

$B^3\Pi_{0_u^+}-X^1\Sigma_g^+$ System of $^{127}\text{I}_2$: Rotational Analysis and Long-range Potential in the $B^3\Pi_{0_u^+}$ State

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The results of detailed rotational and term-value analyses involving some 7000 lines with 58 levels in $B^3\Pi_{0_u^+}$ ($4 \leq v \leq 77$) and 6 levels in $X^1\Sigma_g^+$ ($0 \leq v \leq 5$) are given. For the $B^3\Pi_{0_u^+}$ state the rotational constants B_v can be represented by $B_v = \sum_{n=0}^4 c_n(v + \frac{1}{2})^n$, but neither the vibrational levels nor the centrifugal stretching constants follow simple polynomials in $(v + \frac{1}{2})$. At high v , $(\overline{\Delta G_v})^{10/7}$ is linear in E_v and a short extrapolation leads to a value of the limit, $20\,043.208 \pm 0.033 \text{ cm}^{-1}$, relative to $X^1\Sigma_g^+$ ($v = 0, J = 0$). The highest bound vibrational level has $v = 87$. An RKR potential energy curve has been calculated for the $B^3\Pi_{0_u^+}$ state, and a consistent value of the limit, $20\,043.220 \pm 0.015 \text{ cm}^{-1}$, is obtained from a fit to an attractive part of the curve near the limit, assuming a potential $V(r) = -C_5/r^5 - C_6/r^6 - C_8/r^8$. Values of the long-range interaction constants have been obtained: the term in r^{-6} is not negligible even at internuclear distances as large as 20 \AA . The ground-state dissociation energy, $D_0(\text{I}_2)$ is found to be $12\,440.1 \text{ cm}^{-1}$, corresponding to $35.568 \text{ kcal mol}^{-1}$ or $148.815 \text{ kJ mol}^{-1}$.

The $B^3\Pi_{0_u^+}-X^1\Sigma_g^+$ system of molecular iodine has been much studied in absorption, emission and fluorescence¹⁻¹¹ in part because of its strength and accessibility. The relatively shallow potential energy curve in the upper state and favourable Franck-Condon factors lead to the observation in absorption of a wide range of vibrational levels of the $B^3\Pi_{0_u^+}$ state. Some rotational-vibrational levels can be selectively populated by monochromatic radiation using lasers¹¹⁻¹⁸ and atomic emission lines^{3, 9, 19} so that the B state has often been used for the study of lifetimes,^{20, 21} photodissociation^{22, 23} and photochemical²⁴⁻²⁶ and energy transfer processes.^{9, 11, 19} Fluorescence from monochromatically excited levels in the upper state provides a means of investigating intensity distributions in transitions to different ground state levels and therefore of determining relative Franck-Condon factors which in turn provide tests of the accuracy of the potential energy curves.^{7, 27-29}

In the past few years interest in this system has been stimulated both by the rapid development of tunable lasers^{21, 30} with which molecular hyperfine structures^{16, 31-36} can be studied and by theoretical interest in the long range potential³⁷⁻⁴⁰ near the dissociation limit of the B state.

Despite the importance of the system, it is poorly characterized, especially in respect of the excited state, and this, for example, has led to erroneous identification and assignment of several resonance fluorescence series.^{3, 10-13, 18, 19} Although head measurements² exist for a large number of bands, the rotational structure of relatively few vibrational levels has been analyzed.^{1, 7-10} The present paper reports the rotational and term-value analyses of 64 bands with $4 \leq v' \leq 77$ and $0 \leq v'' \leq 5$ together with the results of a detailed study of the energy levels near the dissociation limit of the B state. We have confined ourselves to $^{127}\text{I}_2$ and the emphasis is on the excited state, although the first six levels of the ground state have also been analyzed. Higher levels of the ground state are best studied by resonance fluorescence.^{5, 6, 41, 42}

ROTATIONAL ANALYSIS AND MOLECULAR CONSTANTS

The experimental details have already been described.¹¹ The analysis was straightforward, for the bands consist of single unperturbed R and P branches, except that there is, especially at high v' , a good deal of overlapping of lines. In some regions the intensity alternation⁴³ with odd J'' strong, even J'' weak (1.4 : 1) is clearly observed. Sixty bands in the region 4985 to 6500 Å with $4 \leq v' \leq 77$, $8 \leq J' \leq 129$ and $0 \leq v'' \leq 5$, $7 \leq J'' \leq 130$ have been analyzed: they are summarized in table 1. A preliminary set of constants was obtained by fitting the observed molecular lines to the expression

$$v_m = v_0 + 2Bm + \Delta Bm(m+1) + 4Dm^3 - \Delta Dm^2(m+1)^2$$

where $m = J+1$ for an R line, $m = -J$ for a P line, v_0 is the band origin, B and D are the lower state constants and $\Delta B = B'' - B'$, $\Delta D = D'' - D'$. Where duplication occurred, the agreement between the present analysis and that given in ref. (10) is generally poor, and we conclude that these reported bands should be ignored. On the other hand, agreement with the analysis given in ref. (7) is reasonably good, generally to within about $\pm 0.02 \text{ cm}^{-1}$.

TABLE 1.—SUMMARY OF ROTATIONAL ANALYSIS OF THE $B^3\Pi_{0,u} - X^1\Sigma_g^+$ SYSTEM OF I_2

v	v	band	v''	rotational range		number of molecular lines	
				J_{\min}	J_{\max}	R branch	P branch
				$B^3\Pi_{0,u}$			
77	77	0	12	26	13	12	
76	76	0	11	28	17	15	
75	75	0	8	30	22	21	
74	74	0	8	38	29	29	
73	73	0	10	41	31	30	
72	72	0	9	42	34	32	
71	71	0	9	45	36	37	
70	70	0	11	47	36	34	
69	69	0	11	51	39	40	
68	68	0	10	53	43	42	
67	67	0	10	54	44	43	
66	66	0	8	51	44	41	
65	65	0	12	58	45	46	
64	64	0	11	65	55	54	
63	63	0	22	66	45	44	
62	62	0	25	66	41	42	
61	61	0	20	62	43	43	
60	60	0	22	67	46	43	
59	59	0	8	61	52	52	
58	58	0	20	62	40	40	
57	57	0	19	59	39	40	
56	56	0	17	62	44	45	
55	55	0	17	67	50	48	
54	54	0	15	73	56	56	
53	53	0	17	73	51	54	
52	52	0	18	64	46	43	
51	51	0	17	62	45	42	
50	50	0	12	50	36	35	
49	49	0	8	82	69	75	
48	48	0	15	82	66	66	
47	47	0	12	99	86	87	

