Description of the absorption spectrum of iodine recorded by means of Fourier Transform Spectroscopy : the (B-X) system

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Classification
Physics Abstracts
33.20K — 31.90

Description of the absorption spectrum of iodine recorded by means of Fourier Transform Spectroscopy : the (B-X) system

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Résumé. — L'analyse de la totalité du spectre d'absorption de la molécule d'iode représenté par le système (B-X) I_2 et enregistré par spectroscopie par transformation de Fourier est présentée. On montre que les 100 000 transitions enregistrées et publiées dans plusieurs Atlas peuvent être recalculées au moyen de 46 constantes : 45 étant les coefficients de Dunham servant à décrire les constantes vibrationnelles et rotationnelles des états X jusqu'à $v'' = 19$ et de l'état B jusqu'à $v' = 80$ (niveau situé à 1,6 cm^{-1} de la limite de dissociation), plus un coefficient empirique permettant de tenir compte des constantes de distorsions négligées (supérieures à M_v). L'erreur quadratique moyenne entre les nombres d'ondes recalculés et mesurés est trouvée égale à 0,002 cm^{-1} en accord avec la comparaison des écarts entre les nombres d'ondes recalculés et les nombres d'ondes absolus de nombreuses raies de l'iode mesurées indépendamment.

Abstract. — An *in extenso* analysis of the (B-X) I_2 iodine absorption spectrum recorded by means of Fourier Transform Spectroscopy is presented. It is shown that the 100 000 recorded transitions covering the 11 000-20 040 cm^{-1} range and published in several Atlases may be recalculated by means of only 46 constants : 45 are Dunham coefficients describing the vibrational and rotational constants of both X state (up to $v'' = 19$) and B state (up to $v' = 80$, situated only at 1.6 cm^{-1} from the dissociation limit of the B state), and one empirical scaling factor which takes account of neglected centrifugal constants higher than M_v. The overall standard error between computed and measured wavenumbers is equal to 0.002 cm^{-1} in agreement with the differences of numerous independent absolute wavenumbers and the computed ones.

1. Introduction.

1.1 HISTORICAL. — First, let us recall that the study of the absorption spectrum of iodine by means of Fourier Transform Spectroscopy (F.T.S.) was undertaken at Aimé Cotton Laboratory, seven years ago, in 1977. At that time, the aim of the work was to test the performances of F.T.S. in the visible range (where the multiplex gain is lost) and to show that F.T.S. remains an excellent tool for emission and absorption studies [1-3], even in cases where the noise is mainly due to the signal itself (photon noise). We concluded our study by the following statement [4] :

« The method (F.T.S.) can be expected to open not only significant new spectroscopic experiments but it also allows a complete high-precision remeasurement of the existing molecular spectra in the visible and U.V. (electronic vibrational transitions). » As usual, we

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were not prophets in our country, and we have felt that the analysis of only a few bands [3, 4] of iodine was not enough to assess the above statement. Thus, we published also an « Iodine Atlas », encompassing a large spectral range from 14 800 to 20 000 cm^{-1} [5b] (note that this atlas was not the first one : Simmons and Hougen, using conventional grating spectroscopy, have published a short time before an « iodine atlas » covering the 18 000-19 000 cm^{-1} range [6]). However, a spectrum, beautiful though it may be, remains solely a collection of numbers, until its complete analysis is achieved. Analysis of the iodine absorption spectrum was a challenge for us, because numerous, extended and careful studies of the (B-X) system were already made at this time [7-11].

Nevertheless, in the fundamental paper published by Barrow and Yee [7], one point remains unexplained : their experimental vibrational constants $G(v)$ do not follow, at least above $v' = 50$, the classical Dunham expression $G(v) = \sum_{n=1} y_{n0}(v + 1/2)^n$. The origin of this difficulty may be either the existence of a

local perturbation, or it has to be ascribed to a lack of precision of the experimental data. Later, Wei and Tellinghuisen [10], adding new data, were able to propose smoothed $G(v)$ and $B(v)$ values following Dunham expressions. However, the use of the constants of Wei and Tellinghuisen, especially for $J > 125$, was found to be in disagreement (~ 0.100 cm^{-1}) with the Fourier data : unambiguous assignments of the whole spectrum were therefore not warranted (see for ex. Ref. [12]). Since Fourier Spectroscopy is practically free from systematic errors [13], the analysis of the Fourier absorption spectrum data of iodine should remove all the above difficulties and prove directly the obvious advantages of using F.T.S., even in the visible range; indeed, we were able to give a description of the (B-X) system in terms of polynomial parameters for the molecular constants G', B', D' and H' for $v' = 1$ up to $v' = 62$ of the B state, and for G'', B'' and D'' for $v'' = 0$ to $v'' = 9$ of the ground state [14]. By means of this collection of effective molecular constants, the wavenumbers of 14 000 assigned transitions belonging to 139 analysed bands were reproduced, with a standard deviation of 0.001, 0.0017 and 0.004 cm^{-1}, for levels involving maximum J values of 50, 100 and 150 respectively. These results clearly show that F.T.S. measurements are, at least, one order of magnitude more reliable than those obtained with conventional spectroscopy. With this success, the instrumental character of our work was considered to be fulfilled [15] and we decided to undertake the study of the (B-X) system for its own sake i.e. to extend the analysis on both sides of the spectrum : (i) to the near infrared where the $(0, v'')$ bands are situated with the aim of reaching the unknown ground level $v' = 0$ of the B state and (ii), to the dissociation limit where the bands $(v', 0)$ with $v' \geqslant 63$ are located, in order to determine the dissociation limit of the B state.

Assignments and analysis of the near infrared region were published in two papers.

The first one, concerning the 12 600-14 000 cm^{-1} range appeared in 1980 [16]; the second one, which contains in addition the 11 600-12 600 cm^{-1} range appeared in 1983 [17]. While in the 1980 paper, RKR procedure, calculation of Centrifugal Distortion Constants (CDC) and Franck-Condon Factors (FCF) were made using programs available from D. L. Albritton (and kindly supplied to us by J. T. Hougen, [18]), in the 1983 paper, we use J. M. Hutson's method for the CDC calculations. Indeed, in the meantime J. M. Hutson (1981 [19]) published an improved computational method which, among other advantages, eliminates summations over excited levels and in which the effects of continuum levels are included exactly, so that the results remain valid for levels very near the dissociation limit (J. M. Hutson *et al.* [20] 1982), (and provided that the Born-Oppenheimer approximation remains also valid in this region).

Point (ii) represents part of the present work.

1.2 PRESENT WORK. — Although data concerning Point (ii) were analysed previously (Ref. [20] up to $v' = 75$, Refs. [21] and [22] up to $v' = 77$), these data were only preliminary and partial. We have recorded again the absorption spectrum of iodine in the range 19 700-20 040 cm^{-1} in order to improve the quality of the previous measurement, especially in the region near the dissociation limit ($D_0 \sim$ 20 043 cm^{-1}). This work is presented in section 2.

Since this last series of measurements close the F.T.S. study of the (B-X) system and that the principal aim of this paper is to give a complete description of the (B-X) system, we collect in the following sections not only the new data for $63 \leqslant v' \leqslant 77$, but also all previous results from $v' = 0$ to $v' = 62$ scattered in several papers.

In addition, throughout this work a quantum mechanical potential curve describing the X state up to $v'' = 19$ was determined by means of the « inverted perturbation approach » method [23, 24] (IPA-potential) using C. R. Vidal's program [25]. Thus, in section 3, the molecular constants of the X state (up to $v'' = 19$) deriving from a quantum mechanical potential will be given, while « effective » molecular constants describing the B state up to $v' = 80$ will be presented. It will be shown that, according to theory, only vibrational constants are needed to recalculate the whole observed spectrum within the experimental uncertainties. Finally, in section 4 an extensive comparison will be made between computed wavenumbers by means of the molecular constants given in section 3 and independent absolute measurements made by interferometric methods other than F.T.S.

2. Experimental.

The experimental set-up was similar to those described in reference [16]; but here, the absorption cell was 0.50 m long (instead of 0.15 m). The cell was maintained at room temperature, where the iodine pressure is about 0.25 torr. A single pass was sufficient to observe the absorption spectrum in the 19 600-20 100 cm^{-1} range. The instrumental width of the · Fourier spectrometer was chosen to be 0.020 cm^{-1}, a value close to the width of the iodine lines : the hyperfine structure of the iodine lines [26, 27] combined with the Doppler width gives a resulting width of about 0.025 cm^{-1} [28]. Each interferogram includes 5×10^5 points; this corresponds to a total path difference of about $\sim$ 33 cm; each step being equal to σ_L, where σ_L is the wavenumber of the reference helium-neon laser stabilized on an iodine hyperfine component ($\sigma_L = 15\,798.0$ cm^{-1}).

Figure 1 compares the last page of the previously published atlas [5b] (A) and the present recordings (B). The gain in signal/noise (approximately a factor of 10) has principally two origins : first, a narrower spectral range (only 500 cm^{-1}) was recorded in one sweep, and second, several selected recordings were added before
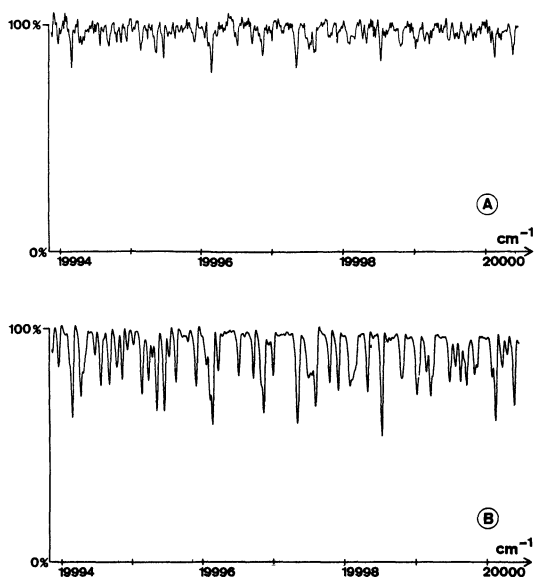
Fig. 1. — Comparison with previous work (Ref. [5a]), showing the gain in signal/noise ratio (approximately a factor 10).

performing the Fourier transform of the resulting interferogram [3].

