RKR Potential, FCF and Mixing Coefficients of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ States of Na_2

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A study of the spin-orbit interaction between the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states of Na_2, based on the collision-induced transitions $(2)^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ recorded with a high resolution Fourier transform spectrometer, had led to the determination of the deperturbed constants of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states [1]. From these constants the Rydberg-Klein-Rees (RKR) potential curves for the $A^1\Sigma_u^+$ ($0 \leqq v \leqq 15$) and $b^3\Pi_u$ ($0 \leqq v \leqq 25$) states and the Franck-Condon factors (FCF) within the range of vibrational levels involved in the interaction of these two states are calculated, together with the mixing coefficients for the pair $(A^1\Sigma_u^+)_{v=4} - (b^3\Pi_u)_{v=10}$.

1. Introduction

In [1] we presented a study of the spin-orbit interaction between the $A^1\Sigma_u^+$ und $b^3\Pi_u$ states of Na_2, resulting from the analysis of high resolution Fourier transform spectra. The experiments were performed by exciting the $B^1\Pi_u$ state from the $X^1\Sigma_g^+$ ground state by the 4880 Å and 4965 Å lines of an Ar^+ laser [4]. This excitation is followed by collisional transfer of energy between the $B^1\Pi_u$ and $(2)^1\Sigma_g^+$ states, populating the rovibrational levels of the $(2)^1\Sigma_g^+$ state [2]. The analysis of the transition $(2)^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ enabled us to study, in detail, the perturbation in levels of the $A^1\Sigma_u^+$ state caused by the $b^3\Pi_u$ state. This analysis was made for levels from $(A^1\Sigma_u^+)_{v=0}$ to $(A^1\Sigma_u^+)_{v=10}$ with J often up to 100 for the most intense series. This led to the calculation of the deperturbed constants of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ state and to a reliable value for the interaction matrix element $\langle {}^3\Pi_u | H_{SO} | {}^1\Sigma_u^+ \rangle$, which was found to be $5.91 \pm 0.14\ cm^{-1}$.

In this paper, which completes the work reported in [1], we give the rotationless potential energy curves for the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states derived from their deperturbed molecular constants as published in [1], and also the Franck-Condon factors between $b^3\Pi_u$ and $A^1\Sigma_u^+$ and the mixing coefficients of these two states.

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2. Results of Calculation

From the Tables 3 and 6 of [1], the Rydberg-Klein-Rees (RKR) potential curves of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states, respectively, have been constructed for levels up to $v=25$ for the $b^3\Pi_u$ state and up to $v=15$ for the $A^1\Sigma_u^+$ state. The vibrational term values $G(v)$ and the turning points of the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states are given in Tables 1 and 2, respectively, and the RKR potential curves are plotted in Figure 1. From these values, the

Table 1. Turning points on the RKR potential curve for the $A^1\Sigma_u^+$ state of Na_2; calculated from results given in [1].

v	$G(v)$ (cm^{-1})	R_{min} (Å)	R_{max} (Å)
−0.5	0.0	3.6373236	
−0.25	29.3132	3.5286595	3.7524617
0	58.5726	3.4854623	3.8021405
1	175.1671	3.3818747	3.9317381
2	291.0524	3.3140427	4.0257147
3	406.2287	3.2609117	4.1051273
4	520.6960	3.2163723	4.1760865
5	634.4542	3.1776342	4.2413847
6	747.5033	3.1431459	4.3025752
7	859.8434	3.1119399	4.3606273
8	971.4745	3.0833652	4.4161940
9	1082.3964	3.0569588	4.4697403
10	1192.6093	3.0323781	4.5216108
11	1302.1132	3.0093608	4.5720698
12	1410.9080	2.9877013	4.6213250
13	1518.9938	2.9672345	4.6695437
14	1626.3704	2.9478258	4.7168625
15	1733.0381	2.9293637	4.7633952

