Pramāṇa, Vol. 22, No. 1, January 1984, pp. 3–9, © Printed in India.

Laser excited fluorescence of Na_2

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MS received 17 September 1983

Abstract. Fluorescence was excited in the $B\,^1\Pi_u - X\,^1\Sigma_g^+$ system of Na_2, using the 488 and 514·5 nm radiations from a cw Ar^+ laser. The fluorescence was monitored through a double monochromator employing photoelectronic detection. In the spectrum resulting from the 488 nm excitation, apart from a large number of fluorescence series, a previously unreported series could be identified. On either side of all the members of the strongest series a large number of collisional satellites were observed and assigned.

Keywords. Laser excitation; fluorescence; vibrational, rotational assignments.

1. Introduction

The $B^1\Pi_u - X^1\Sigma_g^+$ system of sodium has been the subject of numerous investigations in the past. These results are well documented (Kusch and Hessel 1978; Huber and Herzberg 1979; Chandrasekhar 1983). The most exhaustive work is that of Kusch and Hessel (1978) who studied the laser-excited fluorescence (LEF) using all the visible lines of an Ar^+ laser. In the fluorescence spectrum they could measure as many as 25,400 lines including those due to collisional transfers. From a careful and painstaking analysis of this data, they have derived the most accurate molecular constants to date for the B and X states of Na_2.

Recently, we reinvestigated the LEF in the $B - X$ system, using the 488 and 514·5 nm lines of an Ar^+ laser from the point of view of studying the intensity distribution in various fluorescence series. The fluorescence spectrum due to 488 nm excitation revealed a new fluorescence series not reported before. In addition several collisional satellites were seen to accompany the lines belonging to the strongest series. Kusch and Hessel (1978) mentioned the observation of such satellites whose detailed assignments were not given in their paper. Details regarding the new fluorescence series and the assignments of collisional satellites are given in the present paper.

2. Experimental

The sodium dimers were produced in a heat pipe oven made of stainless steel. The construction of the heat pipe oven is on standard lines with minor changes in detail (Chandrasekhar 1983). Argon at 10 torr pressure was used as a buffer gas. During the operation, the temperature of the oven was maintained at 600 ± 5 K. The fluorescence was excited by the 488 and 514·5 nm lines of a commercial Ar^+ laser using a cw power of

800 mW in multimode for each line. The spectrum was recorded on a 0·75 m Spex double monochromator equipped with photon counting detection. Neon atomic spectrum from an electrodeless discharge tube excited by a microwave generator (0–100 W output at 2450 MHz) was simultaneously scanned to provide wavelength calibration. The position of fluorescence lines could be measured to an accuracy of about 0·5 cm^{-1}.

3. Results and discussion

It can be readily appreciated that when a laser line is used to excite fluorescence, it is necessary that there should be an overlap between the line width of the laser and the absorption Doppler profile of the molecular species under study. The situation with reference to the present experiment is illustrated in figure 1. Because of the multimode operation of the laser more than one line coincidence can be expected to occur. This could result in the pumping of many rovibronic levels and hence as many fluorescence series. It is convenient to discuss the results obtained under various sub-headings.

3.1 514·5 *nm excitation*

Figure 2 shows part of the fluorescence series arising from this excitation. Three fluorescence series (previously known) arising out of line coincidence for (2–6) $P(83)$, (1–6) $R(59)$ and (11–14) $Q(49)$ transitions in the B-X system were observed. The first two consist of P-R doublets while the third gives rise to a fragmentary Q series. Calculations based on the molecular constants given by Kusch and Hessel (1978) could reproduce the observed lines to within 0·5 cm^{-1}, confirming their assignments. That $v'' = 6$ is involved in the pumping for both the strong doublet series could be readily established by examining the spectrum in the anti-Stokes' region. The very first doublet members (2–0) $P(83)$, $R(81)$ and (1–0) $P(61)$, $R(59)$ could be identified without ambiguity at their appropriate positions. The J-assignment could be confirmed by

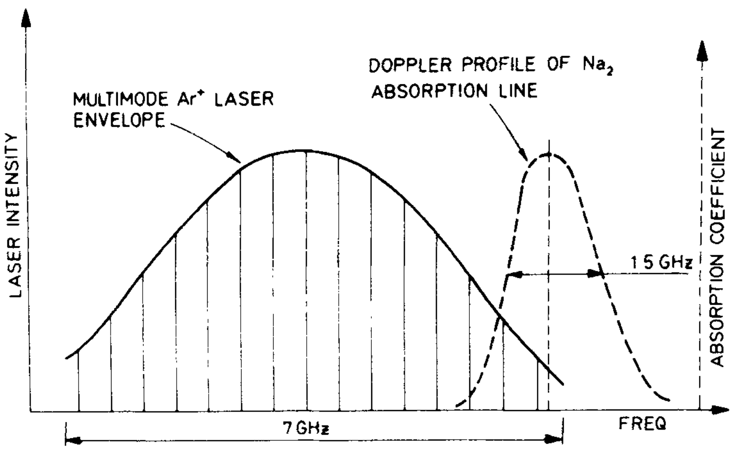

Figure 1. Spectral overlap between multimode laser profile and absorption Doppler profile.