Finally, the absorption spectrum was calibrated by comparing the recorded wavenumbers of unblended, intense and symmetrical lines with the wavenumbers already published [5b] and corrected [28]. To summarize, the absorption spectrum of iodine is now available without discontinuity from $11\ 000\ \mathrm{cm}^{-1}$ to $20\ 035\ \mathrm{cm}^{-1}$.

The recordings are split into four parts :

Part I   : $11\ 000$-$14\ 000\ \mathrm{cm}^{-1}$ [5a]
Part II : $14\ 000$-$15\ 600\ \mathrm{cm}^{-1}$ [5b]
Part III : $14\ 800$-$20\ 000\ \mathrm{cm}^{-1}$ [5b]
Part IV : $19\ 700$-$20\ 035\ \mathrm{cm}^{-1}$ (This work) [5b] .

In addition, the excitation spectrum of iodine induced by laser radiation covering the $15\ 780$-$15\ 815\ \mathrm{cm}^{-1}$ region and the $20\ 022$-$20\ 040\ \mathrm{cm}^{-1}$ region, where for different reasons F.T.S. failed, has been recorded and published recently [21] and [29].

3. Results.

3.1 ANALYSIS OF THE FIFTEEN BANDS $(v', 0)$ WITH $63 \leqslant v' \leqslant 77$.

— In the range $19\ 700$-$20\ 035\ \mathrm{cm}^{-1}$, the wavenumbers and intensities of about 3 600 lines with signal/noise ratio larger than 2 were measured. The recordings, wavenumbers and intensities are given in extenso in Atlas IV [5b].

3.1.1 *Position measurements. Assignments and precision of the measurements.*

— The number of assigned lines for each of the fifteen $(v', 0)$ bands as well as the minimum and the maximum J values detected in each R and P branch are given in table I (between the two horizontal dashed lines).

Estimates of the uncertainties of the measured wavenumbers can be obtained in several ways; but as explained previously (Ref. [5b], Part III, p. X) we prefer to consider the $\Delta_2\ F''(J)$ differences. Table II gives an example of a series of 10 measured differences $\Delta_2\ F''(J) = \sigma_R(J - 1) - \sigma_P(J + 1)$ involving v' values from $v' = 63$ to $v' = 75$. These series, with a value of $J = 33$, were chosen in order to be typical; indeed the intensities of lines with J around 33, have medium intensities ($\sim 40\%$) (see Fig. 2b). The standard deviation of the differences $\Delta_2\ F''(J)$ is $0.0022\ \mathrm{cm}^{-1}$ which corresponds to an average uncertainty of $(0.0022/\sqrt{2})\ \mathrm{cm}^{-1} = 0.0016\ \mathrm{cm}^{-1}$ on the vertex position of each measured line.

These last results, together with both previous F.T.S. data [14, 17] and laser induced spectroscopy data (bands (78, 0), (79, 0) and (80, 0) [21]), lead to a total number of 17 800 assigned lines represented by 174 bands which encompass nearly all the well depth of the B states from $v' = 0$ to $v' = 80$ — the last $v' = 80$ vibrational level being situated only $1.64\ \mathrm{cm}^{-1}$ from the dissociation limit [30]. Only twenty vibrational levels belonging to the ground state are involved in our absorption study $(0 \leqslant v'' \leqslant 19)$. (For the description of the X state from $v'' = 19$ to the dissociation limit $(v'' = 115)$ see Ref. [31]).

3.1.2 *Intensity measurements.*

— Intensity alternation presented by homonuclear molecules of atoms possessing a non-zero spin ($^{127}\mathrm{I} = 5/2$) are remarkably well observed throughout the fifteen analysed bands (see Fig. 2). Evaluation of the « true » intensity of a given line is difficult, and even the precise determination of the ratio of intensities of two lines is not simple. Indeed, it is well known that the « depth » of an absorption line depends, among other factors, on the absorption coefficient and on the ratio of the width of

Fig. 2. — Portion of the iodine spectrum of the analysed region (Fig. 2a). The alternation of intensities results in two different intensity distribution curves according to the parity of the transition (Fig. 2b).

Table I. — Minimum (J_{min}), maximum (J_{max}); J values and number of assigned lines detected in the R and P branches of the 174 analysed bands.

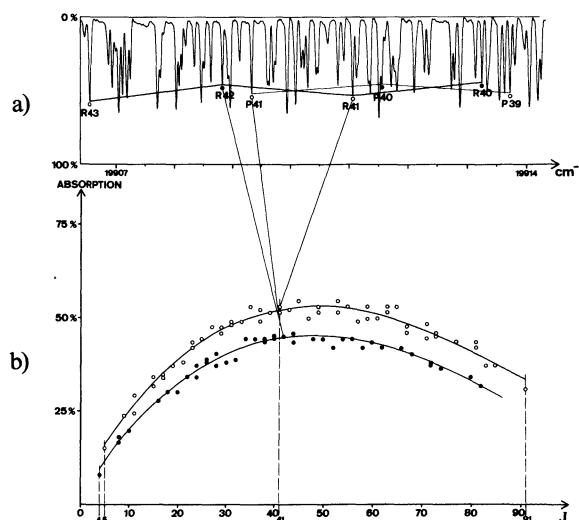|	P BRANCH			R BRANCH			
v', v''	J_{min}	J_{max}	N_P	J_{min}	J_{max}	N_R	N_t
10,0	43	119	13	14	122	16	29
11,0	12	160	26	14	137	27	53
12,0	16	127	34	22	129	27	61
14,0	42	137	30	6	135	35	65
15,0	15	130	33	7	158	31	64
16,0	9	137	39	16	160	39	78
17,0	4	185	48	6	156	42	90
18,0	4	137	56	5	143	60	116
19,0	8	129	54	12	151	60	114
20,0	14	153	66	14	128	48	114
21,0	27	145	44	32	148	46	90
22,0	4	144	34	66	145	37	71
23,0	18	156	71	22	152	55	126
24,0	9	155	66	12	149	75	141
25,0	12	155	80	9	147	74	154
26,0	11	153	84	8	153	83	167
27,0	7	150	73	8	153	83	156
28,0	10	159	78	8	156	74	152
29,0	9	160	72	10	157	85	157
30,0	11	150	82	12	156	77	159
31,0	94	148	25	98	152	23	48
32,0	3	143	53	7	136	56	109
33,0	13	138	68	16	158	78	146
34,0	9	149	84	11	148	85	169
35,0	5	146	75	8	153	83	158
36,0	3	160	67	6	159	84	151
37,0	10	151	62	10	151	67	129
38,0	8	149	61	8	151	63	124
39,0	5	131	58	7	145	62	120
40,0	9	128	61	3	145	67	128
41,0	10	133	46	12	135	41	87
42,0	20	130	38	23	137	45	83
43,0	63	145	26	65	145	31	57
44,0	30	145	35	29	125	29	64
45,0	14	132	38	4	131	44	82
46,0	10	131	42	9	124	41	83
47,0	11	111	33	7	125	27	60
48,0	8	104	32	20	109	27	59
49,0	15	121	28	5	117	26	54
50,0	9	123	26	11	120	20	46
51,0	10	103	17	2	111	27	44
52,0	5	110	34	8	111	26	60
53,0	15	90	18	13	88	27	45
54,0	15	110	37	20	110	31	68
55,0	7	99	37	7	103	40	77
56,0	12	99	33	12	99	33	66
57,0	16	72	26	14	76	26	52
58,0	17	98	19	15	94	26	45
59,0	11	83	25	12	83	31	56
60,0	20	87	26	17	85	36	62
61,0	15	85	35	14	84	33	68
62,0	20	74	23	4	76	19	42
63,0	9	91	57	4	93	49	106
64,0	7	91	39	5	92	50	89
65,0	3	90	52	4	86	42	94
66,0	7	85	39	4	83	42	81
67,0	5	81	45	4	81	43	88
68,0	3	71	36	10	71	35	71
69,0	4	69	38	5	70	35	73
70,0	7	64	36	6	64	34	70
71,0	4	63	34	3	63	34	68
72,0	4	48	26	8	45	26	52
73,0	1	56	25	3	54	32	57
74,0	7	50	26	2	47	33	59
75,0	2	45	30	4	47	30	60
76,0	5	42	19	2	38	17	36
77,0	5	35	10	7	35	14	24
78,0	2	22	9	2	21	8	17
79,0	6	21	7	6	21	8	15
80,0	7	15	6	7	11	4	10
9,1	8	134	40	15	138	39	79
10,1	27	141	48	38	145	45	93
11,1	7	138	45	11	151	43	88
12,1	11	147	51	16	155	58	109
13,1	33	103	37	37	142	43	80
14,1	3	159	37	7	151	31	68
15,1	19	138	58	23	159	49	107
16,1	12	153	56	5	152	53	109
17,1	12	154	64	10	160	51	115
18,1	8	158	48	8	156	41	89
19,1	12	155	45	18	152	40	85
20,1	10	141	53	14	118	57	110
21,1	19	157	54	20	148	49	103
22,1	3	126	20	86	144	20	40
23,1	30	148	48	31	139	39	87
24,1	12	146	52	15	152	53	105
25,1	14	131	47	12	123	43	90
26,1	10	143	40	16	132	46	86
27,1	8	155	32	7	119	36	68
28,1	12	149	32	15	138	29	61
29,1	20	139	16	25	91	12	28
30,1	13	101	20	28	126	15	35
7,2	2	123	35	8	129	37	72
8,2	26	120	47	26	121	37	84
9,2	17	142	47	20	143	35	102
10,2	7	160	56	8	136	61	117
11,2	20	151	54	23	140	45	99
12,2	10	140	47	6	145	60	107
13,2	18	138	54	6	157	50	104
14,2	5	157	29	12	140	21	50
15,2	31	149	57	36	150	51	108
16,2	19	136	52	6	133	60	112
17,2	7	122	50	11	155	55	105
18,2	16	147	36	12	137	38	74
19,2	27	135	26	29	146	29	55
20,2	20	143	23	6	139	36	59
21,2	20	133	27	22	107	21	48
4,3	12	115	41	7	105	44	85
5,3	15	135	57	8	132	56	113
6,3	11	144	47	7	149	53	100
7,3	28	152	64	10	151	54	118
8,3	38	133	33	42	146	50	83
9,3	15	120	54	18	121	43	97
10,3	7	136	57	15	142	50	107
11,3	7	137	61	8	159	57	118
12,3	11	137	45	6	135	51	96
13,3	26	121	42	22	115	27	69
14,3	36	137	22	44	91	23	45
15,3	52	132	23	55	145	25	48
16,3	31	156	22	29	154	20	42
4,4	10	120	75	15	138	72	147
5,4	13	135	88	11	142	76	164
6,4	7	153	103	7	137	97	200
7,4	12	139	101	8	141	100	201
8,4	2	152	56	8	152	62	118
9,4	8	148	78	15	156	84	162
10,4	14	130	43	13	128	53	96
11,4	13	107	30	6	109	27	57
12,4	45	102	14	19	108	16	30
3,5	23	98	41	11	99	43	84
4,5	9	133	62	9	131	74	136
5,5	7	136	81	8	130	85	166
6,5	10	137	97	6	138	99	196
7,5	7	144	98	6	144	95	193
8,5	22	150	62	6	154	64	126
9,5	16	114	51	7	142	45	96
1,6	15	142	48	12	141	51	99
2,6	23	131	30	30	145	49	79
3,6	7	165	45	11	141	29	74
4,6	16	163	78	9	170	98	176
5,6	8	165	83	10	169	89	172
6,6	8	177	83	17	180	76	159
7,6	12	182	74	8	169	74	148
1,7	17	138	33	16	145	46	79
2,7	23	152	58	17	166	78	136
3,7	27	173	82	8	175	80	162
4,7	33	175	75	12	160	73	148
5,7	11	178	87	13	176	96	183
6,7	10	160	56	20	165	55	111
1,8	15	177	50	18	181	68	118
2,8	12	189	95	16	170	94	189
3,8	16	176	91	27	160	84	175
4,8	13	148	58	18	162	65	123
5,8	22	118	36	28	124	44	80
2,9	8	171	101	13	199	107	208
3,9	11	170	91	9	173	92	183
4,9	5	158	33	40	133	28	61
1,10	18	126	62	9	134	82	144
2,10	6	149	57	9	157	60	117
0,11	15	136	47	11	144	48	95
1,11	48	160	55	54	168	48	103
2,11	16	77	38	19	87	47	85
0,12	11	138	94	9	127	89	183
1,12	31	140	74	10	148	101	175
2,12	25	129	49	22	132	49	98
0,13	12	124	76	20	126	84	160
1,13	11	144	60	9	151	68	128
0,14	19	129	79	20	135	75	154
1,14	19	117	59	18	126	63	122
0,15	17	165	144	14	175	146	290
0,16	44	172	121	18	172	120	241
0,17	33	155	84	35	155	91	175
0,18	29	174	132	29	173	129	261
0,19	32	114	57	28	121	56	113