TABLE 1.—*contd.*

ν	ν'	band	ν''	rotational range		number of molecular lines	
				J_{\min}	J_{\max}	R branch	P branch
$B^3\Pi_{0,\pm}$							
46	46		0	22	94	71	71
45	45		0	26	83	56	56
44	44		0	19	68	46	49
43	43		0	12	60	47	45
36	36		0	64	114	47	48
35	35		0	25	129	100	105
34	34		0	12	104	88	88
33	33		0	17	96	75	75
32	32		0	7	87	68	63
29	29		0 ^a	8	70	53	50
25	25		0 ^a	9	58	38	42
21	21		1	57	124	62	68
20	20		1	21	99	77	78
19	19		1	21	111	87	89
18	18		1	22	93	70	65
	18		0	26	98	70	73
17	17		0	12	90	74	79
16	16		0	28	93	64	63
13	13		2 ^a	16	73	45	54
12	12		2 ^a	16	72	54	44
11	11		3	24	105	82	76
	11		1 ^a	25	99	65	32
10	10		4	33	110	68	70
9	9		4	20	120	93	100
	9		2	23	104	81	75
8	8		4	9	67	51	51
	8		3	34	106	65	65
7	7		5	14	88	67	67
	7		4	22	111	82	81
	7		3	9	65	49	49
6	6		3	27	78	44	44
5	5		4	19	72	44	43
	5		3	24	94	63	62
4	4		3	32	90	50	48
$X^1\Sigma_g^+$							
5	7-5			15	87		
4	5 bands			10	120		
3	6 bands			23	105		
2	3 bands			15	103		
1	5 bands			22	125		
0	45 bands			7	130		

^a Bands from ref. (7) with slight revisions.

A final set of molecular constants was obtained from a term-value analysis, using the method devised by Åslund⁴⁴ with a total of 64 bands and about 7000 lines. All bands from the present analysis except the 7-3 band, which is badly blended by mutual overlapping of the R and P branches, were used, along with the slightly revised bands 11-1, 12-2, 13-2, 25-0 and 29-0 from ref. (7). The term values $Y_{v,J}$ for the rotational levels of each vibrational level of the upper and lower states calculated relative to a pair of arbitrary reference levels were fitted by least squares to the expression⁴⁴

$$Y_{v,J} = (-1)^J X + T_0 + B_v J(J+1) - D_v J^2(J+1)^2$$

where X is a constant connecting the two sub-sets of term-values and T_0 is the rotationless vibrational term-value relative to an arbitrary level. The final molecular constants for the two states are given in table 2.

TABLE 2.—SUMMARY OF MOLECULAR CONSTANTS^a (cm^{-1}) OBTAINED FROM TERM VALUES ANALYSIS OF THE $B^3\Pi_{0_u^+} - X^1\Sigma_g^+$ SYSTEM OF I_2

v	$T_{v,J=0}^b$	$10^2 B_v$	$10^8 D_v$
		$B^3\Pi_{0_u^+}$	
77	20 038.162±35	0.4297±180	38.340±20.62
76	36.396±16	0.4560±81	11.890±8.72
75	34.141±5	0.5262±26	33.370±2.75
74	31.473±6	0.5709±22	26.470±1.44
73	28.312±7	0.6092±18	19.470±1.04
72	24.558±4	0.6569±12	16.965±668
71	20.176±4	0.7064±11	17.628±513
70	15.123±8	0.7557±18	17.610±763
69	09.356±4	0.7988±8	14.225±324
68	02.797±5	0.8443±10	12.655±349
67	19 995.385±4	0.8906±8	11.755±277
66	87.080±4	0.9366±8	10.940±296
65	77.826±4	0.9803±7	9.411±194
64	67.543±5	1.0288±6	9.573±132
63	56.222±13	1.0717±12	8.393±259
62	43.803±14	1.1154±13	7.600±268
61	30.230±9	1.1572±10	6.530±237
60	15.416±12	1.2059±11	7.217±230
59	899.356±4	1.2491±6	6.775±178
58	81.998±10	1.2909±12	6.492±277
57	63.273±7	1.3322±9	5.732±245
56	43.133±7	1.3744±8	5.296±196
55	21.559±6	1.4144±7	4.703±139
54	798.455±4	1.4576±4	4.939±72
53	73.843±4	1.4983±4	4.751±74
52	47.667±5	1.5364±5	4.131±117
51	19.840±6	1.5755±8	3.706±190
50	690.358±6	1.6171±12	4.423±462
49	59.166±5	1.6530±4	3.575±62
48	26.194±5	1.6910±4	3.378±54
47	591.417±4	1.7294±2	3.327±26
46	54.808±5	1.7672±3	3.229±32
45	16.359±7	1.8025±5	2.941±64
44	475.966±6	1.8400±6	2.880±113
43	33.666±4	1.8736±5	2.022±143

TABLE 2.—*contd.*

v	$T_{v,J=0^b}$	$10^2 B_v$	$10^8 D_v$
$B^3\Pi_{0^+}$			
36	081.049±14	2.1099±4	2.104±21
35	22.466±4	2.1398±1	1.985±7
34	18 961.744±2	2.1690±1	1.824±10
33	898.901±2	2.1982±1	1.701±15
32	33.951±6	2.2264±3	1.517±35
29	626.423±3	2.3114±4	1.611±76
25	320.695±5	2.4116±8	0.432±253
21	17 982.338±15	2.5104±4	1.141±20
20	892.948±6	2.5290±3	0.839±31
19	01.497±6	2.5506±3	0.798±31
18	708.114±4	2.5727±2	0.867±28
17	612.850±4	2.5945±3	1.013±35
16	515.711±7	2.6142±4	0.875±38
13	213.115±3	2.6707±3	0.125±59
12	108.716±4	2.6924±4	0.743±67
11	002.563±4	2.7124±2	0.952±20
10	16 894.664±5	2.7292±2	0.834±14
9	785.033±3	2.7472±1	0.844±8
8	673.690±4	2.7656±2	0.885±20
7	560.715±3	2.7816±1	0.791±9
6	446.071±6	2.7971±4	0.529±50
5	329.769±3	2.8153±2	0.766±21
4	211.859±9	2.8315±5	0.725±51
$X^1\Sigma_g^+$			
5	1 054.072±3	3.6741±2	0.575±21
4	845.732±3	3.6859±1	0.551±6
3	636.130±4	3.6985±2	0.624±18
2	425.307±3	3.7087±1	0.507±15
1	213.302±5	3.7199±2	0.409±12
0	0.0	3.73129±7	0.459±4

^a Error limits in this table and throughout the paper are one standard error. ^b $T_{v,J=0}$ is the vibrational term value relative to $X^1\Sigma_g^+$ ($v=0, J=0$).

