An analysis of the $A\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ band system of $^7\mathrm{Li}_2$[a)]

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A new analysis of the $A\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ band system of $^7\mathrm{Li}_2$ has been made. The analysis extends from $v' = 0$ to $v' = 25$, from $v'' = 0$ to $v'' = 14$, and up to $J = 78$. The dissociation energy of the A state is found to be 8940 cm^{-1}, considerably less than any earlier estimate of that energy. The RKR potential curves for the A and X states are given, together with the Franck–Condon factors for the A–X transition.

INTRODUCTION

The present work is a reanalysis of the $A\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ band system of $^7\mathrm{Li}_2$. The data on which the analysis is based is that used by Hsu[1] in an analysis of the same system. Our interest[2] in the A–X system of Na_2 led us to examine the A–X system of Li_2. We were given access to the data for Li_2 and the inadequacy of the initial analysis became apparent.[3] The experimental procedures that were used in photographing the absorption spectrum of Li_2, as well as the procedures for obtaining a tabulation of line frequencies from the photographic plates, are discussed by Hsu. The resulting data are of high quality. Approximately 18 000 lines within a frequency range of 7180 cm^{-1} were measured for the A–X system. The mean separation between adjacent lines is then about 0.400 cm^{-1}, although the density of lines varies considerably throughout the spectrum. There are obviously many instances of the merging of several lines into a single, perhaps broad line, and of marginally resolved lines.

The high density of lines is, of course, an invitation to the misassignment of lines through the statistical occurrence of coincidences between preliminary calculated line frequencies and observed lines. The probability of a coincidence depends on the range of allowed deviations of the observed line frequencies from those calculated from an accepted formula. The effect of such assignment was[1] a distribution in J without the expected high density at the most probable J'', the paucity of R–P pairs with the same J'' or J', the more or less constant number of lines assigned to each v', v'', and excessive deviations between observed and calculated line frequencies as judged by the deviations of line frequencies in regions at low v' where the assignments are correct.

THE ANALYSIS

The analysis of Hsu, an extension of that of McKellar and Jenkins,[4] is essentially correct through $v' = 7$. By the use of combination differences and manual extrapolation from the observed line frequencies in this range we were able to identify bands up through $v' = 19$. One criterion for the initial assignment of lines was that both members of the R, P pair (J', $J'' = J' - 1$) and (J', $J'' = J' + 1$) must occur and that the difference $\Delta_2 F''$ must be closely the same as that found for $v' < 7$ for the same v''. It was also required that several sequential R, P pairs be observed. When a body of data with a large presumption of correctness had been developed for some v' and some v'', the presumption of correctness became a certainty when a body of data for another v'' and the same v' was found; the additional test that could then be made was that the difference $\Delta_2 F'$ between the frequencies of the lines ($J' = J'' + 1$, J'') and ($J' = J'' - 1$, J'') be the same for a particular v' and all v''. With the extensive data from the manual extrapolation a least squares solution was made to determine the constants in the Dunham equation. The equation then predicted frequencies which were a sound guide to further assignments. We have been able to make unambiguous assignments through $v' = 25$.

The final determination of the Dunham coefficients is based on 2306 lines that were chosen from a much larger number of assigned lines. The data include 2136 lines in R, P pairs with a common J', 75 lines not included in 2136 but which are members of R, P pairs with a common J'', and 95 lines whose J' or J'' do not appear elsewhere in the set of chosen lines for a particular v', v''.

We have not systematically tried to identify all the lines that fit the formula and are part of a reasonably continuous array of lines.

For $v' = 1$ we find 681 lines that fit the final formula with a deviation δ, $|\delta| \leq 0.015$ cm^{-1}, and 169 lines that fit with $0.016 \leq |\delta| \leq 0.025$ cm^{-1}, so that 850 lines can be assigned; 195 of these lines are used as input data to the least squares solution. For $v' = 2$, 634 lines have $|\delta| \leq 0.015$ cm^{-1} and 159 lines have $0.016 \leq |\delta| \leq 0.025$ cm^{-1}, to yield 793 total assigned lines; 107 of these lines are used in the least squares solution . For $v' = 7$, 375 lines may be assigned and 146 appear in the analysis.

In Table I the Franck–Condon factors for transitions between v' and v'' are shown. The underlined Franck–Condon factors indicate those bands that were used in the final determination of the Dunham coefficients.