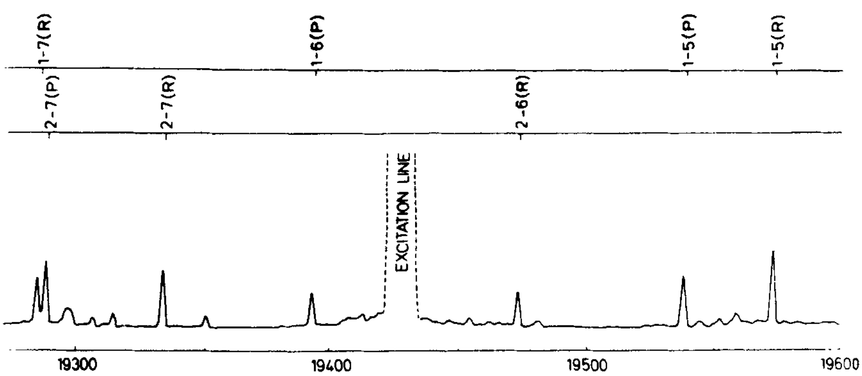

Figure 2. Part of the fluorescence spectrum in the $B^1\Pi_u - X^1\Sigma_g^+$ system of Na_2 excited by the 514·5 nm line of Ar^+ laser. The laser operated in multimode and mainly pumped the (2–6) $P(83)$ and (1–6) $R(59)$ transitions.

Table 1. Some of the strong transitions in the *B-X* system of Na_2 excited by Ar^+ laser.

Laser wavelength (nm, air)	Laser frequency (cm^{-1}, vac.)	Transition excited	Calculated frequency (cm^{-1}, vac.)
		(1–6) R (59)	19430·06
514·531	19429·83	(2–6) P (83)	19429·89
		(11–14) Q (49)	19429·97
487·986	20486·66	(6–3) Q (43)	20486·73
		(7–4) Q (25)*	20486·63

* Reported for the first time.

measuring the *P-R* separation in each case. The relation used was (Herzberg 1950)

$$\Delta\nu_{P,R} = 4B_{v''}(J'+1/2) - 8D_{v''}(J'+1/2)^3. \tag{1}$$

Our observations also conform with earlier investigations (Demtröder *et al* 1976).

3.2 488 *nm excitation*

Five relatively intense fluorescence series which were previously reported by Kusch and Hessel (1978) and Demtröder *et al* (1976) have been observed. The laser line coincidences responsible for these series are listed in table 1. A portion of the spectrum is displayed in figure 3. A closer scrutiny of the spectrum revealed a new, moderately strong fluorescence series not reported earlier. This series is included in figure 3. It is surprising that this series had eluded the observation of Kusch and Hessel (1978) who could recognise as many as 16 series, strong and weak, in their spectrum. In order to propose assignments for the new series, the members were followed into the anti-Stokes' region. This suggested that $v'' = 4$ was involved in the pumping. With this clue and using the molecular constants provided by Kusch and Hessel (1978) it could be established that the new series arose because of line coincidence for the (7–4) $Q(25)$ transition. Members could be traced to $v'' = 17$. These assignments were confirmed by

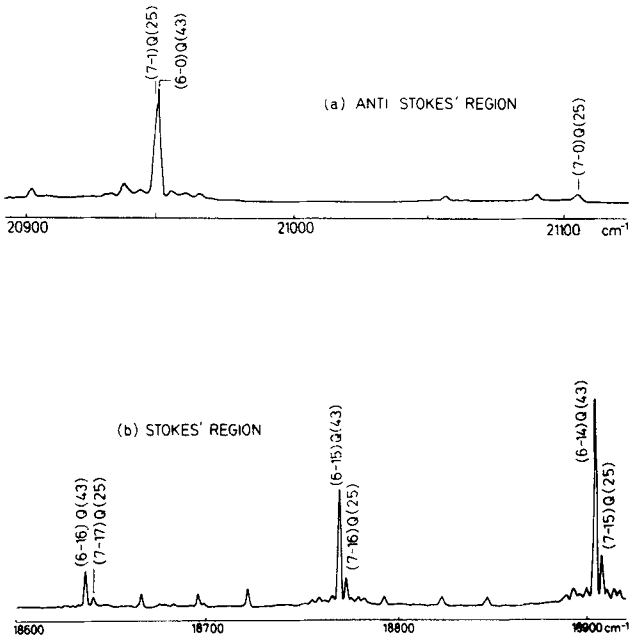

Figure 3. Portion of the fluorescence spectrum of Na_2 excited by the 488 nm line of Ar^+ laser, showing the new (7-v'') $Q(25)$ series in addition to the known (6-v'') $Q(43)$ series. Little peaks surrounding the strong lines are collisional satellites.