The experimental values for the ground state can be represented adequately by two-constant expressions

$$G_v = \omega_e(v + \frac{1}{2}) - x_e \omega_e (v + \frac{1}{2})^2$$

$$B_v = B_e - \alpha_e (v + \frac{1}{2})$$

$$D_v = D_e + \beta_e (v + \frac{1}{2})$$

and the constants are given in table 3. The small constant β_e is, of course, not well determined, but the value of D_e , $(4.25 \pm 0.42) \times 10^{-9} \text{ cm}^{-1}$, is in good agreement with the Kratzer value, $4.54 \times 10^{-9} \text{ cm}^{-1}$. All the ground state constants agree reasonably well with published values.

TABLE 3.—MOLECULAR CONSTANTS (cm^{-1}) FOR GROUND STATE $X^1\Sigma_g^+$ OF I_2 range of $v = 0-5$

(a) vibrational constants

$$\omega_e = 214.5016 \pm 0.014; \quad x_e\omega_e = 0.614\ 68 \pm 0.002.$$

(b) rotational constants

$$B_e = 3.737\ 19 \times 10^{-2} \pm 4.7 \times 10^{-6}$$

$$\alpha_e = 1.1376 \times 10^{-4} \pm 1.37 \times 10^{-6}$$

$$r_e = 2.6663_4 \text{ \AA} \text{ with } \mu = 63.4502 \text{ a.m.u.}$$

$$10^9 D_e = 4.25 \pm 0.42$$

$$10^9 \beta_e = 0.321 \pm 0.122$$

$$D_e \text{ (Kratzer)} = 4.54 \times 10^{-9}$$

The vibrational term-values in the upper state extend over such a wide range, $4 \leq v \leq 77$, that they cannot be fitted to a simple polynomial in $(v + \frac{1}{2})$. The values for $4 \leq v \leq 50$ have been fitted by least-squares to the expression $G_v = \sum_{n=0}^5 c_n (v + \frac{1}{2})^n$ and the values of the coefficients are given in table 4. The fit of B_v to the polynomial $\sum_{n=0}^4 c_n (v + \frac{1}{2})^n$ is reasonably satisfactory and the results are given in table 4.

TABLE 4.—MOLECULAR CONSTANTS (cm^{-1}) FOR $B^3\Pi_{0,+}$ STATE OF I_2 (a) vibrational constants: $0 \leq v < 50$

$$G_v = \sum_{n=0}^5 C_n (v + \frac{1}{2})^n$$

$$C_1 = 125.697\ 08 \pm 3.71 \times 10^{-2}; \quad C_2 = -7.642\ 44 \times 10^{-1} \pm 3.60 \times 10^{-3};$$

$$C_3 = -1.775\ 98 \times 10^{-3} \pm 1.54 \times 10^{-4}; \quad C_4 = -7.379\ 43 \times 10^{-5} \pm 2.99 \times 10^{-6};$$

$$C_5 = 1.030\ 60 \times 10^{-6} \pm 2.16 \times 10^{-8}.$$

$$T_{0,0} = 15\ 724.57; \quad T_e = 15\ 769.01.$$

(b) rotational constants

$$B_v = \sum_{n=0}^4 C_n (v + \frac{1}{2})^n \quad 0 \leq v < 77$$

$$C_0 = 2.903\ 87_6 \times 10^{-2} \pm 2.07 \times 10^{-5}; \quad C_1 = -1.581\ 90 \times 10^{-4} \pm 3.25 \times 10^{-6};$$

$$C_2 = -3.363\ 18 \times 10^{-7} \pm 1.53 \times 10^{-7}; \quad C_3 = -4.777\ 27 \times 10^{-8} \pm 2.76 \times 10^{-9};$$

$$C_4 = 3.262\ 87 \times 10^{-10} \pm 1.67 \times 10^{-11}.$$

$$r_e = 3.0248_1 \text{ \AA}$$

$$10^9 D_e = 5.43 \pm 1.44$$

$$10^9 \beta_e = 0.300 \pm 0.186 \quad 0 \leq v < 10$$

$$D_e \text{ (Kratzer)} = 6.20 \times 10^{-9}.$$

The variation of the values of B_v and D_v with v is illustrated in fig. 1. D_v changes little with v below about $v = 20$, but increases very rapidly at $v > 30$. The values of D_v over the whole range of v , cannot be fitted to a simple polynomial. A limited linear fit for $v \leq 10$ gives $D_e = (5.43 \pm 1.44) 10^{-9} \text{ cm}^{-1}$, in reasonable agreement with the Kratzer value $6.2 \times 10^{-9} \text{ cm}^{-1}$.

It is clear that representation of the molecular constants for the $B^3\Pi_{0,+}$ state over the wide range of v by simple polynomials in $(v + \frac{1}{2})$ is not very successful, and the experimental values of $T_{v,J=0}$, B_v and D_v should be used for both states, B and X . Missing values of G_v and of B_v in the excited state can be calculated using the coefficients in table 4. Similarly missing values of D_v can be calculated or obtained from the curve in fig. 1.

The extensive lists of molecular lines and vibrational rotational term-values are too lengthy to publish here but may be obtained on request. Alternatively lines and term-values can be generated using the constants in tables 2, 3 and 4: these are capable of reproducing the observed unblended lines to within $\pm 0.02 \text{ cm}^{-1}$.