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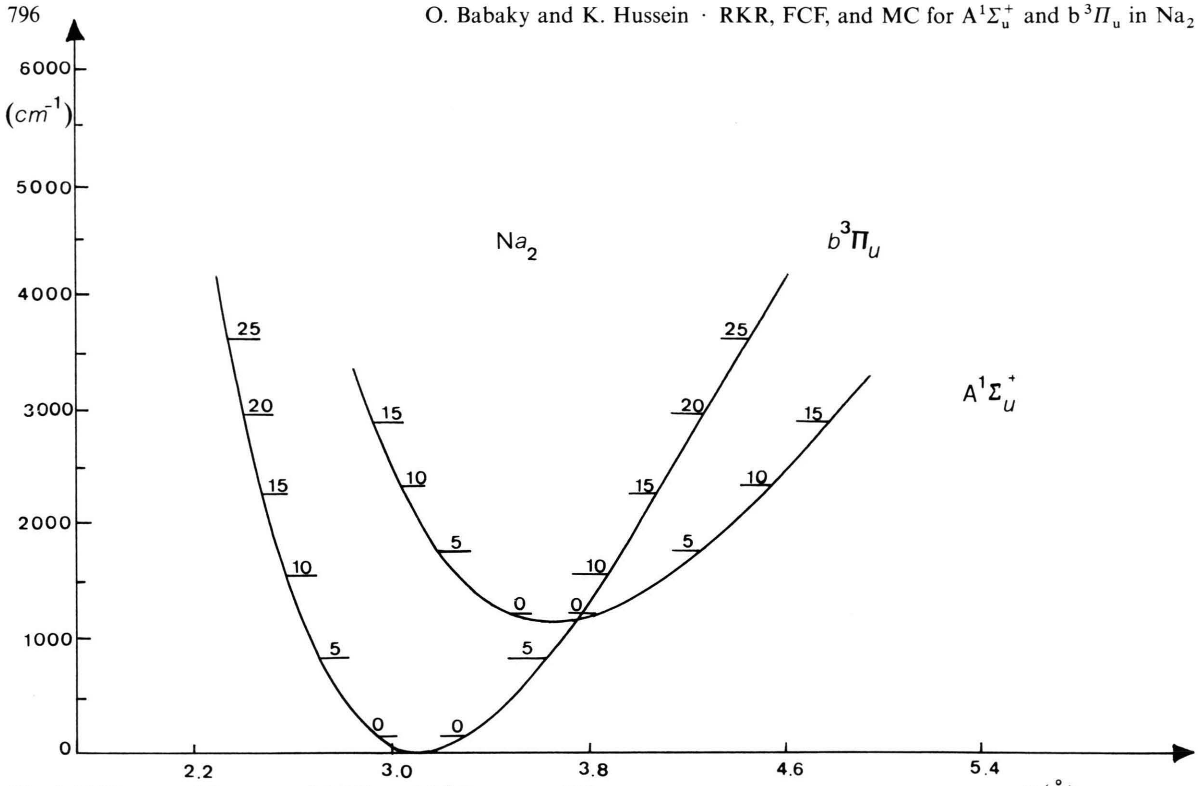

Fig. 1. RKR potential curves of $A^1\Sigma_u^+$ and $b^3\Pi_u$ states of Na_2.

Table 2. Turning points on the RKR potential curve for the $b^3\Pi_u$ state of Na_2; calculated from results given in [1].

