$23-3$	$16 \le J'' \le 86$	m	$19 \le J'' \le 75$	w
$24-3$	$16 \le J'' \le 56$	m	$21 \le J'' \le 75$	w
$25-3$	$14 \le J'' \le 56$	m		
$21-4$	$22 \le J'' \le 76$	m		
$22-4$	$24 \le J'' \le 88$	m	$19 \le J'' \le 65$	w
$23-4$	$8 \le J'' \le 98$	m	$9 \le J'' \le 69$	m
$24-4$	$4 \le J'' \le 98$	s	$11 \le J'' \le 67$	w
$25-4$	$4 \le J'' \le 98$	vs	$9 \le J'' \le 71$	w
$26-4$	$14 \le J'' \le 88$	m	$9 \le J'' \le 71$	w
$23-5$	$14 \le J'' \le 72$	w		
$24-5$	$6 \le J'' \le 72$	s		

$v'-v''$	Excitation by Ar^+ $\lambda \le 4880$ Å J''	Intensity[a]	Excitation by Ar^+ $\lambda \le 4965$ Å J''	Intensity[a]
$25-5$	$6 \le J'' \le 72$	vs	$7 \le J'' \le 63$	w
$26-5$	$6 \le J'' \le 78$	s	$5 \le J'' \le 61$	m
$27-5$	$6 \le J'' \le 78$	m	$5 \le J'' \le 65$	w
$25-6$	$10 \le J'' \le 64$	m		
$26-6$	$10 \le J'' \le 74$	m	$17 \le J'' \le 55$	w
$27-6$	$10 \le J'' \le 74$	m	$17 \le J'' \le 55$	m
$28-6$	$10 \le J'' \le 72$	m	$19 \le J'' \le 55$	w
$29-6$	$10 \le J'' \le 74$	m	$17 \le J'' \le 55$	vw
$23-7$	$20 \le J'' \le 68$	w		
$28-7$	$12 \le J'' \le 74$	m		
$29-7$	$10 \le J'' \le 72$	m		
$30-7$	$8 \le J'' \le 80$	m		
$31-7$	$12 \le J'' \le 76$	m		
$32-7$	$20 \le J'' \le 68$	w		
$24-8$	$14 \le J'' \le 68$	w		
$25-8$	$14 \le J'' \le 72$	w		
$29-8$	$16 \le J'' \le 62$	w		
$30-8$	$14 \le J'' \le 72$	w		
$31-8$	$14 \le J'' \le 72$	w		
$32-8$	$14 \le J'' \le 72$	w		
$25-9$	$18 \le J'' \le 52$	w		
$26-9$	$14 \le J'' \le 52$	w		
$27-9$	$18 \le J'' \le 70$	w		
$31-9$	$26 \le J'' \le 56$	w		
$32-9$	$18 \le J'' \le 70$	w		
$33-9$	$18 \le J'' \le 66$	w		
$34-9$	$16 \le J'' \le 70$	w		
$28-10$	$30 \le J'' \le 62$	w		
$29-10$	$30 \le J'' \le 62$	w		
$34-10$	$30 \le J'' \le 48$	vw		

[a] vs, very strong; s, strong; m, mean; w, weak; vw, very weak.

for levels $v'' = 1-6$ (these bands posses odd and even J'' lines). Examples of these two relations are illustrated in Figs. 4 and 5, respectively, for the level $v'' = 1$. The bands from $v'' = 1$ to $v'' = 6$, which have all lines provide better description of the perturbed levels, for example, the crossing points of Fig. 5, are located much more precisely to a unity, while those of Fig. 4 are located with an error of two units. In Fig. 6, the values $T(v,J) = T_e + G(v) + F(J)$ of the different vibrational levels of the perturbing $b^3\prod_u$ and the perturbed $A^1\Sigma_u^+$ states are plotted against $J(J+1)$. The points of intersection are the positions of maximum perturbation. This figure represents the perturbations within the observed range for $6 < (b^3\prod_u, v) < 15$ and $0 < (A^1\Sigma_u^+, v) < 10$. Because of the triplet character of the perturbing $b^3\prod_u$ state, each interaction represents, in fact, a group of three perturbations. This representation in Fig. 6 agrees very well with those in Figs. 3, 4 and 5.

All the curves of the relative intensities of the observed bands excited by the Ar^+ line 4880 Å pass through a maximum for the same value of $J' = 44$. This maximum is more important and accentuated for the bands arising from the upper vibrational level $v' = 25$ or from the neighbouring level of the transition $\left((2)^1\Sigma_g^+, v'\right) - (A^1\Sigma_u^+, v'')$, as seen in the case of the bands ($v' = 25 - v'' = 5$), ($v' = 25 - v'' = 4$). But this maximum becomes less important when the upper vibrational level v' of a band departs from the level $v' = 25$. This can be observed at the band ($v' = 30 - v'' = 7$). When the upper level of the band is found far away from the level $v' = 25$ the curve becomes approximately flat. An example are the bands ($v' = 34 - v'' = 9$) and ($v' = 15 - v'' = 1$). This result leads us to believe that the level ($v' = 25 - J' = 44$) of the $(2)^1\Sigma_g^+$ state is the collisional resonant level with the $B^1\prod_u$ state. This agrees well with the scheme in Figure 2.