calculating the individual line positions which could be reproduced to within 0·5 cm^{-1}. Further, the Franck–Condon factors $q(v' J', v'' J'')$ for the various members of the series were calculated (Chandrasekhar 1983). The line positions of the members of the new series, their FCF s and observed intensities are displayed in table 2. That no member of this series on either side of the exciting line was inadvertently omitted could be established by considering the sum of the FCF s *i.e.* $\sum_{v''} q(v' J', v'' J'')$ which turned out to be 0·97 for all the observed members of the new series. This shows that the members not included in the progression contribute only 3% to this sum and hence would be too weak to be observed.

3.3 *Collisional satellites*

As may be seen from figure 3, the strongest series (6-v'') $Q(43)$ produced by 488 nm excitation displays many satellites accompanying each member. These were subsequently recognised to be due to collisional transfers and arise for the following reasons. The laser line selectively builds up a large population in the $v' = 6$, $J' = 43$ rovibronic level of the $B\,^1\Pi_u$ state. Due to collisions brought about mainly by the buffer gas, a certain amount of population is transferred to the adjacent J levels from which fluorescence to levels of the ground state is possible. From a detailed calculation using the molecular parameters of Kusch and Hessel (1978) it was possible to assign all these collisional satellites. Some typical, strong collisional satellites and their assignments are given in table 3.

From the analysis of the spectrum, it was found that collisional transfers for ΔJ upto

Table 2. The new (7-v'') $Q(25)$ series in the B-X system of Na_2. Fluorescence was excited using the 488 nm line of the Ar^+ laser. Laser line coincidence occurs for (7–4) $Q(25)$.

v''	ν_{obs} (cm^{-1} vac)	$\nu_{obs}-\nu_{calc}$ (cm^{-1})	FCF (× 1000)	I_{obs} (arb. units)
0	21106·3	+0·14	29·9	13
1	*	—	107·0	—
2	*	—	51·0	—
3	w	—	1·7	—
4	ϕ	—	64·8	—
5	—	—	6·3	—
6	*	—	59·4	—
7	w	—	15·6	—
8	*	—	40·3	—
9	19746·0	−0·06	51·1	26
10	w	—	3·6	—
11	19460·5	−0·23	80·0	25
12	19320·3	−0·17	42·0	12
13	w	—	5·3	—
14	19044·8	0·00	99·7	51
15	18909·4	−0·12	155·7	65
16	18776·0	+0·11	109·4	38
17	18643·9	−0·07	45·4	13

* overlapped by the lines of (6-v'') $Q(43)$; ϕ, excitation; w, too weak to be observed.

Table 3. Positions and assignments of typical collisional satellites.

$\Delta J'$	Assignment	Around (6–1) $Q(43)$ line		Around (6–14) $Q(43)$ line	
		ν_{obs} (cm^{-1}, vac)	$\nu_{obs}-\nu_{calc}$ (cm^{-1})	ν_{obs} (cm^{-1}, vac)	$\nu_{obs}-\nu_{calc}$ (cm^{-1})
−7	$P(37)$	*	—	*	—
	$R(35)$	20824·1	−0·12	18927·8	+0·14
−6	$Q(37)$	20810·8	+0·09	18916·3 b	+0·19
−5	$P(39)$	*	—	*	—
	$R(37)$	20819·8	+0·10	18925·2	+0·13
−4	$Q(39)$	20805·8	+0·30	18913·0 b	+0·16
−3	$P(41)$	20790·3	−0·10	*	—
	$R(39)$	20815·0	+0·06	18922·4	+0·12
−2	$Q(41)$	20800·0	+0·09	*	—
−1	$P(43)$	20784·0	−0·19	18895·5	−0·29
	$R(41)$	20810·0	+0·09	18919·5	+0·17
0	$Q(43)^m$	20794·1	−0·17	18905·9	+0·04
+1	$P(45)$	20777·3	−0·42	18891·5	−0·10
	$R(43)$	20804·8	+0·18	18916·3 b	+0·09
+2	$Q(45)$	20788·2	−0·05	18902·0	−0·13
+3	$P(47)$	20770·8	−0·19	18887·1	−0·14
	$R(45)$	20799·0	−0·05	18913·0 b	+0·07
+4	$Q(47)$	20782·0	+0·04	18898·2	0·00
+5	$P(49)$	w	—	18882·5	−0·25
	$R(47)$	*	—	*	—
+6	$Q(49)$	20775·1	−0·29	*	—

m—main fluorescence; *—overlapped by a strong line; b—blended; w—weak.