Table II. — $\Delta_2 F''(J)$ differences and estimation of the accuracy of the wavenumber measurements.

v', v''	$\sigma_R(J-1)\,(cm^{-1})$	$\sigma_P(J+1)\,(cm^{-1})$	$\Delta_2 F''(J)\,(cm^{-1})$	Deviations (cm^{-1})
63, 0	19 928.7527	19 923.7544	4.9983	0.0002
64, 0	39.5586	34.5605	4.9981	0.0
65, 0	49.3040	44.3054	4.9986	0.0005
66, 0	58.0391	53.0422	4.9969	0.0012
67, 0	65.8152	60.8145	5.0007	0.0026
70, 0	83.9602	78.9619	4.9983	0.0002
71, 0	88.4663	83.4666	4.9997	0.0016
72, 0	92.2932	87.2922	5.0010	0.0029
73, 0	95.4932	90.4963	4.9969	0.0012
75, 0	20 000.2458	95.2527	4.9931	0.0050
		Average :	4.9981	S.D. : 0.0022

the line to the instrumental width. However, the difficulties do not prevent us from localizing the maximum of the intensity of a given band. At room temperature ($T = 293$ K) this maximum should lie around $J \sim 51$ for all (v', 0) bands. This is the case for the (63, 0) bands (Fig. 2 and Fig. 3), but for $v' \geqslant 63$ the maximum is shifted to lower J values : for the (77, 0) band the maximum occurs for $J \sim 23$. These anomalies are not isolated features; they are also observed in the ^{79}Br₂ spectrum by Barrow et al. [32]. The J dependence of the calculated FCF does not explain these observations; probably they have to be related to the relative strong variation of the magnetic hyperfine constant C' with the vibrational quantum number v' (see Ref. « 1 » of Table VII) and to perturbation with other states in this region [33, 34].

3.2 LEAST SQUARES ANALYSIS METHOD.

— In order to determine the vibrational and rotational molecular constants, the global fit of the 17 800 assigned lines was done following the method described in recent papers. We recall that in this method the CDC value of D, H, L and M which are needed to calculate the energies of the rovibrational levels $E(v, J)$ are not « experimental » values but are those obtained from theory [19]. The energies $E(v, J)$ levels are given by equations (1) and (2) [35] :

$$E(v', J) = E_{v'}(0) + B_{v'} K - D_{v'} K^2 + H_v K^3 +$$
$$+ L_{v'} K^4 + M_v K^5 \quad (1)$$

$$E(v'', J) = E_{v''}(0) + B_{v''} K - D_{v''} K^2 + H_{v''} K^3 \quad (2)$$

where $K = J(J + 1)$,

and the fitting process concerns only the vibrational $G(v)$ and rotational $B(v)$ constants. Of course, the use of this method is based on the assumption that the analysed X and B states can be described in terms of a single rotationless potential curve. This requirement can be considered to be fulfilled for the lower part of the rotationless potential of the X state containing the first twenty vibrational levels; indeed, the IPA
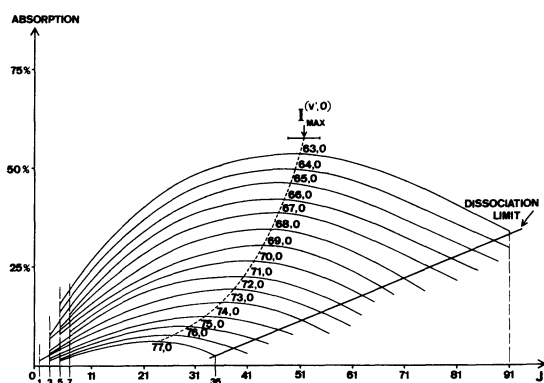
potential up to $v'' = 19$ is in excellent agreement with the RKR ones determined previously [17]. The eigenvalues $G(v'')$ and the expectation values $B(v'')$ reproduce the experimental ones (given in Ref. [17]) within 0.001 cm⁻¹ and 10⁻⁷ cm⁻¹ respectively. But in the case of the B state the situation is different : near the dissociation limit perturbations of different origins are present [33, 34]. However in the global fit of the data, these perturbations will be ignored for two reasons : first these perturbations are small [30] and second in the iterative procedure (Fig. 4) the vibrational and rotational constants are essentially considered, in a first step, as free parameters; the principal aim of the global fit of the data being to attempt to describe the whole observed spectrum from 11 000 to 20 040 cm⁻¹ with a minimum of parameters. Accordingly, the vibrational $G(v'')$ and rotational $B(v'')$ constants belonging to the first twenty levels of the ground state can be considered as « true » molecular constants while the $G(v')$ and $B(v')$ constants of the B state should be considered, in a first step, as « effective » constants (see discussion, Section 5).

A flow diagram of the iteration procedure is shown in figure 4. This procedure is essentially the same as that used by Tellinghuisen et al. for the X state of I₂ [36] (and earlier by Burns et al. [9]), except that the method used there for calculating CDC would not be adequate
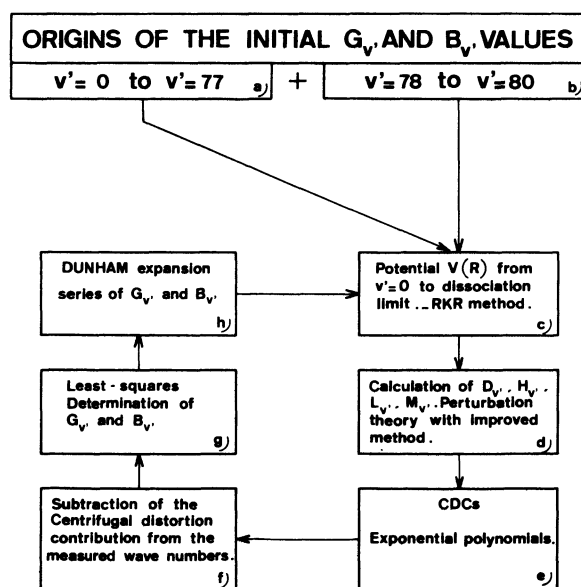

Fig. 4. — The iteration procedure : a) Origin of the spectroscopy data [14, 16, 17]. b) Laser Induced Fluorescence data [21]. c) RKR program of J. Tellinghuisen [36]. d) Differential equation method of Hutson [19]. e) Determination of the exponential polynomials for « compact » representation of the computed CDC according Le Roy [37]. f) subtraction of the quantities $(-D_v K^2 + H_v K^3 + L_v K^4 + M_v K^5)$ yields « distortion-free wavenumbers ». g) Solution of the 17 800 simultaneous equations with 182 unknowns (81 G_v and 81 B_v). h) Determination of Dunham expansion coefficients of the G_v and B_v values.