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TABLE I. Franck–Condon factors[a] for the $A\,^1\Sigma_u^+$–$X\,^1\Sigma_g^+$ transition of $^7Li_2$ for $J=0$. (The v' and v'' of the FCF that are underlined identify the bands used in the analysis.)

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0	$\underline{52}$	$\underline{176}$	$\underline{270}$	$\underline{250}$	$\underline{156}$	$\underline{68}$	$\underline{21}$	5	1						
1	$\underline{134}$	$\underline{197}$	$\underline{58}$	9	$\underline{134}$	$\underline{211}$	$\underline{159}$	$\underline{72}$	22	4	1				
2	$\underline{187}$	$\underline{79}$	15	$\underline{127}$	$\underline{56}$	8	$\underline{129}$	$\underline{197}$	$\underline{135}$	$\underline{53}$	13	2			
3	190	3	$\underline{98}$	$\underline{45}$	25	$\underline{112}$	25	31	$\underline{163}$	$\underline{180}$	$\underline{95}$	28	5		
4	$\underline{157}$	18	$\underline{90}$	4	$\underline{92}$	9	61	$\underline{85}$		$\underline{92}$	$\underline{192}$	$\underline{139}$	50	9	1
5	$\underline{113}$	$\underline{68}$	27	$\underline{60}$	30	39	62	5	95	30	30	$\underline{171}$	$\underline{176}$	77	16
6	$\underline{73}$	$\underline{102}$			2	$\underline{71}$	2	75	9	57	71	1	$\underline{128}$	199	107
7	$\underline{43}$	$\underline{105}$	21	$\underline{37}$	44	19	48	22	39	46	14	91	7	$\underline{81}$	$\underline{208}$
8	$\underline{24}$	$\underline{88}$	56	3		3	54	8	55	5	67		80	31	42
9	13	$\underline{64}$	$\underline{78}$	6	$\underline{39}$	37	11	50	3	55	3	59	13	52	57
10	7	42	$\underline{80}$	31	7	55	4	40	19	27	29	25	32	37	24
11	3	$\underline{26}$	68	$\underline{55}$	1	37	33	5	47		47	5	46	9	55
12	2	$\underline{15}$	$\underline{51}$	$\underline{66}$	17	10	48	5	28	29	8	43	1	51	
13	1	$\underline{8}$	$\underline{35}$	$\underline{64}$	39		34	30	2	41	6	28	24	13	39
14		$\underline{4}$	22	$\underline{53}$	$\underline{53}$	9	11	42	7	18	33		39	6	30
15		2	$\underline{14}$	$\underline{40}$	$\underline{56}$	27		31	28		34	14	11	35	
16		1	$\underline{8}$	$\underline{28}$	$\underline{51}$	42	5	12	37	8	11	34	1	26	21
17		1	5	$\underline{18}$	$\underline{42}$	49	19	1	28	26		26	21	2	33
18			2	$\underline{12}$	$\underline{31}$	48	33	3	12	33	10	7	31	6	12
19			1	$\underline{7}$	$\underline{22}$	$\underline{41}$	41	13	1	25	25		19	24	
20			1	4	$\underline{15}$	$\underline{33}$	43	26	1	11	30	10	3	27	12
21				2	9	$\underline{24}$	39	35	9	2	23	23	1	13	25
22				1	$\underline{6}$	$\underline{17}$	$\underline{33}$	38	20	1	11	27	11	1	22
23				1	$\underline{4}$	$\underline{12}$	$\underline{26}$	$\underline{36}$	29	6	2	21	22	2	9
24					2	$\underline{8}$	$\underline{19}$	32	33	15		11	25	11	
25					1	$\underline{5}$	$\underline{14}$	$\underline{27}$	$\underline{34}$	23	4	3	19	20	2

[a] The Franck–Condon factors are multiplied by 10^3.

There are several bands characterized by a high FCF which have not been included in the analysis. In the case of $v'=3$, $v''=0$ the R line $J'=J''+1$, J'' and the P line $J'=J''-6$, $J''-5$ coincide within 0.100 cm^{-1} or less up to $J''=40$. Beginning with $J''=47$, both the R and P branches are well resolved. In the case of $v'=6$, $v''=3$ there is a very close overlap of R and P branches up to at least $J''=80$ for R and $J''=75$ for P.

In general, the number of assigned lines decreases with increasing v', since the large Franck–Condon factors occur at relatively high v'', where the thermal population is small.

The maximum J' that has entered into our solution decreases approximately monotonically from 78 at $v'=0$ to 41 at $v'=24$. The maximum J'' decreases approximately monotonically from 79 at $v''=0$ to 57 at $v''=10$, after which it decreases more rapidly.