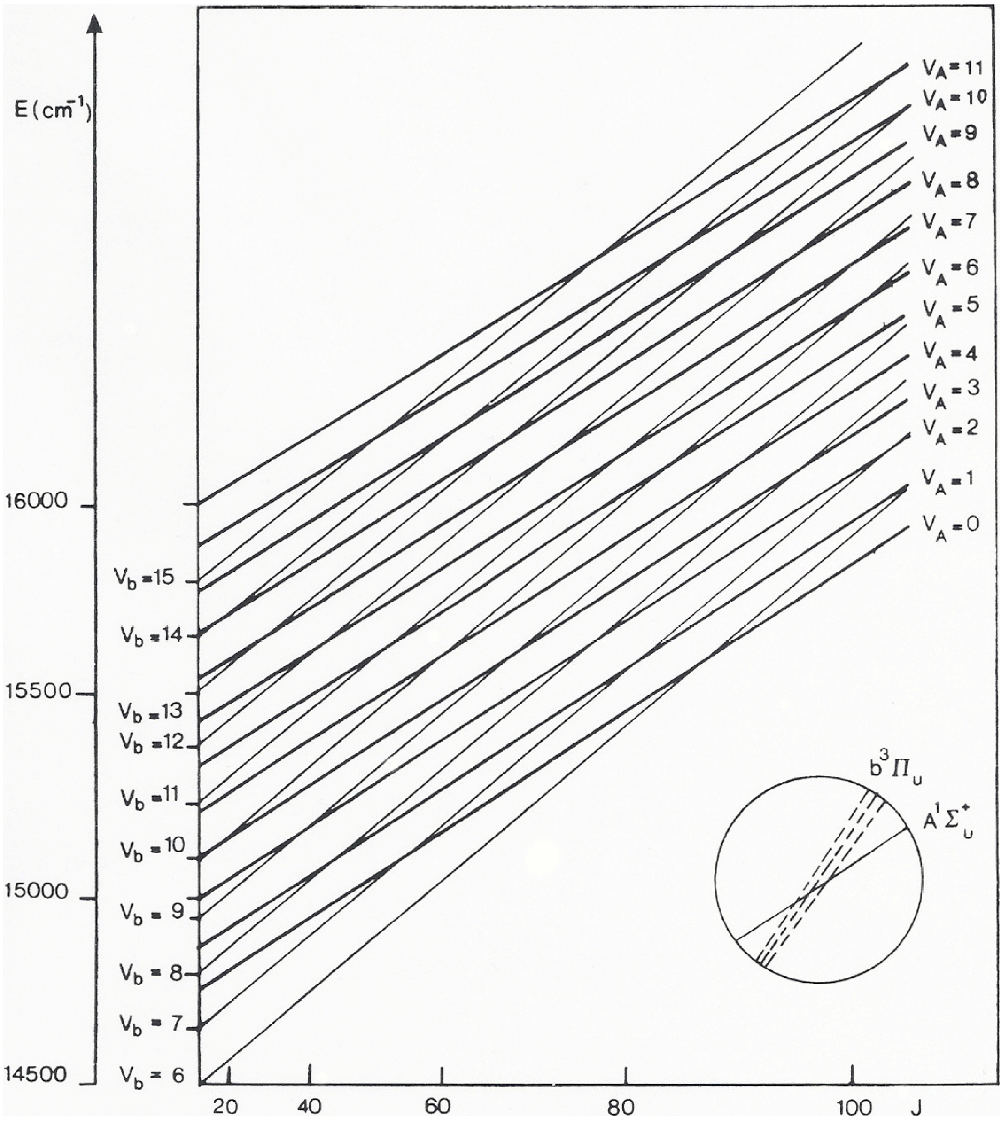

Fig. 6. Variations of term values $T(v) = T_e + G(v) + F(J)$ against $J(J+1)$ for the $A^1\Sigma_u^+$ and $b^3\prod_u$ state of Na_2.

In the case of the excitation by the Ar^+ line 4965 Å it was found that the levels ($v' = 23 - J' = 30$) and ($v' = 26 - J' = 42$, or $J' = 44$) of the $(2)^1\Sigma_g^+$ state are the collisional resonant levels with the $B^1\prod_u$ state.

The process is found to be resonant, with cross-sections strongly depending on the ΔE energy transfer, being maximal when $\Delta E \approx 0$ with selection rules $\Delta J = 0, \pm 2$ for the excitation line at 4880 Å and negligible when $\Delta E \geq 300\ \text{cm}^{-1}$ at $T = 770$ K. At the same time the experimentally observed spectra indicate that both resonant and nonresonant channels contribute to the collisional energy transfer. The quantitative characteristics of these processes can be interpreted by calculations based on a first-order dipole-dipole and second-order interaction potentials, using the Born approximation [9].

3. Conclusion

Our work concerns the perturbation of the $A^1\Sigma_u^+$ state, which is essentially different from those of Kusch and Hessel [4] and Engelke et al. [2]. We report a detailed analysis of 11 perturbed vibrational levels of the $A^1\Sigma_u^+$ state. 60 bands of the $(2)^1\Sigma_g^+ - A^1\Sigma_u^+$

system are attributed with the help of the Fourier transform spectroscopy technique, which enables a precise study of the perturbations of the $A^1\Sigma_u^+$ state. It permitted also the description, in detail, of the interaction of the $b^3\Pi_u - A^1\Sigma_u^+$ states, which was published in [5–8], and the study of the ground state $X^1\Sigma_g^+$ [9].

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