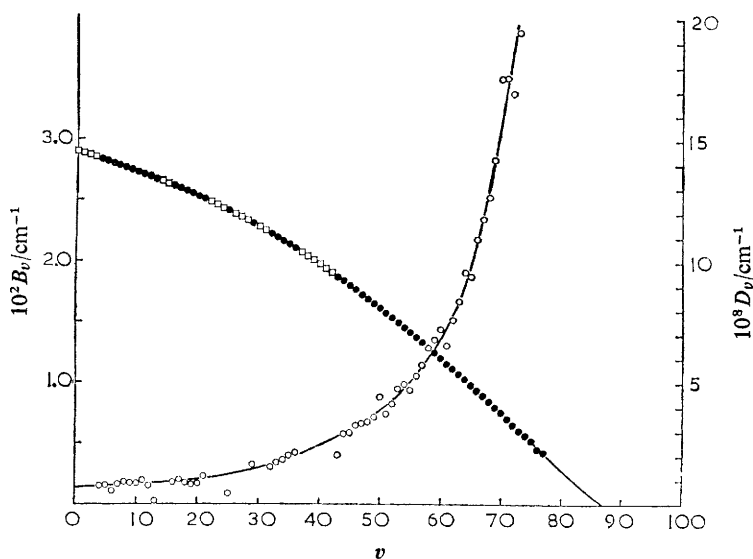


FIG. 1.—The variation of B_v with v (left-hand scale) and D_v with v (right-hand scale) for the $B^3\Pi_{0,u}$ state of I_2 . The B_v values represented by open squares are calculated from the constants given in table 4.

ANALYSIS OF THE LONG-RANGE POTENTIAL IN THE $B^3\Pi_{0,u}$ STATE

A. VIBRATIONAL ENERGY LEVELS NEAR THE DISSOCIATION LIMIT

Recently LeRoy and Bernstein³⁷ have derived an expression

$$G_v = D - [(v_D - v)H_m]^{2m/(m-2)}, \quad m \neq 2 \quad (1)$$

which relates the distribution of vibrational eigenvalues G_v near the dissociation limit D to the attractive long-range part of the internuclear potential

$$V(r) = - \sum_{m \geq n} C_m / r^m \quad (2)$$

Here v_D is an effective vibrational index, in general non-integral, at the dissociation limit, and H_m is a constant depending on the reduced mass μ , the long-range coefficient C_m and the local value m in (2) where n is the asymptotic value of the inverse powers of the internuclear distance r . Truncating v_D to an integer gives the highest bound vibrational level supported by the internuclear potential.

The applicability of (1) is limited to cases where the Birge-Sponer plot⁴⁵ shows positive curvature for the levels near D , as appears for the B state of I_2 (fig. 2).

If, in the region near the dissociation limit the density of vibrational levels is sufficiently great, the dissociation energy can be determined with the use of the approximate expression³⁷

$$(\overline{\Delta G_v})^{2n/(n+2)} = [D - G_v](K_n)^{2n/(n+2)} \quad (3)$$

where $\overline{\Delta G_v} = \frac{1}{2}(G_{v+1} - G_{v-1})$, and, with $m = n$ in (1), $K_n = [2n/(n-2)]H_n$. If the

conditions for (1) and (3) are satisfied and n is known⁴⁶ the long-range parameters D , v_D , H_n , K_n and hence C_n can be obtained graphically. We used

$$G_v = D - k[\overline{\Delta G}_v]^{2n/(n+2)} \quad (4)$$

$$v = v_D - h[D - G_v]^{(n-2)/2n} \quad (5)$$

where $k = 1/[K_n]^{2n/(n+2)}$ and $h = 1/H_n$.

LeRoy and Bernstein have concluded that for the $B^3\Pi_{0,u}$ states of the halogens $n = 5$. The effect of using different values of n in the least-squares fitting of (4) is shown in table 5 for $65 \leq v \leq 76$. Relatively large systematic deviations are found for $n = 4, 5.5$ and 6 and we conclude in agreement with LeRoy and Bernstein that the effective value of n is 5. The effect of different assumptions about the value of n on the extrapolated value of D is given in table 6.

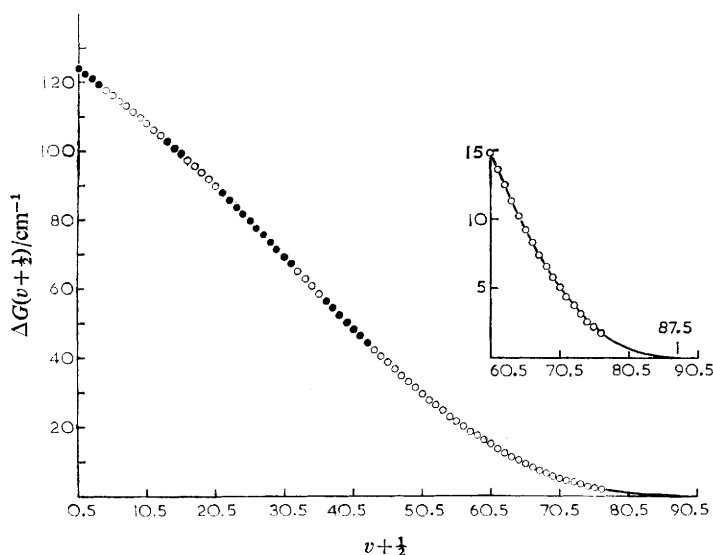


FIG. 2.—The variation of $\Delta G_{v+\frac{1}{2}}$ with $v+\frac{1}{2}$ for the $B^3\Pi_{0,u}^+$ state of I_2 showing positive curvature at the high vibrational levels. The values represented by filled circles are calculated from the constants given in table 4.

TABLE 5.—EFFECT OF USING DIFFERENT VALUES OF n IN THE LEAST-SQUARES FITTING OF EQN (4) FOR $B^3\Pi_{0,u}^+$ STATE OF I_2

v	$n = 5$	$[E_v(\text{obs.}) - E_v(\text{calc.})]/\text{cm}^{-1}$		$n = 6$
		$n = 4$	$n = 5.5$	
76	0.020	-0.526	0.235	0.423
75	0.054	-0.276	0.188	0.305
74	-0.124	-0.267	-0.063	-0.008
73	-0.077	-0.033	-0.089	-0.097
72	0.040	0.245	-0.036	-0.100
71	0.067	0.387	-0.057	-0.163
70	0.002	0.384	-0.149	-0.279
69	-0.019	0.362	-0.171	-0.304
68	0.058	0.355	-0.065	-0.173
67	0.059	0.180	0.005	-0.045
66	-0.032	-0.194	0.025	0.073
65	-0.047	-0.617	0.175	0.367

The plot of G_v against $(\overline{\Delta G_v})^{10/7}$ is illustrated in fig. 3. To within the experimental errors this plot is linear in the range $65 \leq v \leq 76$, but for $v < 64$ the slope becomes increasingly negative as v decreases. The value of D obtained by linear extrapolation of (4) is, therefore, an upper bound. However the extrapolation from the last observed level with $v = 76$ is only some 7 cm^{-1} and this, together with the relative insensitivity of the extrapolated value of D to the assumed value of n , suggests that the systematic errors in D are likely to be small.