v	$G(v)$ (cm^{-1})	R_{min} (Å)	R_{max} (Å)
−0.5	0.0	3.1066226	
−0.25	38.3651	3.0118052	3.2073735
0	76.6724	2.9738877	3.2506307
1	229.3370	2.8827148	3.3632278
2	381.0979	2.8227973	3.4446750
3	531.9552	2.7757295	3.5133795
4	681.9088	2.7361704	3.5746830
5	830.9587	2.7016807	3.6310269
6	979.1050	2.6709040	3.6837688
7	1126.3477	2.6429942	3.7337563
8	1272.6867	2.6173821	3.7815600
9	1418.1221	2.5936629	3.8275863
10	1562.6538	2.5715368	3.8721366
11	1706.2818	2.5507746	3.9154415
12	1849.0062	2.5311962	3.9576828
13	1990.8270	2.5126573	3.9990064
14	2131.7441	2.4950402	4.0395318
15	2271.7575	2.4782472	4.0793518
16	2410.8673	2.4621965	4.1185692
17	2549.0735	2.4468184	4.1572363
18	2686.3760	2.4320533	4.1954208
19	2822.7748	2.4178496	4.2331762
20	2958.2700	2.4041622	4.2705494
21	3092.8615	2.3909518	4.3075817
22	3226.5494	2.3781833	4.3443101
23	3359.3336	2.3658258	4.3807674
24	3491.2142	2.3538514	4.4169835
25	3622.1921	2.3422354	4.4529853

Franck-Condon factors (FCF) at $J=0$ between the $A^1\Sigma_u^+$ and $b^3\Pi_u$ states for the observed range of vibrational levels ($A^1\Sigma_u^+$) ($0 \leq v \leq 10$) and ($b^3\Pi_u$) ($6 \leq v \leq 15$) have been derived; the results are given in Table 3.

The molecular orbital configurations which give the electronic states $A^1\Sigma_u^+$ and $b^3\Pi_u$ are

$$A^1\Sigma_u^+: \quad [(1\sigma_g 1s)^2(1\sigma_u 1s)^2(2\sigma_g 2s)^2(2\sigma_u 2s)^2(3\sigma_g 2p)^2 \cdot (3\sigma_u 2p)^2(1\pi_u 2p)^4(1\pi_g 2p)^4](4\sigma_g 3s)^1(5\sigma_u 3p)^1,$$

$$b^3\Pi_u: \quad [\qquad](4\sigma_g 3s)^1(2\pi_u 3p)^1.$$

The wave functions of these states can be formally written as:

$$|A^1\Sigma_u^+\rangle = 1/\sqrt{2}\,[|---\bar{\sigma}_g\,\sigma_u| - |---\sigma_g\,\bar{\sigma}_u|],$$

$$|b^3\Pi_{0u}\rangle = 1/\sqrt{2}\,[|---\bar{\sigma}_g\,\bar{\pi}_u^+| - |---\sigma_g\,\bar{\pi}_u|].$$

The phenomenon of mixing coefficients between the $A^1\Sigma_u^+$ state and the sub-states $b^3\Pi_0$, $b^3\Pi_1$ and $b^3\Pi_2$ is characterized by the squares (C_i^2) of the development coefficients (C_i) of the total wave function of the $A^1\Sigma_u^+$ state. This is perturbed on the basis of pure wave function $b^3\Pi_{0e}$, $b^3\Pi_{1e}$, $b^3\Pi_{2e}$ and $A^1\Sigma_u^+$ states, which are calculated in the case of the parity *e* matrix.

For example, the evolution with J of the numerical values of the development coefficients C_i and of the

Table 3. Franck-Condon factors for $b^3\Pi_u - A^1\Sigma_u^+$ ($v-v''$) transitions of Na_2 for $J=0$.