± 8 could be observed. An interesting observation has been that transfers for which $\Delta J = \pm 2, \pm 4, \ldots\ldots$ (even), gave rise to Q satellite series whereas those for which $\Delta J = \pm 1, \pm 3, \ldots.$ (odd), series consisting of P-R doublets resulted. The reason for this is not far to seek. It rests on the circumstance that the symmetry rule for homonuclear molecules, namely $a \leftrightarrow a, s \leftrightarrow s, a \not\leftrightarrow s$, is a rigorous one holding not only for radiative transitions but also for transitions brought about by collisions. The situation would become clear by a reference to figure 4. Due to Λ doubling in the $B^1\Pi_u$ state, each J level is doubled with opposite parity and with opposite a and s character. It is known that in the $B^1\Pi_u - X^1\Sigma_g^+$ transition, the Q lines arise out of the lower set of Λ components while the P and R lines emanate from the upper set of Λ components. The level that is pumped initially by the laser is the antisymmetric (a), + parity component of $v' = 6, J' = 43$. Application of the symmetry rule $a \leftrightarrow a, s \leftrightarrow s, a \not\leftrightarrow s$, for collisions, at once shows that transfers of the kind $\Delta J = \pm 1, \pm 3, \ldots$ (odd) would result in populating the upper Λ components. Hence a P-R doublet series should result from each of these collisionally populated levels. In the case of transfers with $\Delta J = \pm 2, \pm 4, \ldots$ (even),

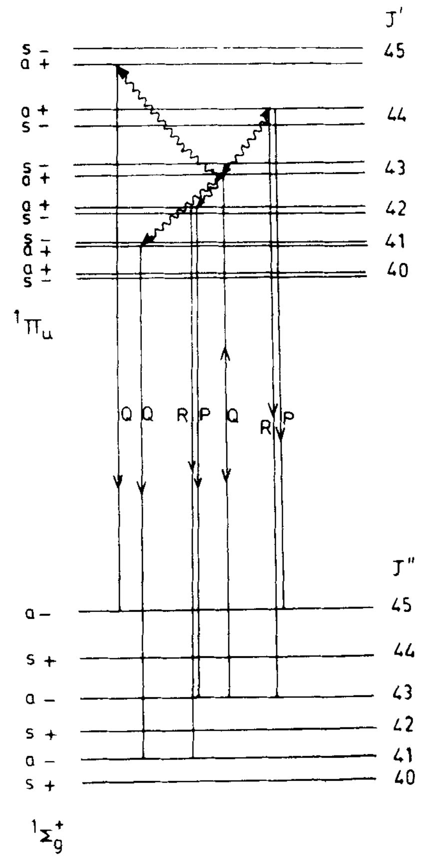

Figure 4. Occurrence of collisional satellites in the laser excited fluorescence of Na_2. The 488 nm line populates the lower Λ component of $J' = 43$, + parity antisymmetric level *via* the transition (6–3) $Q(43)$. J changing collisions can transfer population only to antisymmetric levels. This means that for ΔJ odd the upper Λ component would be populated leading to P, R doublets. For ΔJ even the lower Λ components are populated and Q lines result.

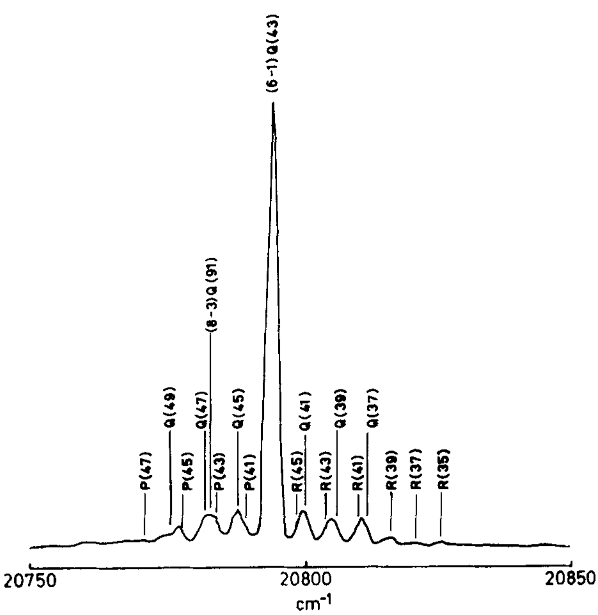

Figure 5. Collisional satellites around (6–1) $Q(43)$ and their assignments. Line assigned as (8–3) $Q(91)$ is due to another main, overlapping series.

populations are transferred to the lower Λ components and hence only Q series should arise. Based on the above reasoning all the collisional lines could be successfully assigned. The satellites surrounding the (6–1) $Q(43)$ line and their assignments are illustrated in figure 5.

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