Fig. 3. — Observed intensity distribution of the analysed bands corresponding to transitions with odd J values. Note the sharp displacement of the intensity maxima as v increases.

in the present case [19]. For inclusion in the least squares fits the CDC values belonging to the B state for $0 \leqslant v' \leqslant 80$, were represented by exponential polynomials and noted « CDC_s » :

$$D_v = \exp \sum_{i=1} C_{di}(v + 1/2)^{i-1}$$

$$- H_v = \exp \sum_{i=1} C_{hi}(v + 1/2)^{i-1}$$

$$- L_v = \exp \sum_{i=1} C_{li}(v + 1/2)^{i-1}$$

$$- M_v = \exp \sum_{i=1} C_{mi}(v + 1/2)^{i-1}$$

obtained from fits of the calculated values according to Hutson's method. Only exponentials provide an adequate representation of the calculated CDC values, without loss of precision. Indeed these constants increase rapidly at high v and finally diverge at dissociation [37].

The vibrational and rotational constants (as well as the CDC of the ground state up to $v'' = 19$) are accurately represented by the classical Dunham expansion series [38]

$$\sum y_{il}(v + 1/2)^i , \quad \text{where}$$

$$\begin{cases} l = 0 \text{ and } i = 1, 2, ... i \text{ for } G_v \\ l = 1, 2, 3, ... \text{ and } i = 0, 1, 2, ... i \text{ for } B_v, D_v, H_v . \end{cases}$$

The input data of the least squares fit are the 17 800 measured wavenumbers which obey equation (3) or (4). (These equations are derived from Eqs. (1) and (2), $\sigma_R(J)$ for $\Delta J = -1$ and $\sigma_P(J)$ for $\Delta J = +1$.)

$$\sigma_R(J) = T_e + G_{v'} + B_{v'} \alpha +$$
$$+ [- D_{v'} \alpha^2 + H_{v'} \alpha^3 + L_{v'} \alpha^4 + M_{v'} \alpha^5]$$
$$- (G_{v''} + B_{v''} \gamma - D_{v''} \gamma^2 + H_{v''} \gamma^3) \quad (3)$$

$$\sigma_P(J) = T_e + G_{v'} + B_{v'} \alpha +$$
$$+ [- D_{v'} \beta^2 + H_{v'} \beta^3 + L_{v'} \beta^4 + M_{v'} \beta^5]$$
$$- (G_{v''} + B_{v''} \gamma - D_{v''} \gamma^2 + H_{v''} \gamma^3) \quad (4)$$

(where $\alpha = (J + 1)(J + 2)$, $\gamma = J(J - 1)$, $\beta = J \times (J - 1)$ and $T_e = T_{0,0} + G_0'' - G_0'$; $T_{0,0}$ being the distance between the ground level $v'' = 0$, $J = 0$ of the X state and the level $v' = 0$, $J = 0$ of the B state), the unknowns being the molecular constants. If the CDC values of the B state are known from theory, the centrifugal distortion contribution (quantities in brackets, Eqs. (3) and (4)) can be subtracted from the « raw » measured wavenumbers $\sigma_R(J)$ and $\sigma_P(J)$ leading to « distortion-free » wavenumbers. A further simplification of the system is obtained by assuming that the ground state's constants are well known and are equal to those deduced from the IPA potential (Table III). Finally it remains to fit a system containing 17 800 corrected wavenumbers to an expression with 162 unknowns : the 81 vibrational $G_{v'}$ constants and the 81 rotational constants $B_{v'}$ belonging to the B state with $0 \leqslant v' \leqslant 80$. The principal problem consists of

Table III. — *Dunham coefficients describing the vibrational and rotational molecular constants of the* B *state* (*valid up to* $v' = 80$) *and* X *state* (*valid up to* $v'' = 19$). *The number of significant digits necessary to recalculate the wavenumbers of the transition belonging to the* (B-X) I_2 *system is given in parentheses :* $y_{i0}(12)$, $y_{i1}(11)$.

	i	y_{i0}	i	y_{i1}
			0	0.37368125593374800-01
	1	0.2145292253831637D+03	1	-.1138151197256179D-03
X state	2	-.6129731614337341D+00	2	-.3061638399475614D-06
	3	-.1027340004155040D-03	3	-.4093271255246214D-08
$0 \leqslant v'' \leqslant 19$	4	-.1427228811574466D-03	4	0.954261758786540D-10
	5	0.8765347546885206D-05	5	-.466472158656780D-11
	6	-.3036676438177481D-06		
	7	0.4241664120510493D-08		

	i	y_{i0}	i	y_{i1}
			0	0.2900072710830-01
	1	0.1256686951781330+03	1	-.1494374068110-03
	2	-.7503998360394800+00	2	-.126039916187D-05
	3	-.4144041450207300-02	3	0.360843852404D-07
	4	0.2248931580864800-03	4	-.118936764784D-07
	5	-.3228682530208200-04	5	0.160836460759D-08
B state	6	0.2827402678223100-05	6	-.140149921572D-09
	7	-.1697605952591200-06	7	0.817082273146D-11
$0 \leqslant v' \leqslant 80$	8	0.7248339198431400-08	8	-.329526101021D-12
	9	-.2236683436162100-09	9	0.937259316176D-14
	10	0.5024159532913000-11	10	-.189281067061D-15
	11	-.8183150076487400-13	11	0.269875228921D-17
	12	0.9520574918516400-15	12	-.265723409355D-19
	13	-.7683789243394700-17	13	0.172032143518D-21
	14	0.4075803322639100-19	14	-.659290444078D-24
	15	-.1275286930700500-21	15	0.113349602297D-26
	16	0.1780620741121100-24		

determining good initial $G_{v'}$ and $B_{v'}$ values in order to start the iterative procedure (Fig. 4). For this purpose a preliminary least squares fit is made with the raw measured wavenumbers where only the molecular constants $G_{v'}$, $B_{v'}$, $D_{v'}$ and $H_{v'}$ are taken into account. The centrifugal distortion constants $L_{v'}$ and $M_{v'}$ are too small for empirical determination, hence they were set to be equal to zero in the preliminary fit. Once a set of $G_{v'}$ and $B_{v'}$ constants are known, their Dunham expansion parameters are determined and a RKR [39] curve may be constructed [40] and used to generate centrifugal distortion constants [19, 41]. An iterative approach is then necessary to obtain a self-consistent set of vibrational, rotational and centrifugal distortion constants [9, 19].

However transitions connected to rotational levels with high J values (levels situated between the two full lines $- M_v K^5 = 0.001$ cm^{-1} and $- M_v K^5 = 0.025$ cm^{-1} $(K = J(J + 1)$ in Fig. 5) require distortion constants higher than $M_{v'}$ in order to be accurately recalculated). By means of effective $M_v^* = kM_v$ constants, which take account of the neglected higher N_v, O_v... constants (see Ref. [20]), and where k is an empirical scaling factor equal to 2.2, it was possible to handle the whole field of data (Table I and Figs. 5 and 6) in one sweep.

Including the $M_v^* = kM_v$ effective constants in the fits, the procedure represented by figure 4 converges rapidly and only two iterations were required. The resulting overall standard error $\hat{\sigma}$ between the 17 800 computed wavenumbers and the measured ones was 0.002 cm^{-1}. The least squares fits were unweighted
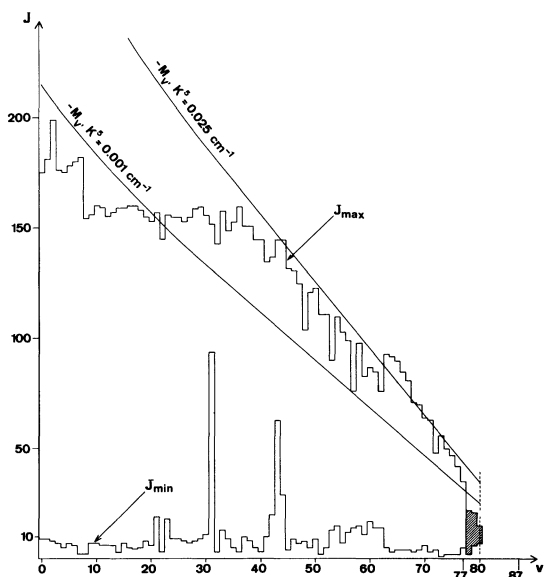
Fig. 5. — Observed data field of the B state. High J and high v values are located between the two full lines $- M_v K^5 = 0.001$ cm^{-1} and $- M_v K^5 = 0.025$ cm^{-1} ($K = J(J + 1)$).
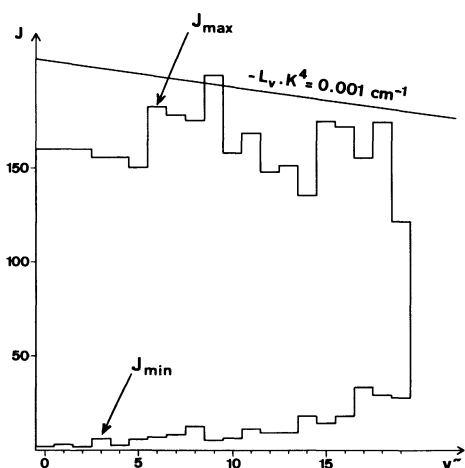

Fig. 6. — Observed data field of the X state. The contribution of the $L_{v''}$ constants can be neglected, the data field being situated almost outside and below the full line $- L_v K^4 = 0.001$ cm^{-1} ($K = J(J + 1)$).

fits made with data of different qualities depending on the experimental conditions in which they were recorded as well as on the nature (density) of the spectrum. Thus, the actual significance of the overall standard error $\hat{\sigma} = 0.002$ cm^{-1} must be redefined according to the analysis of the 17 800 residuals (or differences $(\sigma_{cal} - \sigma_{meas})$).