Using the value of D determined from (4) with $n = 5$ a plot of v against $[D - G_v]^{3/10}$ may be used to determine v_D and h (fig. 4). The long-range parameters obtained from a least-squares fit for $64 \leq v \leq 77$ are given in table 6. The previous results obtained by LeRoy and Bernstein³⁷ using Brown's band-head data² (with the revised

TABLE 6.—LONG-RANGE PARAMETERS OBTAINED FROM EQN (4) AND (5) FOR THE $B^3\Pi_{0,u^+}$ STATE OF I_2

n	v_H^a	v range ^c	$10^{-5} C_n/\text{cm}^{-1} \text{ \AA}^n$	v_D	dissociation energy/ $\text{cm}^{-1} e$	ref.
4	77	64-77	2.8861 ^d	87.345 ± 0.007	$20\ 045.010 \pm 0.21$	} this work
5	77				$20\ 043.20_8 \pm 0.033$	
5.5	77				$20\ 042.550 \pm 0.07$	
6	77				$20\ 042.000 \pm 0.13$	
5	72^b	55-72 ^b	$3.10_6 \pm 0.16$	$87.74_5 \pm 0.38$	$20\ 044.040 \pm 1.2$	37

^a v_H is the highest analyzed vibrational level; ^b vibrational analysis only (ref. (2)); ^c range of v used in analysis; ^d obtained from $1/H_n = 6.376 \pm 0.002_7$ in eqn (5); ^e energy relative to $X^1\Sigma_g^+$ ($v = 0, J = 0$) (see table 2).

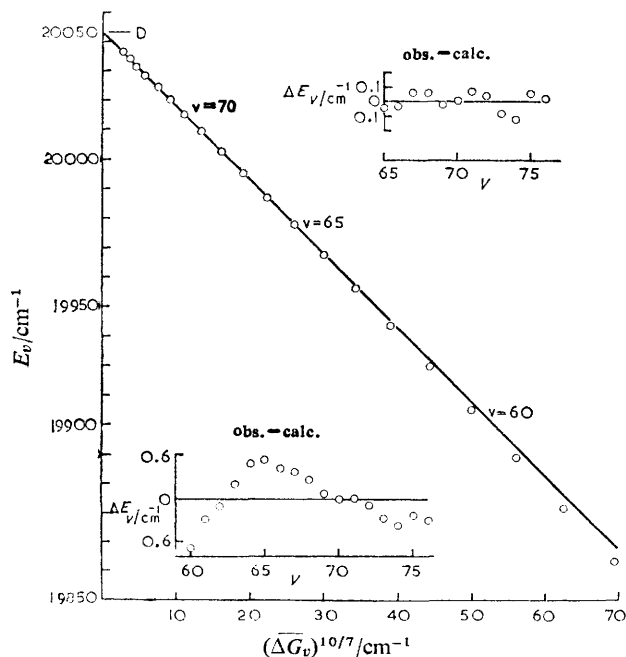


FIG. 3.—Plot of E_v against $(\overline{\Delta G_v})^{10/7}$ according to eqn (4) near the dissociation limit of $B^3\Pi_{0,u^+}$ of I_2 . E_v is the vibrational energy relative to $X^1\Sigma_g^+$ ($v = 0, J = 0$). The relatively large systematic errors resulting from a least-squares fit for $60 \leq v \leq 76$ are shown in the bottom inset. The small random errors resulting from a fit for $65 \leq v \leq 76$ are shown in the top inset.

v' numbering ^{7, 47}) agree well with the present results. The separation ${}^2P_{3/2} - {}^2P_{1/2}$ in I is 7603.15 cm^{-1} ⁴⁸: the value of D_0 becomes $12\,440.06 \text{ cm}^{-1}$. This confirms the estimate of LeRoy and Bernstein,^{37, 49} but, since it is based on band-origins rather than band-heads, should be more precise. The value $D_0 = 12\,452.5 \pm 1.5 \text{ cm}^{-1}$ obtained by Verma^{41, 50} from the analysis of fluorescence series seems to be too large by about 12.5 cm^{-1} .

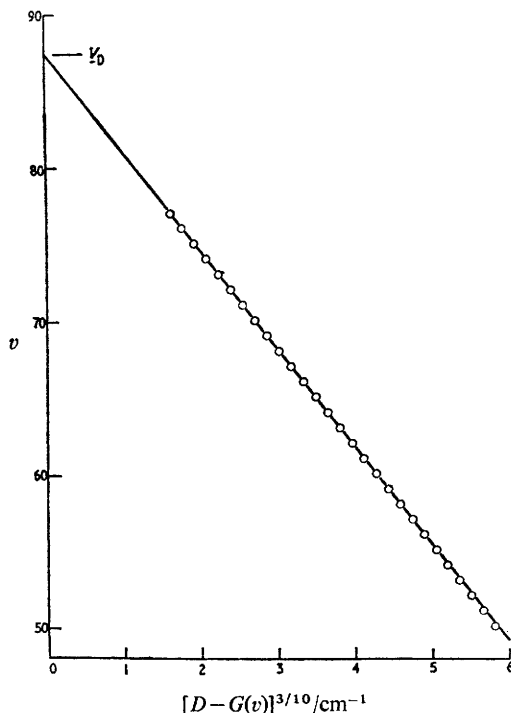


FIG. 4.—Plot of v against $[D - G(v)]^{3/10}$ according to eqn (5) near the dissociation limit of $B^3\Pi_{0,+}$ of I_2 .

B. ANALYSIS OF LONG-RANGE POTENTIAL

With the constants given in tables 2 and 4, an RKR potential energy curve was constructed to the highest observed vibrational level $v = 77$ using a programme devised by Chandler, Richards and Todd of this laboratory. The potential was extended to $v = 85$ using the extrapolated energies given in table 7 together with values of B_v extrapolated graphically. Large-scale graphical extrapolation of the r_{\min} limb of the RKR potential at high v was necessary because the calculations are very sensitive to small errors in B_v . This extrapolation is straightforward since the r_{\min} limb is almost vertical at these levels and $\Delta r = r_{\max} - r_{\min}$ depends only on the vibrational levels.⁵¹ The RKR turning points of the $B^3\Pi_{0,+}$ state for $0 \leq v \leq 85$ in the range 2.63 to 27.63 \AA are given in table 8. A part of the attractive potential near the dissociation limit is shown in fig. 5.