Our assigned line frequencies to specified quantum numbers are higher than those of Hsu by about 44 cm^{-1} for $v'=23$, and about 66 cm^{-1} for $v'=25$; there is a considerable dependence of the difference on J.

RESULTS

The 2306 line frequencies that entered into the least squares solution to determine the coefficients in the Dunham expansion are reproduced by the final expansion with an rms deviation of 0.0126 cm^{-1}. Presumably, this could be decreased by rejecting lines that are described in the data as broad, overlapped, as wings on a strong line, etc.

In Table II are tabulated the coefficients in the conventional Dunham expansion. They are recorded as generated by the computer; the large number of digits that describe each coefficient is not an indication of its detailed accuracy. Experience in other contexts has shown us that essentially trivial additions to or deletions from the input data can modify the constants far beyond the rms uncertainties in the constants. The addition of further constants or the deletion of constants with an rms uncertainty that approaches the value of the constant may also alter other constants far beyond the calculated rms uncertainties.

TABLE II. The Dunham coefficients that describe two electronic states of $^7Li_2$ for J up to 78. (The quantities in parentheses are the exponents of 10 in the multiplying factor.)

i,k	$Y'_{i,k}(A\,^1\Sigma_u^+)$, cm^{-1} Fit of data from $v'=0$ to 25	Standard error	$Y''_{i,k}(X\,^1\Sigma_g^+)$, cm^{-1} Fit of data from $v''=0$ to 14	Standard error
T_e	1.4068307 (+4)	4.5 (−3)		
1,0	2.5546730 (+2)	2.1 (−3)	3.5141581 (2)	4.1 (−3)
2,0	−1.5813606 (0)	4.5 (−4)	−2.5827623 (0)	1.7 (−3)
3,0	3.1279089 (−3)	4.0 (−5)	−6.4041995 (−3)	2.8 (−4)
4,0	−3.4636432 (−5)	1.6 (−6)	−7.3938699 (−5)	2.1 (−5)
5,0	−1.1889202 (−6)	2.4 (−8)	−7.6540631 (−6)	5.7 (−7)
0,1	4.9742376 (−1)	1.2 (−5)	6.7244814 (−1)	1.2 (−5)
1,1	−5.4806486 (−3)	2.2 (−6)	−7.0617658 (−3)	4.6 (−6)
2,1	2.0050727 (−5)	3.0 (−7)	−2.7060594 (−5)	1.2 (−6)
3,1	−1.5581199 (−7)	1.6 (−8)	−9.4563226 (−7)	1.2 (−7)
4,1	−1.1224970 (−8)	2.8 (−10)	−5.2529751 (−8)	4.0 (−9)
0,2	−7.4686053 (−6)	4.7 (−9)	−9.7223890 (−6)	4.9 (−9)
1,2	6.5422452 (−8)	6.8 (−10)	−3.0986819 (−8)	1.5 (−9)
2,2	−6.7280669 (−10)	5.4 (−11)	−2.6753859 (−9)	2.9 (−10)
3,2	−2.6735925 (−11)	1.7 (−12)	−7.4907372 (−11)	1.3 (−11)
0,3	9.7508943 (−11)	5.2 (−13)	1.1692368 (−10)	5.3 (−12)
1,3	−1.6434785 (−12)	6.4 (−14)	−3.6571198 (−15)	1.5 (−13)
2,3			6.0005462 (−14)	2.3 (−14)

TABLE III. RKR potential curve for $^7Li_2$.