3.3 ANALYSIS OF THE 17 800 RESIDUALS. — The histogram of the $n = 17\,800$ residuals given on figure 7 shows that the distribution of the errors of the measurements is not a normal one. The width of each interval is $l = \hat{\sigma}/5$ with $\hat{\sigma} = 0.002$ cm^{-1}, the solid curve is the
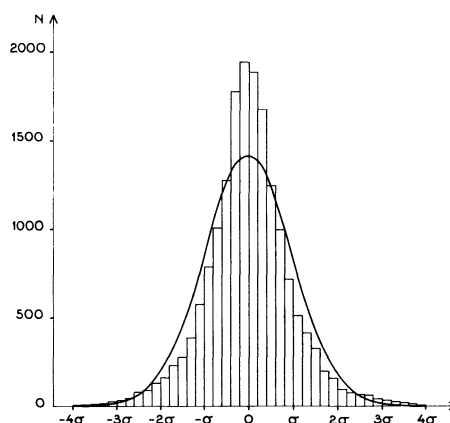

Fig. 7. — Histogram of the 17 800 residuals. The solid curve is a normal distribution with $N = 17\,800$, $l = \hat{\sigma}/5$, $\mu = 0$ and $\hat{\sigma} = 0.002$ cm^{-1} (see text).

Gaussian curve according to the equation ([42] p. 28)

$$\varphi(x) = \frac{nl}{\hat{\sigma}(2\pi)^{1/2}} \exp\left[-\frac{1}{2}\left(\frac{x - \mu}{\hat{\sigma}}\right)^2 \right]$$

when μ is taken equal to zero.

To explain the non normal distribution, i.e. an excess of the number of residuals between $- \hat{\sigma}$ and $+ \hat{\sigma}$, two additional plots were made.

a) A plot of the standard errors associated with each J value, from $J = 10$ to $J = 199$ (Fig. 8). Some systematic, but expected, trends are visible : for low
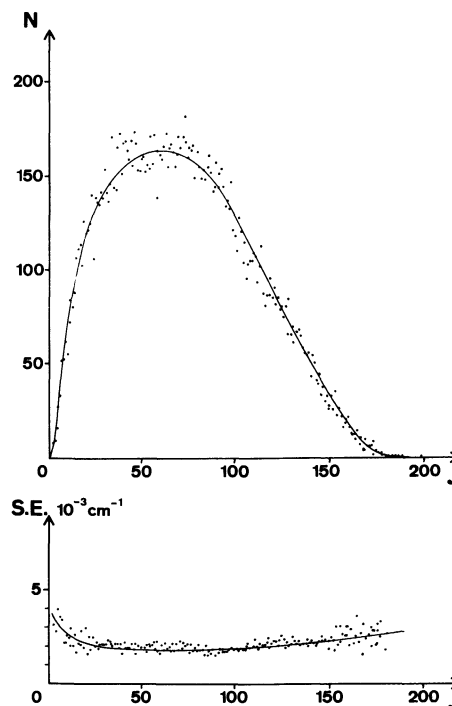

Fig. 8. — Distribution of the standard errors (S.E.) as a function of J. Note the « rotational » aspect of this distribution. $N =$ number of observed J values.

and high J values the standard errors increase according to the rotational distribution of the intensities in each observed band. Note that the « sampling distribution » of the 17 800 lines as a function of the number N of observed J values shows a flat maximum localized between $J = 50$ and $J = 100$.

This flat maximum reflects the experimental conditions in which the absorption spectrum was recorded. For an absorption cell at room temperature ($T = 293$ K, Atlas, Part III and IV), or heated at $T = 523$ K (Atlas, Part II), or heated at $T = 773$ K (Atlas, Part I), the observed maxima of the intensities of the rotational lines are located respectively at $J \sim 51$, $J \sim 69$ and $J \sim 84$.

Thus, the number of « intense » lines predominates, in a natural way, inside the sampled 17 800 lines. In principle, least squares fits which are weighted according to the intensities of the lines should remove the « non normal » residual distribution, but the following plot shows that the neglected intensity parameter is far from being the principal factor which gives rise to the observed distribution.

b) A plot of the wavenumbers of the 174 band origins associated with the standard error of each band (Fig. 9). This representation gives the key to the non Gaussian distribution observed in figure 7. In fact we have mixed in the global least squares fits three different sources of data :

i) The infrared data, recorded in Atlas I, covering the 11 000-14 000 cm^{-1} region where the (v', v'') bands, with $v' = 0, 1, 2$ and $11 \leqslant v'' \leqslant 19$, are localized. The corresponding wavenumbers of the 2 648 assigned lines in this region are reproduced within a standard error of 0.003 cm^{-1} (Fig. 9 and Refs. [16, 17]).

ii) The visible data [14], recorded in Atlas II, III and IV and spread out from 14 000 cm^{-1} to 20 000 cm^{-1}, contains the (v', v'') bands, with $1 \leqslant v' \leqslant 74$ and $0 \leqslant v'' \leqslant 10$. The 14 936 wavenumbers of the assigned lines are reproduced with a Standard Error (S.E.) steadily increasing from a value of 0.001 cm^{-1} represented by crosses in figure 9 to a value of 0.002 cm^{-1} (full circles, Fig. 9).

iii) Data (221 assigned lines) belonging to weak $(v', 0)$ bands where $v' \geqslant 75$, situated above 20 000 cm^{-1} (end of Atlas IV and fluorescence data [26]). Here the S.E. increases to 0.008 cm^{-1}.

It follows that the central part of the residual distribution corresponds mainly to part ii) of the spectrum, while the wings are mainly populated with the
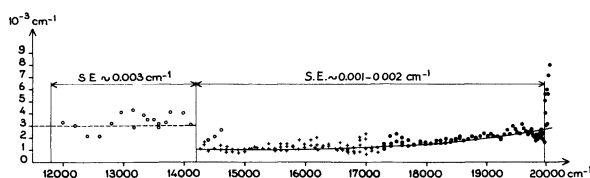
data of part i) as can easily be verified directly by inspection of the origins of the residuals; the low number of assigned lines of part iii) has no noticeable influence on the total distribution. Thus, weighted least squares fits taking into account both the intensities of the lines and the origin of the three different populations should, in principle, be made. This amount of work was considered to be unnecessary and illusory : unnecessary because the coupling between the data of parts i) and ii) is weak, only the levels $v' = 1$ and $v' = 2$ being involved in these two parts; and illusory because the weight of a given line depends not only on the intensity of the line, but also on some hidden parameters as for example the noise in the vicinity of the line [15], and/or overlapping of very weak absorption lines and uncertainties on the centre positions induced by the presence of a non negligible hyperfine structure according to the parity of the transitions [26, 27]. Briefly, valuable criteria defining *a priori* the quality of a given line in the iodine absorption spectrum are difficult to find, if not impossible.

To summarize, analysis of the residuals acts as a detector of the different uncertainties associated with the different experimental conditions in which the absorption spectrum was recorded. The overall standard error $\hat\sigma = 0.002$ cm^{-1} characterizes the major part of the spectrum (region ii), the visible part) which contains $\sim 90 \%$ of the assigned lines; but the two extremities of the spectrum ($\sigma < 14\,200$ cm^{-1} and $\sigma > 20\,000$ cm^{-1}) are known with less accuracy. But in any case, the computed wavenumbers always reproduce the experimental ones within three times the respective standard errors quoted in figure 9. It should also be noted that from figures 8 and 9, the standard errors increase with both J and v. The data field which corresponds to high J and v values lies between the two full lines $- M.K^5 = 0.001$ cm^{-1} and $- M.K^5 = 0.025$ cm^{-1}. The most plausible explanation of this behaviour is either to assume that some systematic error is introduced by the use of effective $M_v^* = kM_v$ constants in the fits or by the iterative procedure itself. This latter point will be examined in section 5.

3.4 MOLECULAR CONSTANTS AND « COMPACT REPRESENTATION ». — The final Dunham coefficients for the G_v and B_v expansion of the B state are given in table III, and for the sake of completeness we add those describing the X state for $0 < v'' < 19$. Briefly, only 45 Dunham coefficients are needed to recalculate the observed absorption spectrum of the (B-X) system ; the CDC_s are not independent parameters since they are determined by the knowledge of $G(v)$ and $B(v)$ [19]. Table III is central to our work : it represents the most compact representation that it is possible to reach of the absorption (B-X) I_2 spectrum. Indeed, by means of the above 45 Dunham coefficients, the wavenumbers of more than the 100 000 recorded lines

Fig. 9. — Observed values of standard errors (S.E.) of each band plotted in function of the band origin wavenumbers.

contained in the four published atlases, can be recalculated within experimental error. However, these recalculations involve the use of Hutson's program which gives access to the needed CDC_s; but, *a posteriori*, CDC_s can also be represented in a « compact » form by the coefficients of their exponential polynomials : they are given in table IV (which contains also the Dunham coefficients for $D_{v''}$ and $H_{v''}$). Finally table V presents, *in extenso*, the molecular constants appearing in equations (3) and (4) for $0 \leqslant v' \leqslant 80$ and $0 \leqslant v'' \leqslant 19$.