It was implicitly assumed that only the leading term (asymptotic value n) in the inverse power long-range expansion of (2) need be considered in the applications of (4), (5) to the analysis of the experimental data for the levels $64 \leq v \leq 77$, corresponding to $6.2 \lesssim r_{\max} \lesssim 10.0 \text{ \AA}$ (table 8). The effects of higher terms in the expansion are now

considered. Theory^{40, 52-54} shows that for $I_2(B^3\Pi_{0,u})$ the binding energy in the attractive long-range potential is given by

$$D - G_v = C_5/r_v^5 + C_6/r_v^6 + C_8/r_v^8 + \dots \quad (6)$$

where C_5 , C_6 and C_8 are constants (positive) and r_v is $r_{v,\max}$. Values of C_6 and of C_8 have been determined using a known value of D and a theoretical estimate⁴⁰ of C_5 . In the present analysis all three constants were determined by a simultaneous least-squares fit using r_{\max} values for $64 \leq v \leq 77$ and values of $D - G_v$ from tables 2 and 6. The long-range constants were also determined from the r_{\max} values for $64 \leq v \leq 85$, with D unknown. The results are given in table 9. The value derived in this way for the limit, $20\,043.22_0 \text{ cm}^{-1}$, relative to $X^1\Sigma_g^+$ ($v = 0, J = 0$), is in very good agreement with that given in table 6. The two extrapolations, one based on the values of ΔG_v , and the other on the values of r_{\max} , are therefore consistent.

TABLE 7.—ENERGY LEVELS (cm^{-1})^a NEAR THE DISSOCIATION LIMIT OF $B^3\Pi_{0,u}$ STATE OF I_2 CALCULATED ACCORDING TO EQN (1) WITH $m = n$

v	calc. ^b	energy level	obs.
87	20 043.208		
86	43.202		
85	43.172		
84	43.092		
83	42.930		
82	42.653		
81	42.224		
80	41.605		
79	40.756		
78	39.632		
77	38.189		38.162
76	36.382		36.396
75	34.162		34.141
74	31.480		31.473
73	28.286		28.312
72	24.527		24.558
71	20.152		20.176
70	15.105		15.123
69	09.332		09.356
68	02.776		02.797
67	19 995.379		95.385
66	87.083		87.080
65	77.829		77.826
64	67.557		67.543

^a Energy relative to $X^1\Sigma_g^+$ ($v = 0, J = 0$); ^b calculated energies for levels $v \leq 63$ become progressively too small as v decreases (see fig. 4).

Although the value of C_5 derived in the present RKR analysis is in reasonably good agreement with the theoretical value, those of C_6 and C_8 are significantly different from the values obtained by LeRoy and Cummings.⁴⁰ A graphical comparison between the two sets of long-range constants is given in fig. 6. According to both sets, the contribution of the leading term in r^{-5} is only about 50 % of the binding energy at $v = 65$ and less than 70 % at the highest analyzed level $v = 77$. This result is of

course contrary to the assumptions which have been made in respect of the applicability of (4) and (5) for the levels $64 \leq v \leq 77$. The apparent paradox arises from a fortuitous cancellation when the powers of the first two potential terms in (2) differ by unity,⁴⁰ so that the forms of (4) and (5) are effectively unchanged for the high vibrational levels. The values of C_n derived from the slopes k and h may not then be pure C_5 , and this may explain the difference between the two estimates derived in the present analysis (tables 6 and 9). It seems that the deviation from linearity for $v < 64$ shown in fig. 3 arises from the increasing contribution of C_8/r^8 as illustrated in fig. 6. If so, the values of C_6 and C_8 obtained by LeRoy and Cummings appear to be slightly too high and too low, respectively.

TABLE 8.—RKR POTENTIAL TURNING POINTS FOR THE $B^3\Pi_{0,+}$ STATE OF I_2

v	$G(v)/\text{cm}^{-1}$	$R_{\min}/\text{\AA}$	$R_{\max}/\text{\AA}$	v	$G(v)/\text{cm}^{-1}$	$R_{\min}/\text{\AA}$	$R_{\max}/\text{\AA}$
0	62.66	2.963 07	3.093 44	43	3771.72	2.649 86	4.467 32
1	186.82	2.921 73	3.148 71	44	3814.02	2.648 15	4.517 16
2	309.44	2.895 00	3.189 57	45	3854.41	2.646 61	4.568 85
3	430.49	2.874 24	3.224 65	46	3982.86	2.645 04	4.622 94
4	549.97	2.856 96	3.256 45	47	3929.47	2.643 64	4.679 10
5	667.88	2.842 03	3.286 14	48	3964.25	2.642 31	4.737 57
6	784.18	2.828 80	3.314 36	49	3997.22	2.641 04	4.798 88
7	898.83	2.816 90	3.341 53	50	4028.41	2.639 80	4.863 07
8	1011.82	2.806 06	3.367 94	51	4057.89	2.638 70	4.930 09
9	1123.17	2.796 16	3.393 50	52	4085.72	2.637 71	5.000 02
10	1232.80	2.786 95	3.418 88	53	4111.90	2.636 73	5.073 79
11	1340.72	2.778 34	3.444 09	54	4136.51	2.635 88	5.150 98
12	1446.90	2.770 35	3.469 00	55	4159.61	2.635 21	5.231 71
13	1551.33	2.762 81	3.493 88	56	4181.19	2.634 45	5.317 70
14	1653.97	2.755 75	3.518 68	57	4201.33	2.633 81	5.408 17
15	1754.80	2.749 06	3.543 55	58	4220.05	2.633 19	5.503 80
16	1853.81	2.742 76	3.568 49	59	4237.41	2.632 57	5.605 59
17	1950.96	2.736 76	3.593 61	60	4253.47	2.632 07	5.713 17
18	2046.22	2.731 09	3.618 94	61	4268.28	2.631 63	5.827 36
19	2139.61	2.725 71	3.644 53	62	4281.86	2.631 17	5.950 68
20	2231.06	2.720 59	3.670 40	63	4294.27	2.630 77	6.082 18
21	2320.58	2.715 71	3.696 66	64	4305.60	2.630 47	6.222 33
22	2408.13	2.711 06	3.723 28	65	4315.88	2.630 17	6.372 80
23	2493.70	2.706 64	3.750 38	66	4325.13	2.629 87	6.537 51
24	2577.28	2.702 40	3.777 94	67	4333.44	2.629 60	6.715 86
25	2658.83	2.698 39	3.806 08	68	4340.85	2.629 35	6.908 62
26	2738.35	2.694 53	3.834 77	69	4347.41	2.629 15	7.121 19
27	2815.82	2.690 86	3.864 11	70	4353.18	2.629 00	7.355 02
28	2891.23	2.687 36	3.894 12	71	4358.23	2.628 88	7.609 53
29	2964.57	2.683 99	3.924 86	72	4362.61	2.628 78	7.891 93
30	3035.82	2.680 78	3.956 39	73	4366.37	2.628 65	8.209 87
31	3104.98	2.677 73	3.988 78	74	4369.56	2.628 58	8.566 61
32	3172.04	2.674 79	4.022 05	75	4372.25	2.628 52	8.970 17
33	3236.99	2.671 99	4.056 32	76	4374.47	2.628 46	9.433 06
34	3299.83	2.669 30	4.091 59	77	4376.27	2.628 40	9.970 48
35	3360.55	2.666 71	4.127 99	78	4377.72	2.628 3 ₅	10.602 1 ₅
36	3419.14	2.664 21	4.165 66	79	4378.84	2.628 3 ₁	11.360 0 ₃
37	3475.69	2.661 90	4.204 26	80	4379.69	2.628 2 ₈	12.292 4 ₈
38	3530.16	2.659 68	4.244 22	81	4380.31	2.628 2 ₇	13.465 3 ₁
39	3582.55	2.657 52	4.285 72	82	4380.74	2.628 2 ₆	15.005 4 ₃
40	3632.89	2.655 47	4.328 64	83	4381.01	2.628 2 ₅	17.169 8 ₉
41	3681.18	2.653 51	4.373 16	84	4381.17	2.628 2 ₄	20.900 1 ₅
42	3727.45	2.651 65	4.419 35	85	4381.25	2.628 2 ₃	27.627 6 ₆