v \ v''	0	1	2	3	4	5	6	7	8	9	10
6	0.18250	0.002548	0.09090	0.01996	0.01342	0.06064	0.02013	0.002778	0.03663	0.04167	0.01179
7	0.14350	0.05325	0.06424	0.008098	0.06725	0.01454	0.01330	0.04994	0.02195	0.000451	0.02588
8	0.09331	0.11890	0.007354	0.06655	0.02671	0.01533	0.05427	0.009358	0.01210	0.04292	0.02130
9	0.05084	0.01436	0.01390	0.07101	0.003672	0.06129	0.008160	0.02257	0.04420	0.005181	0.01245
10	0.02345	0.12050	0.07756	0.01593	0.05764	0.02205	0.02162	0.04625	0.000743	0.02836	0.03521
11	0.009221	0.07712	0.12610	0.006073	0.06728	0.005715	0.05699	0.001154	0.03635	0.02876	0.000692
12	0.003109	0.03942	0.12250	0.06356	0.01487	0.05939	0.01182	0.03427	0.03118	0.003514	0.04068
13	0.000902	0.01651	0.08474	0.11710	0.006903	0.05914	0.01374	0.04791	0.001788	0.04557	0.08382
14	0.000226	0.005758	0.04498	0.11850	0.06540	0.008079	0.06490	0.002109	0.04770	0.01152	0.02082
15	0.000049	0.001690	0.01906	0.08252	0.11570	0.01368	0.04553	0.02929	0.03054	0.01576	0.03892

Table 4. Mixing coefficients $(C_i)^2$ of the $A^1\Sigma_u^+$ ($v=4$) state of Na_2.

J	$^1\Sigma_u^+$		$^3\Pi_2$		$^3\Pi_1$		$^3\Pi_0$	
	C_i	$(C_i)^2$	C_i	$(C_i)^2$	C_i	$(C_i)^2$	C_i	$(C_i)^2$
41	0.9997	0.9994	0.0008	0.0000	0.0043	0.0000	0.0252	0.0006
42	0.9996	0.9992	0.0010	0.0000	−0.0050	0.0000	0.0268	0.0007
43	0.9996	0.9992	0.0013	0.0000	−0.0058	0.0000	0.0285	0.0008
44	0.9995	0.9990	0.0018	0.0000	−0.0070	0.0000	0.0306	0.0009
45	0.9994	0.9988	0.0024	0.0000	−0.0085	0.0001	0.0332	0.0011
46	0.9993	0.9986	0.0034	0.0000	−0.0106	0.0001	0.0363	0.0013
47	0.9991	0.9982	0.0051	0.0000	−0.0136	0.0002	0.0403	0.0016
48	0.9988	0.9976	0.0082	0.0001	−0.0185	0.0003	0.0456	0.0021
49	0.9981	0.9962	0.0146	0.0002	−0.0273	0.0007	0.0535	0.0029
50	0.9960	0.9920	0.0321	0.0010	−0.0477	0.0023	0.0678	0.0046
51	0.9732	0.9471	0.1322	0.0175	−0.1464	0.0214	0.1184	0.0140
52	0.9805	0.9614	−0.1596	0.0255	0.1146	0.0131	0.0093	0.0001
53	0.9930	0.9860	−0.0942	0.0089	0.0337	0.0011	0.0624	0.0039
54	0.9884	0.9769	−0.1076	0.0116	0.0004	0.0000	0.1073	0.0115
55	0.9476	0.8979	−0.2121	0.0450	−0.0707	0.0050	0.2283	0.0521
56	0.9003	0.8105	0.2876	0.0827	0.2147	0.0461	−0.2463	0.0607
57	0.9833	0.9669	0.1191	0.0142	0.1263	0.0160	−0.0540	0.0029
58	0.9879	0.9759	0.0902	0.0081	0.1251	0.0157	0.0164	0.0003
59	0.9713	0.9434	0.1069	0.0114	0.1825	0.0333	0.1085	0.0118
60	0.7161	0.5128	0.2064	0.0426	−0.4395	0.1932	−0.5015	0.2515
61	0.9750	0.9506	−0.0512	0.0026	−0.1223	0.0150	−0.1785	0.0319
62	0.9927	0.9855	−0.0211	0.0004	−0.0570	0.0032	−0.1040	0.0108
63	0.9966	0.9932	−0.0114	0.0001	−0.0343	0.0012	−0.0747	0.0056
64	0.9980	0.9960	−0.0070	0.0000	−0.0233	0.0005	−0.0588	0.0035
65	0.9987	0.9974	−0.0047	0.0000	−0.0170	0.0003	−0.0486	0.0024
66	0.9990	0.9980	−0.0033	0.0000	−0.0130	0.0002	−0.0415	0.0017
67	0.9993	0.9986	−0.0025	0.0000	−0.0103	0.0001	−0.0363	0.0013
68	0.9994	0.9988	−0.0019	0.0000	−0.0084	0.0001	−0.0322	0.0010
69	0.9996	0.9992	−0.0015	0.0000	−0.0070	0.0000	−0.0289	0.0008
70	0.9996	0.9992	−0.0012	0.0000	−0.0059	0.0000	−0.0262	0.0007