Thus the calculation of the molecular constants by means of a simple computer program can be done by the use of the coefficients of table III and table IV which in turn permits the recalculation of the wavenumbers of the whole (B-X) I₂ system (Such simple programs are available from us, at Aimé Cotton Laboratory). Table V is useful for people who need to identify a few transitions, as frequently occurs in laser spectroscopy, and also gives a check of the calculated molecular constants deduced using the coefficients given in tables III and IV or from the use of Hutson's program [19].

3.5 ACCURACY OF THE VIBRATIONAL AND ROTATIONAL MOLECULAR CONSTANTS.

— The uncertainties in the $G(v)$ constants, or more precisely in the $E(v)$ constants where

$$E(v) = T_{0,0} + G(v) - G(0) = G(v) + 15\ 661.9408\ \text{cm}^{-1}$$

listed in table V, column 1 are not easy to evaluate for the following reasons :

(i) These $E(v)$ values are « smoothed » ones which reproduce more or less faithfully the $E(v)$ values resulting from the last step of the Global Fit (G.F.) in the iterative procedure. The differences $E(v) - E(v)_{G.F.}$ are within $\pm$ 0.001 cm^{-1} up to $v = 72$ and within $\pm$ 0.0045 cm^{-1} in the $73 \leqslant v \leqslant 80$ range, reflecting the decrease of the accuracy of the wavenumber measurements near the dissociation limit.

(ii) The $E(v)_{G.F.}$ values which represent the band origins are not measured directly; the accuracy of $E(v)_{G.F.}$ depends on :

a) the uncertainties of the wavenumber measurements (noise and calibration),

b) the « fitting » procedure : the reliability of the fits depends partially on the validity of the CDC_s constants which are calculated *a priori* by Hutson's method and partially for each band origin $E(v)$ on the number of unblended lines which are assigned in every band, together with the lowest values detected in every band (for a complete discussion of this latter point see Ref. [42]).

Errors due to the finite value of the signal to noise ratio of the lines can easily be estimated by the consideration of the $\Delta_2 F_J''$ combination differences (Section 3.1); the calibration of the spectrum was made

Table IV. — *Dunham coefficients describing the D" and H" constants according to $D'', H'' = \sum_{i=0} y_{il} \times (v + 1/2)^i$ with $l = 2, 3$; and exponential coefficients describing the CDC_s of the B state.*
The number of significant digits necessary to recalculate the wavenumbers of the transition belonging to the (B-X) I₂ system is given in parentheses : $y_{i2}(10)$, $y_{i3}(9)$, $C_{di}(10)$, $C_{hi}(9)$, $C_{li}(8)$, $C_{mi}(7)$.

y_{i2}	y_{i3}
0.45353679538848400-08	-.50207688405839991D-15
0.24310683753169780-10	-.21450634511712290-16
0.57037424644064170-13	0.25912233508729340-18
0.84736023494025630-13	-.11989817453310800-18
-.85288656961385350-14	0.87845253090812590-20
0.45723693000126940-15	-.29417135709469230-21
-.94293077060302580-17	

X state

C_{di}	C_{hi}	C_{li}	C_{mi}
-.189024223360+02	-.33718944650+02	-.473050709D+02	-.598483130+02
0.175716102030-01	0.77704316200-01	0.109273874D+00	0.772788710-01
0.146926005210-03	0.104229675 80-02	0.456705023D-02	0.174494450-01
0.491824300750-04	-.25639672930-03	-.802422429D-03	-.158147450-02
-.735276143810-05	0.35991552530-04	0.711468387D-04	0.754760300-04
0.732259496430-06	-.28306619930-05	-.355923537D-05	-.203184750-05
-.486777663430-07	0.13695908530-06	0.106987914D-06	0.310466700-07
0.223304629000-08	-.42618198050-08	-.197187575D-08	-.250030260-09
-.720473417820-10	0.86705863470-10	0.218610546D-10	0.825358240-12
0.164186869140-11	-.11452402780-11	-.133994869D-12	
-.262426680710-13	0.94600773520-13	0.349444102D-15	
0.287833721810-15	-.44418160370-16		
-.206482606200-17	0.90585760130-19		
0.873110097150-20			
-.165046951130-22			

B state

by means of selected iodine lines the wavenumbers of which are known precisely and independently (they are given in Section 4). It turns out that the estimated uncertainties due to these different sources — use of Dunham expansion series, internal coherence of the wavenumber measurements (noise) and external coherence of the wavenumber measurements (calibration) are sensibly equal, as one would expect, to the standard deviation of $\sigma_{cal} - \sigma_{meas}$. Since the values of $E(v)_{G.F.}$ are deduced from a substantial number of lines belonging to several bands it follows that an upper limit for the uncertainties of the vibrational energies can be taken equal to the value of the standard deviation of $\sigma_{cal} - \sigma_{meas}$ quoted in each band. Table VI summarizes the estimated upper limit for uncertainties $\delta E(v)$ characterizing the vibrational energies for the $v = 0$-80 range. Similarly the $\delta B(v)$ uncertainties correspond to changes in $B(v)$ values which induce variations of the order of $\delta E(v)$ on the rotational energies. The uncertainties given in table VI appear to us to be much more realistic than the associated uncertainties resulting from the global fits of the data which are deemed small, as usual [36, 42].

4. Comparison with independent interferometric wavenumber measurements : a test for the molecular constants.

Since 1975, the number of wavenumbers of iodine lines which are measured independently (i.e. not by F.T.S.) with precision (interferometric methods in general),

Table V. — *Energies* (E_v), *rotational* (B_v) *and* CDC_s *of the* B *and* X *state* $(E_v = T_{0,0} + G(v) - G(0))$.