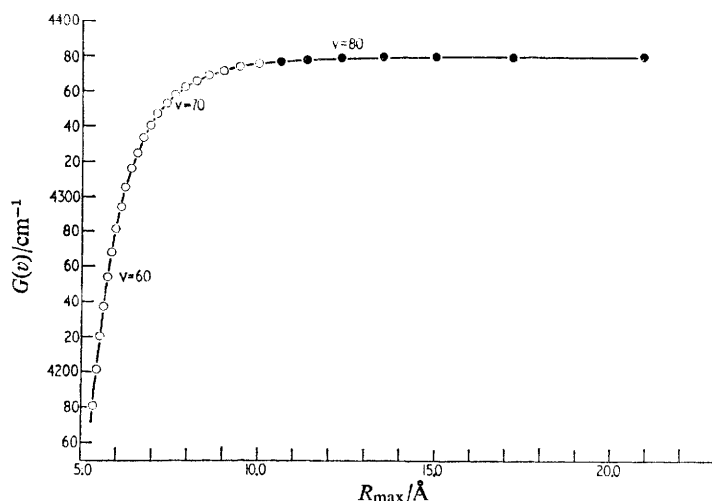


FIG. 5.—A portion of the attractive RKR potential energy curve near the dissociation limit of the $B^3\Pi_{0_u^+}$ state. The turning points for $v > 77$ as indicated by filled circles are calculated using the extrapolated energies given in table 7. The dissociation limit relative to the potential minimum is $D_e = 4381.29 \text{ cm}^{-1}$.

TABLE 9.—RESULTS OF RKR LONG-RANGE POTENTIAL ANALYSIS FOR $B^3\Pi_{0_u^+}$ STATE OF I_2

v range	r range/Å	dissociation energy/ cm^{-1} ^a	$10^{-5} C_5$ ^b	$10^{-6} C_6$	$10^{-8} C_8$	note
64-77	6.2-10.0		3.43 ± 0.13	1.064 ± 0.133	0.46 ± 0.02	<i>d</i>
64-85	6.2-27.6	4381.293 ± 0.015	3.40 ± 0.13 (3.68) ^c	1.100 ± 0.13 1.850 ± 0.2	0.45 ± 0.02 0.19 ± 0.04	<i>d</i> ref. (40)

^a Energy relative to the equilibrium position of the potential curve of $B^3\Pi_{0_u^+}$ state. The value relative to $X^1\Sigma_g^+$ ($v = 0, J = 0$) is $20\,043.220 \text{ cm}^{-1}$; ^b the C_m ($m = 5, 6, 8$) coefficients are in $\text{cm}^{-1} \text{Å}^m$; ^c theoretical value; ^d values obtained using eqn (6).

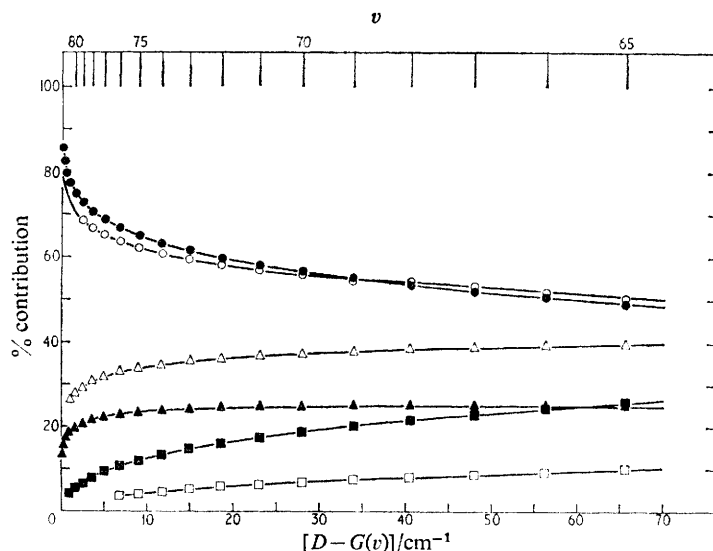


FIG. 6.—The percentage contribution of each term C_m/r^m in eqn (6) for $m = 5, 6$ and 8 to the binding energy $[D - G(v)]$ near the dissociation limit of $B^3\Pi_{0_u^+}$ is indicated by \bullet , \blacktriangle and \blacksquare , respectively. The corresponding values shown by \circ , \triangle and \square are calculated from the constants obtained by LeRoy and Cummings (table 9).