mixing coefficient C_i^2 are given in Table 4 for the interaction $A^1\Sigma_u^+$ ($v=4$) − $b^3\Pi_u$ ($v=10$). The curves of the variation of C_i^2 versus J are illustrated in Figure 2.

3. Discussion

The results reported here for the RKR potential curve with the vibrational term values $G(v)$ for the deperturbed levels of the A state are in very good agreement with those obtained by Kaminsky [3]. Our estimates of $G(v)$ are smaller, on the average, than those of Kaminsky by about (0.018 cm^{-1}) for $0 \leqq v \leqq 7$ and larger by about (0.031 cm^{-1}) for $8 \leqq v \leqq 15$. This is due to the slight differences between our B_v constants published and discussed in [1], and those of Kaminsky [3]. The RKR potential curve of the $b^3\Pi_u$ state is

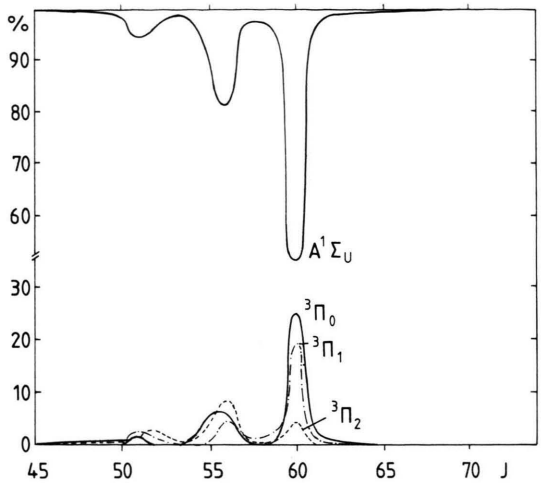

Fig. 2. Variation with J of the percentage of $b^3\Pi_{0e}$ ($v=10$), $b^3\Pi_{1e}$ ($v=10$) and $b^3\Pi_{2e}$ ($v=10$) character in the perturbed $A^1\Sigma_u^+$ ($v=4$) level.

derived from constants which satisfy the results of earlier work [5, 6], and give a good representation of the deperturbed levels of the $b^3\Pi_u$ state in the range $v=6$ to $v=25$ [1]. The values of the Franck-Condon factors between the A and b states, given in Table 3, reflect the observed strength of interaction rather well within the range of the observed vibrational levels; cf. e.g. the perturbations of the $(A^1\Sigma_u^+)_{v=4}-(b^3\Pi_u)_{v=10}$ and $(A^1\Sigma_u^+)_{v=1}-(b^3\Pi_u)_{v=8,7}$ levels, which are illustrated in the Figs. 3 and 4 of [1], respectively. The variation with J of the percentage of $^3\Pi_{0e}$ ($v=10$), $^3\Pi_{1e}$ ($v=10$) and $^3\Pi_{2e}$ ($v=10$) character in the perturbed $A^1\Sigma_u^+$ ($v=4$) level, given in Table 4, was fitted for the interaction illustrated in the Fig. 3 of [1]. This is in close agreement with the curves illustrated in Figure 2.

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