v'	$E_{v'}$	$B_{v'}$	$D_{v'}$	$-H_{v'}$	$-L_{v'}$	$-M^\bullet_{v'}$
0	15724.5871	0.2892569710D-01	0.623184071D-08	0.236059709D-14	0.301891905D-20	0.106365241D-25
1	15848.7424	0.2873807040D-01	0.634498863D-08	0.255494386D-14	0.339067474D-20	0.118424920D-25
2	15971.3641	0.2861948270D-01	0.646390069D-08	0.276699292D-14	0.382234284D-20	0.134878319D-25
3	16092.4323	0.2846265160D-01	0.658936697D-08	0.299730171D-14	0.431548074D-20	0.156148979D-25
4	16211.9276	0.2830320720D-01	0.672194237D-08	0.324712735D-14	0.487312647D-20	0.182822101D-25
5	16329.8305	0.2814103630D-01	0.686208169D-08	0.351828987D-14	0.549996849D-20	0.215614715D-25
6	16446.1208	0.2797602890D-01	0.701022026D-08	0.381305617D-14	0.620256031D-20	0.255362733D-25
7	16560.7781	0.2780807890D-01	0.716681823D-08	0.413404624D-14	0.698953410D-20	0.303021172D-25
8	16673.7813	0.2763708070D-01	0.733238172D-08	0.448416290D-14	0.787179347D-20	0.359676671D-25
9	16785.1091	0.2746292520D-01	0.750747024D-08	0.486654557D-14	0.886268189D-20	0.426572538D-25
10	16894.7398	0.2728549690D-01	0.769269693D-08	0.528454767D-14	0.997813192D-20	0.505146923D-25
11	17002.6518	0.2710467250D-01	0.788872567D-08	0.574173652D-14	0.112368044D-19	0.597084729D-25
12	17108.8231	0.2692032120D-01	0.809626788D-08	0.624191446D-14	0.126602265D-19	0.704383883D-25
13	17213.2315	0.2673230560D-01	0.831608011D-08	0.678915959D-14	0.142729375D-19	0.829436694D-25
14	17315.8550	0.2654048340D-01	0.854896312D-08	0.738788420D-14	0.161026496D-19	0.975127447D-25
15	17416.6714	0.2634470940D-01	0.879576237D-08	0.804290883D-14	0.205409358D-19	0.114494794D-24
16	17515.6584	0.2614483730D-01	0.905736950D-08	0.875954939D-14	0.232226556D-19	0.134313350D-24
17	17612.7938	0.2594072070D-01	0.933472447D-08	0.954371438D-14	0.262628241D-19	0.157482286D-24
18	17708.0558	0.2573221390D-01	0.962881752D-08	0.104020092D-13	0.297251563D-19	0.184624651D-24
19	17801.4224	0.2551917240D-01	0.994069070D-08	0.113418442D-13	0.336458409D-19	0.216494888D-24
20	17892.8722	0.2530145300D-01	0.102714384D-07	0.123715432D-13	0.380880215D-19	0.254005129D-24
21	17982.3842	0.2507891330D-01	0.106222064D-07	0.135004496D-13	0.431200222D-19	0.298256361D-24
22	18069.9377	0.2485141200D-01	0.109941901D-07	0.147390275D-13	0.488131426D-19	0.350575430D-24
23	18155.5130	0.2461880840D-01	0.113886305D-07	0.160989561D-13	0.552523731D-19	0.412559046D-24
24	18239.0911	0.2438096350D-01	0.118068096D-07	0.175932160D-13	0.625340690D-19	0.486126191D-24
25	18320.6538	0.2413774010D-01	0.122500445D-07	0.192361681D-13	0.707695536D-19	0.573580707D-24
26	18400.1843	0.2388900460D-01	0.127196813D-07	0.210436261D-13	0.800885008D-19	0.676886275D-24
27	18477.6669	0.2363462840D-01	0.132170885D-07	0.230329254D-13	0.906430138D-19	0.801756694D-24
28	18553.0874	0.2337449000D-01	0.137436522D-07	0.252229941D-13	0.102612626D-18	0.949765250D-24
29	18626.4332	0.2310847090D-01	0.143007709D-07	0.276344336D-13	0.116210323D-18	0.112647822D-23
30	18697.6935	0.2283649170D-01	0.148898547D-07	0.302896189D-13	0.131689806D-18	0.133761931D-23
31	18766.8595	0.2255584470D-01	0.155123256D-07	0.332128328D-13	0.149354233D-18	0.159007402D-23
32	18833.9246	0.2227427580D-01	0.161696229D-07	0.364304519D-13	0.169566755D-18	0.189214641D-23
33	18898.8844	0.2198392900D-01	0.168632122D-07	0.399712054D-13	0.192763252D-18	0.225388451D-23
34	18961.7370	0.2168737850D-01	0.175946007D-07	0.438665326D-13	0.219467754D-18	0.268749668D-23
35	19022.4833	0.2138461780D-01	0.183653576D-07	0.481510676D-13	0.250311205D-18	0.320789002D-23
36	19081.1269	0.2107566230D-01	0.191771415D-07	0.528632851D-13	0.286054391D-18	0.383336751D-23
37	19137.6741	0.2076054930D-01	0.200317341D-07	0.580463410D-13	0.327616067D-18	0.458654473D-23
38	19192.1344	0.2043933660D-01	0.209310816D-07	0.637491472D-13	0.376107648D-18	0.549553870D-23
39	19244.5204	0.2011210130D-01	0.218773428D-07	0.700277217D-13	0.432876190D-18	0.659563941D-23
40	19294.8475	0.1977892367D-01	0.228729448D-07	0.769468565D-13	0.499557954D-18	0.793128221D-23
41	19343.1343	0.1943995050D-01	0.239206455D-07	0.845821533D-13	0.578145519D-18	0.955904190D-23
42	19389.4024	0.1909526090D-01	0.250236030D-07	0.930224813D-13	0.671072385D-18	0.115513807D-22
43	19433.6763	0.1874499320D-01	0.261854525D-07	0.102372922D-12	0.781320317D-18	0.140018365D-22
44	19475.9832	0.1838927670D-01	0.274103892D-07	0.112758268D-12	0.912556444D-18	0.170320603D-22
45	19516.3530	0.1802824070D-01	0.287032577D-07	0.124327264D-12	0.106930958D-17	0.208014494D-22
46	19554.8181	0.1766201090D-01	0.300696490D-07	0.137257451D-12	0.125719862D-17	0.255204147D-22
47	19591.4129	0.1729070680D-01	0.315160040D-07	0.151761224D-12	0.148323046D-17	0.314687716D-22
48	19626.1741	0.1691443810D-01	0.330497240D-07	0.168092862D-12	0.175619147D-17	0.390214018D-22
49	19659.1400	0.1653330290D-01	0.346792900D-07	0.186557087D-12	0.208716555D-17	0.486843002D-22
50	19690.3504	0.1614738510D-01	0.364143905D-07	0.207519395D-12	0.249022455D-17	0.611455583D-22
51	19719.8466	0.1575567537D-01	0.382660587D-07	0.231418646D-12	0.298335492D-17	0.773479699D-22
52	19747.6709	0.1536146140D-01	0.402468213D-07	0.258782507D-12	0.358971029D-17	0.985931567D-22
53	19773.8664	0.1496154490D-01	0.423708590D-07	0.290246517D-12	0.433931657D-17	0.126691964D-21
54	19798.4772	0.1455702570D-01	0.446541820D-07	0.326577828D-12	0.527140992D-17	0.164183282D-21
55	19821.5480	0.1414791150D-01	0.471148212D-07	0.368704986D-12	0.643766649D-17	0.214654816D-21
56	19843.1241	0.1373418880D-01	0.497730397D-07	0.417755631D-12	0.790669836D-17	0.283217039D-21
57	19863.2512	0.1331587650D-01	0.526515687D-07	0.475104663D-12	0.977036282D-17	0.372209285D-21
58	19881.9758	0.1289293090D-01	0.557758756D-07	0.542436409D-12	0.121526919D-16	0.507261119D-21
59	19899.3449	0.1246535110D-01	0.591744750D-07	0.621825688D-12	0.152226450D-16	0.688903221D-21
60	19915.4059	0.1203313720D-01	0.628793010D-07	0.715844732D-12	0.192124993D-16	0.945038537D-21
61	19930.2072	0.1159630800D-01	0.669261601D-07	0.827705783D-12	0.244446499D-16	0.130977838D-20
62	19943.7980	0.1115491160D-01	0.713553235D-07	0.961453506D-12	0.313711182D-16	0.183447759D-20
63	19956.2281	0.1070900361D-01	0.762122829D-07	0.112222770D-11	0.406325388D-16	0.259737387D-20
64	19967.5484	0.1025882070D-01	0.815487852D-07	0.131662627D-11	0.531474864D-16	0.371924957D-20
65	19977.8108	0.980446757D-02	0.874242437D-07	0.155321297D-11	0.702499197D-16	0.538937621D-20
66	19987.0680	0.934625284D-02	0.939076958D-07	0.184336427D-11	0.939045055D-16	0.790944200D-20
67	19995.3737	0.888453519D-02	0.101080529D-06	0.220166265D-11	0.127050903D-15	0.117697738D-19
68	20002.7823	0.841976193D-02	0.109040280D-06	0.264867177D-11	0.174167121D-15	0.177852696D-19
69	20009.3488	0.795247025D-02	0.117905900D-06	0.321190625D-11	0.242215770D-15	0.273453277D-19
70	20015.1287	0.748328234D-02	0.127825023D-06	0.392975364D-11	0.342280970D-15	0.428892043D-19
71	20020.1774	0.701289274D-02	0.138983904D-06	0.485650558D-11	0.492495300D-15	0.688447771D-19
72	20024.5504	0.654204679D-02	0.151620922D-06	0.607029682D-11	0.723471116D-15	0.113561577D-18
73	20028.3027	0.607150964D-02	0.166044732D-06	0.768581392D-11	0.108880621D-14	0.193480847D-18
74	20031.4884	0.560202657D-02	0.182658459D-06	0.987504344D-11	0.168637376D-14	0.342612043D-18
75	20034.1607	0.513427726D-02	0.201991541D-06	0.129020606D-10	0.270379230D-14	0.635363441D-18
76	20036.3714	0.466882962D-02	0.224740947D-06	0.171831317D-10	0.452149406D-14	0.124528523D-17
77	20038.1708	0.420610297D-02	0.251823084D-06	0.233937676D-10	0.796277466D-14	0.260788865D-17
78	20039.6076	0.374635616D-02	0.284436013D-06	0.326669994D-10	0.149496889D-13	0.591170582D-17
79	20040.7289	0.328972386D-02	0.324126855D-06	0.469742748D-10	0.303862079D-13	0.147289758D-16
80	20041.5795	0.283633486D-02	0.372847922D-06	0.698933973D-10		0.410613097D-16

v''	$E_{v''}$	$B_{v''}$	$D_{v''}$	$H_{v''}$
0	0.000	0.3731114098671146D-01	0.4547547628207550D-08	-.5127518681623231D-15
1	0.2133022927376437D+03	0.3719670067802829D-01	0.4572208485138791D-08	-.5340322291154361D-15
2	0.4253742356725109D+03	0.3708161358474350D-01	0.4597534338572310D-08	-.5556429468721693D-15
3	0.6362102686971426D+03	0.3696586585838189D-01	0.4623730064958021D-08	-.5779567669609448D-15
4	0.8458033825751230D+03	0.3684941526048041D-01	0.4650910671516871D-08	-.6012238577098949D-15
5	0.1054145613786457D+04	0.3673226380482058D-01	0.4679135797367788D-08	-.6256071108097138D-15
6	0.1261228397284109D+04	0.3661438399566286D-01	0.4708437425553093D-08	-.6512174418765087D-15
7	0.1467042796610772D+04	0.3649575486689795D-01	0.4738840805962358D-08	-.6781490910465117D-15
8	0.1671579634153874D+04	0.3637635411248850D-01	0.4770378589154715D-08	-.7065149233796305D-15
9	0.1874829538716789D+04	0.3625615750588612D-01	0.4803098171079618D-08	-.7364817297409002D-15
10	0.2076782938784253D+04	0.3613513836108117D-01	0.4837062248696054D-08	-.7683055270447346D-15
11	0.2277430015859961D+04	0.3601326696242798D-01	0.4872342586490214D-08	-.8023668589770773D-15
12	0.2476760643454347D+04	0.3589050100695991D-01	0.4909006993891650D-08	-.8392060965263935D-15
13	0.2674764331700520D+04	0.3576683004462276D-01	0.4947099513587618D-08	-.8795587385465209D-15
14	0.2871430199176310D+04	0.3564218491850814D-01	0.4986613820736552D-08	-.9243907123195215D-15
15	0.3066746993310694D+04	0.3551652720508696D-01	0.5027459833079082D-08	-.9749336741185325D-15
16	0.3260703180751734D+04	0.3538980365444274D-01	0.5069423531948184D-08	-.1032720309770618D-14
17	0.3453287129075440D+04	0.3526195463050510D-01	0.5112119994177510D-08	-.1099619635219621D-14
18	0.3644487401212121D+04	0.3513291355128313D-01	0.5154939634908213D-08	-.1177872297089012D-14
19	0.3834293183969065D+04	0.3500260832909881D-01	0.5196987661294230D-08	-.1270125873244746D-14