C. LONG-RANGE DEPENDENCE OF B_v

LeRoy³⁹ has examined the problem of the variation of B_v with v near the dissociation limit and obtained a relation which may be written

$$v = v_D - q[B_v]^{(n-2)/4} \quad (7)$$

where $q = 1/[Q_n]^{(n-2)/4}$ and Q_n is a constant depending on the reduced mass, n and the long-range constant C_n . For $n = 5$, $B_v^{3/4}$ should then be linear in v . However the approximations made in the derivation of (7) are expected to be less well satisfied than in the corresponding relation connecting ΔG_v with v (5) and the results plotted in fig. 7

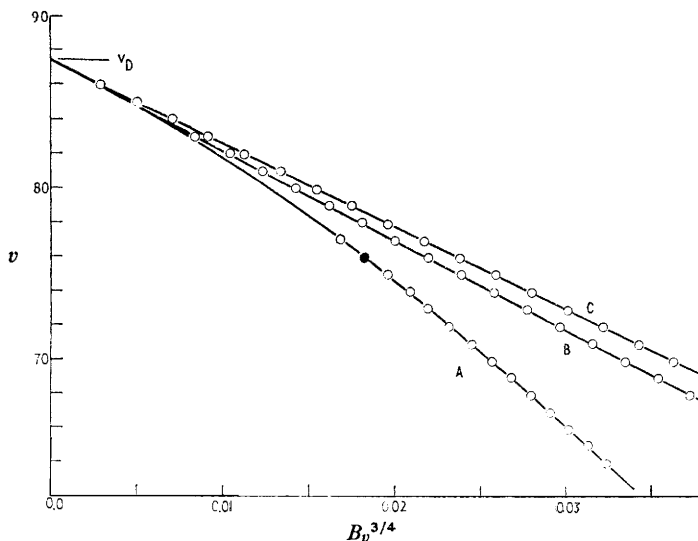


FIG. 7.—The variation of $(B_v)^{3/4}$ with v . A, observed values together with the calculated value for $v = 76$ using the constants given in table 4; B, calculated with $C_5 = 3.40 \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$ obtained from the analysis of long-range RKR potential (table 9); C, calculated with $C_5 = 2.886 \times 10^5 \text{ cm}^{-1} \text{ \AA}^5$ obtained with the use of eqn (5) (table 6).

show that the values of B_v calculated from (7) are too large. Moreover the variation of B_v with v near dissociation illustrated in fig. 1, where dB_v/dv is found to decrease only slightly with increasing v , shows that the power to which B_v is to be raised in an expression of the type of (7) to obtain a region of linear variation with v is close to one. It seems that the long-range dependence of B_v requires further attention. Meanwhile estimates of B_v for $v > 77$ can readily be obtained, either graphically, or by polynomial extrapolation as shown in table 10.

CONCLUSIONS

The present work began with the aims of determining the dissociation limit in the $B^3\Pi_{0,+}$ state and of deriving experimental data to test the theory of the long-range interaction between $I(^2P_{3/2})$ and $I(^2P_{1/2})$. In the course of this work it became clear that the accepted assignments for many of the laser excited fluorescence series were incorrect and the rotational analysis was extended to include most of the commonly used laser and other excitation lines. The result has provided a consistent rotational analysis covering the greater part of the range of bound levels in the B state.

TABLE 10.—COMPARISON OF OBSERVED AND CALCULATED B_v VALUES (cm^{-1}) NEAR THE DISSOCIATION LIMIT OF $B^3\Pi_{0_u}$ STATE OF I_2

v	obs. ^a	calc. ^b $10^2 B_v$	calc. ^c
87	0		0.006 (0.006)
86	[0.031]		0.036 (0.040)
85	[0.066]	0.063	0.075 (0.083)
84	[0.107]	0.108	0.120 (0.134)
83	[0.150]	0.154	0.170 (0.190)
82	[0.194]	0.199	0.224 (0.250)
81	[0.240]	0.245	0.282 (0.314)
80	[0.286]	0.291	0.342 (0.382)
79	[0.331]	0.337	0.406 (0.453)
78	[0.376]	0.383	0.472 (0.526)
77	0.4297	0.4293	0.540 (0.603)
76	0.4560	0.4757	0.611 (0.681)
75	0.5262	0.5221	0.684 (0.763)
74	0.5709	0.5685	0.759 (0.846)
73	0.6092	0.6149	0.835 (0.932)
72	0.6569	0.6612	0.914 (1.019)
71	0.7064	0.7075	0.994 (1.109)
70	0.7557	0.7536	1.076 (1.200)
69	0.7988	0.7996	1.159 (1.293)
68	0.8443	0.8454	1.244 (1.388)
67	0.8906	0.8910	1.331 (1.485)
66	0.9366	0.9364	1.419 (1.583)
65	0.9803	0.9816	1.508 (1.682)
64	1.0288	1.0265	1.599 (1.784)

^a Values in square brackets are graphically extrapolated; ^b values calculated using the constants obtained from a least-squares polynomial fit (table 4); ^c calculated using eqn (7), with $C_5 = 3.40 \times 10^5$. Values in parentheses are with $C_5 = 2.8861 \times 10^5$ (table 6).

The first direct conclusion is that, over the extended range of v , neither the vibrational levels nor the centrifugal stretching constants, D_v , can adequately be expressed by simple polynomials in $(v + \frac{1}{2})$. This situation has already been recognized in the cases of, amongst others, the ground states of H_2 ⁵⁵ and of HF .⁵⁶ B_v can be represented by a five-term polynomial, but the behaviour of B_v at high values of v is not well represented by current theory based on the long-range potential.

The results have been used to construct an RKR potential curve extending to the dissociation limit of the B state. The interaction at large distances may be represented by a potential $-(C_5/r^5 + C_6/r^6 + C_8/r^8)$ and the analysis shows that even at distances as large as 20 Å, the contribution of the term in C_6/r^6 is not negligible. Independent determination of uncorrelated values of C_5 , C_6 and C_8 is, however, difficult, so that not too much weight should be attached to the precise values so far obtained.

In the long-range region, the approximations (4) and (5) are found to hold and provide good estimates of D and of v_D : this is for the reasons (i) that there is positive curvature in the Birge-Sponer plot and (ii) that the first two terms in the potential differ in power by unity. Both these terms, in r^{-5} and r^{-6} , are significant in the working range, so that the values of the constants C_n derived from eqn (4) and (5) are not pure C_5 .

Regardless of the precise significance of the values of the long-range constants, the

dissociation limit is well-defined and leads to the ground state value $D_0(I_2) = 12\,440.1\text{ cm}^{-1}$. This value is inconsistent with that derived by Verma from long fluorescence series, $12\,452.5 \pm 1.5\text{ cm}^{-1}$, and it is concluded that these series require revision.

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