	$A\,^1\Sigma_u$ state			$X\,^1\Sigma_g$ state		
V	$G(v')$, cm^{-1}	r_{min}, Å	r_{max}, Å	$G(v'')$, cm^{-1}	r_{min}, Å	r_{max}, Å
−0.5	0	3.10821		0	2.67328	
0	127.068	2.92572	3.31424	175.032	2.51723	2.84898
1	379.382	2.80523	3.48214	521.261	2.41389	2.99213
2	628.561	2.72829	3.60688	862.264	2.34761	3.09889
3	874.621	2.66912	3.71422	1197.997	2.29646	3.19120
4	1117.578	2.62028	3.81163	1528.413	2.25414	3.27546
5	1357.446	2.57838	3.90253	1853.457	2.21775	3.35457
6	1594.237	2.54154	3.98881	2173.072	2.18570	3.43021
7	1827.964	2.50858	4.07164	2487.191	2.15700	3.50342
8	2058.635	2.47872	4.15185	2795.742	2.13099	3.57495
9	2286.258	2.45140	4.23000	3098.641	2.10720	3.64533
10	2510.838	2.42622	4.30653	3395.798	2.08529	3.71501
11	2732.380	2.40287	4.38177	3687.109	2.06499	3.78434
12	2950.883	2.38109	4.45601	3972.462	2.04609	3.85365
13	3166.347	2.36069	4.52946	4251.731	2.02845	3.92321
14	3378.766	2.34151	4.60232	4524.776	2.01193	3.99331
15	3588.135	2.32343	4.67477			
16	3794.444	2.30634	4.74694			
17	3997.679	2.29014	4.81898			
18	4197.825	2.27475	4.89101			
19	4394.862	2.26011	4.96316			
20	4588.768	2.24616	5.03553			
21	4779.516	2.23285	5.10826			
22	4967.075	2.22013	5.18144			
23	5151.413	2.20797	5.25522			
24	5332.491	2.19634	5.32968			
25	5510.266	2.18519	5.40497			

The approximate relationship $4(Y_{0,1})^3\ (Y_{0,1})^{-2} \simeq Y_{0,2}$ offers a test of the consistency of the solution. For the upper, A state $Y'_{0,2}(\text{obs}) = -7.469\times10^{-6}$ cm^{-1}; the calculated value is -7.543×10^{-6} cm^{-1}. The discrepancy is 1%. For the lower, X state $Y''_{0,2}(\text{obs}) = -9.722\times10^{-6}$ cm^{-1}; the calculated value is -9.864×10^{-6} cm^{-1}. The discrepancy is 1.5%. In both cases the discrepancy is much greater than that which is allowed by the rms uncertainties of the constants. Nevertheless, the agreement of the calculated and observed values of $Y_{0,2}$ is satisfactory because of the strong coupling between the constants.

The RKR potential curve, together with the vibrational term values $G(v')$ and $G(v'')$, are given for both the A and X states in Table III. The curves are calculated only for the range of levels we have observed.

The intervals between the vibrational levels of the A state become zero at $v' = 59$ as determined from our $Y'(n, 0)$. This leads to a dissociation energy D'_e of 8940 cm^{-1}, where the uncertainties in the Dunham coefficients lead to an uncertainty of about ± 50 cm^{-1} in D'_e. The vibrational energy is 5510 cm^{-1} for $v' = 25$, the highest observed state. Hsu states that the molecule dissociates at $v' = 45$ and that $D'_e = 9469$ cm^{-1}. This requires that the mean vibration interval be 208 cm^{-1}, where the first interval is 255 cm^{-1} and the last interval is zero. This is clearly impossible.

Dissociation of the X state occurs at $v'' = 40$ where the vibrational energy becomes $D''_e = 8541$ cm^{-1}. This is in agreement with the conclusion of Stwalley[5] that the best estimate of D''_e is 8615 ± 100 cm^{-1}. With this value of D''_e, the atomic excitation energy of 14904 cm^{-1} and $T_e = 14068$ cm^{-1}, we find $D'_e = 9451$ cm^{-1}. This is in marked disagreement with $D'_e = 8940$ cm^{-1} obtained from the analytic extrapolation to dissociation of the energies of the vibrational levels of the A state. There are, of course, other possible ways of extrapolating vibrational energies to dissociation. The present well defined discrepancy may serve as a guide in formulating a valid procedure for extrapolating to dissociation.

There is a substantial residual problem related to the A–X system. It is well developed at a lower temperature than the B–X system, and its origin is more than 5000 cm^{-1} below that of the B–X system. The net effect is that the A–X system is virtually isolated from the B–X system.

A very rough approximation of the number of lines that can be confidently assigned in the framework and range of the present analysis is about 8000. There are undoubtedly many instances of the assignment of two or more sets of quantum numbers to a single line. There must also be accidental assignments. This leaves very approximately 10 000 unassigned lines mostly at the high frequency end of the spectrum. There can be no doubt of the quality of the data at high frequencies since many lines have been assigned from this region of the spectrum. Within the limitations imposed by the thermal population of levels in the X state and the FCF for transitions, it is unlikely that another 8000 lines could be assigned.

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ham University, 1974, University Microfilms, Ann Arbor, Michigan.

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[3] One of us (P. K.) sent a detailed criticism of the analysis to Hsu early in 1976. He has not reexamined the problem.

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