Table VI. — *Estimates of the uncertainties $\delta E(v)$ and $\delta B(v)$ of the vibrational energies $E(v)$ and of the rotational constants, respectively.*

v' Range B State	$\delta E(v')$ (cm^{-1})	$\delta B(v')$ (cm^{-1})
0-2	0.003	2×10^{-7}
3-72	0.002	10^{-7}
73-76	0.003	10^{-6}
77-79	0.005	10^{-5}
80	0.010	5×10^{-5}
v'' Range X State	$\delta E(v'')$ (cm^{-1})	$\delta B(v'')$ (cm^{-1})
0-10	0.002	10^{-7}
11-19	0.003	2×10^{-7}

is growing slowly but steadily. So far, we have collected a list of 38 lines spread between 15 233.3 and 19 926.17 cm^{-1} (but we don't claim that the list given in Table VI is exhaustive !). Only a few of them were used to calibrate our data [21, 28] ; thus a comparison between the recalculated wavenumbers by means of the molecular constants of table V and the independent measured ones, becomes of crucial importance. Inspection of table VII, column 5, shows that the differences ($\sigma_{meas} - \sigma_{cal}$) are within three times the standard deviation $\hat{\sigma} = 0.002$ cm^{-1} excepted for the P56(73-0) transition for which the difference reaches $- 0.0165$ cm^{-1} (Table VII, column 5). It is a good illustration of the difficulties encountered for transitions connected to levels situated beyond the field delimited by the $- M_v K^5 = 0.001$ cm^{-1} full line (see Fig. 5). As mentioned in section 3.2, the scaling factor k ($M_v^* = kM_v$) was taken equal to 2.2 for all bands ; actually the scaling factor is « band dependent » ; with a value of $k = 2.8$ full agreement is observed for the P56(73-0) transition (Table VII, column 6), but the one for the R98(58-1) is now destroyed ($+ 0.016$ cm^{-1}). Apart from the two transitions P56(73-0) and R98(58-1), both of which arise from levels situated near the dissociation limit, table VII shows that the residuals ($\sigma_{meas} - \sigma_{cal}$) depend weakly on the exact value of k provided that the rotational levels involved in the considered transitions are situated below the dissociation limit. It should be noted that, in any case, the chosen value $k = 2.2$ does not prevent us from identifying the P56(73-0) transition correctly ; the disagreement in this case ($- 0.0165$ cm^{-1}) being half the value of the Doppler width of the line. In addition, L. Hlousek and W. M. Fairbank, Jr., have recently [43] compared the F.T.S. measurements of 27 transitions with the absolute measurements that they have made using saturation spectroscopy in the 15 233.36-17 360.6 cm^{-1}

range. The agreement between the F.T.S. and the absolute measurements was found to be better than 0.0015 cm^{-1}, see reference [43], footnote n° 3. To conclude, the good agreements between σ_{cal} and σ_{obs} show the « external » coherence of the molecular constants of table V : the recalculated wavenumbers are absolute wavenumbers (in vacuum) obtained without any corrections (with a final standard error of $\pm$ 0.002 cm^{-1}) at least in the tested region 15 223-19 926 cm^{-1}. For the region below 15 233 cm^{-1}, i.e. in the 11 000-15 233 cm^{-1} range, independent measurements of iodine transitions involving a large scale of J values, should be a further valuable test of the molecular constants.

5. Discussion.

In a recent paper [44] J. W. Tromp and R. J. Le Roy, suggest that the relatively high value of the scaling factor $k = 2.2$ ($M_v^* = kM_v$) is not only due to the truncation of the centrifugal distortion series up to $M_{v'}$ but also may be caused by some inadequacies of the model used to fit the data ; for example errors may be expected to arise in the CDC calculated quantum mechanically [44], but based on an RKR potential which is only « exact » within the first order JWKB approximation.

To check this last possibility the IPA potential of the B state was computed, using as a starting point the RKR potential defined by the Dunham and CDC coefficients determined in this work (Tables II and III) [30]. It turns out that the IPA potential of the B state reproduces correctly the quantum calculated eigenvalues for $0 \leqslant v' \leqslant 40$ and for $60 \leqslant v' \leqslant 80$, but in the medium region $40 \leqslant v' \leqslant 60$ the agreement is less satisfactory but remains fairly good (Fig. 10, Ref. [30]). Nevertheless, we repeat the quantum mechanical computation of the CDC$_s$ of the B state using
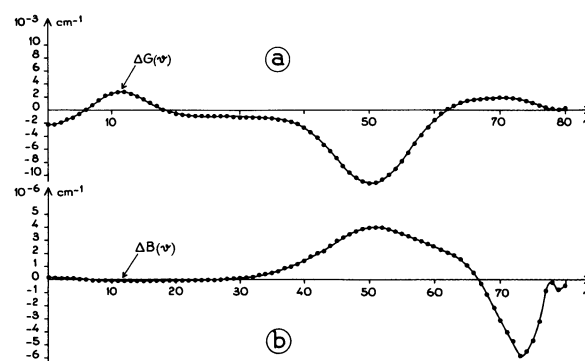
Fig. 10. — a) Differences between the calculated eigenvalues $G(v)$ (see Ref. [30]) and the « experimental » ones described by the Dunham coefficients given in first column of table III. The discrepancy in the region $40 < v' < 60$ is obvious. b) Differences between the expectation values $\langle B(v) \rangle$ deduced from the IPA potential (see Ref. [30]) and the « experimental » ones described by the Dunham coefficients given in table III, column 2.

Table VII. — *Comparison between computed wavenumbers and absolute wavenumbers measurements made by interferometric methods other than F.T.S.*

Assignments		Wavenumbers (cm^{-1})			$[\sigma_{meas} - \sigma_{cal}]$ (10^{-3} cm^{-1})	
		σ_{meas}	σ_{cal} $k = 2.2$	σ_{cal} $k = 2.8$	$k = 2.2$	$k = 2.8$
R73(5-5)	(a)	15 233.3641	.3646	.3646	− 0.5	− 0.5
P33(6-3)	(b)	15 797.9763	.9756	.9756	+ 0.7	+ 0.7
R127(11-5)	(c)	.9996	.0005	.0004	− 0.9	− 0.8
P48(11-3)	(d)	16 340.6316	.6314	.6314	+ 0.2	+ 0.2
R48(15-5)	(d)	.6487	.6490	.6490	− 0.3	− 0.3
R47(9-2)	(e)	.6547	.6533	.6533	+ 1.4	+ 1.4
P62(13-1)	(f)	16 955.6930	.6910	.6910	+ 2.0	+ 2.0
R67(13-1)	(f)	.8022	.8002	.8002	+ 2.0	+ 2.0
R119(14-1)	(f)	.8610	.8598	.8598	+ 1.2	+ 1.2
P114(14-1)	(f)	16 956.1518	.1506	.1506	+ 1.2	+ 1.2
R59(15-2)	(f)	.3909	.3894	.3893	+ 1.5	+ 1.6
P54(15-2)	(f)	.5333	.5316	.5316	+ 1.7	+ 1.7
P107(14-1)	(f)	16 973.2316	.2304	.2304	+ 1.2	+ 1.2
R43(15-2)	(f)	.2849	.2832	.2832	+ 1.7	+ 1.7
P38(15-2)	(f)	.3760	.3755	.3755	+ 0.5	+ 0.5
R105(16-2)	(f)	.4938	.4925	.4925	+ 1.3	+ 1.3
P47(13-1)	(f)	.7950	.7931	.7931	+ 1.9	+ 1.9
P142(15-1)	(f)	.8224	.8225	.8224	− 0.1	− 0.1
R52(13-1)	(f)	.8914	.8895	.8895	+ 1.9	+ 1.9
R85(16-2)	(f)	17 014.5701	.5683	.5683	+ 1.8	+ 1.8
P80(16-2)	(f)	17 015.0616	.0598	.0598	+ 1.8	+ 1.8

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directly the IPA potential. Again the new CDC$_s$ values were in excellent agreement with those calculated by means of an RKR potential, for all v' levels. Thus, it is impossible to ascribe the value of the scaling factor k to cumulative errors due to calculating quantum mechanically of CDC$_s$ based on RKR potentials. On another hand, the use of k is restricted to the recalculation of the energies of levels where high v' and J' values are involved, i.e., above the full line $- MK^5 = 0.001$ cm^{-1} of figure 5. In the regions of high v' and J' values, situated near the dissociation limit, represented also on figure 3, a breakdown of the Born-Oppenheimer approximation should occur; and the use of both Hutson's method for the CDC calculations and Dunham series may be no more valid. Thus, the relative high value of the scaling factor k should be ascribed not only to the neglected high order CDC values, but also to violations of the Born-Oppenheimer approximation. Indeed, if we consider the Coriolis effect alone, the actual B_v values have to be smaller than the mechanical values implied by the B state potential energy curve [22]. For example, for $v' = 78$ the correction ΔB on B'_{78} was estimated to be 1.5×10^{-5} ([22], Table I) and according to J. Vigué (private communication), the ΔB calculated corrections [22] have to be multiplied by a factor 2, because the

Table VII (continued).

Assignments		Wavenumbers (cm^{-1})			$[\sigma_{meas} - \sigma_{cal}]\,(10^{-3}\ cm^{-1})$	
		σ_{meas}	σ_{cal} $k = 2.2$	σ_{cal} $k = 2.8$	$k = 2.2$	$k = 2.8$
P62(17-1)	(g)	17 352.2475	.2448	.2448	+ 2.7	+ 2.7
P117(21-1)	(h)	17 594.799	.7963	.7963	+ 2.7	+ 2.7
P133(27-3)	(i, g)	.8474	.8453	.8449	+ 2.1	+ 2.5
R98(43-2)	(h, i, g)	18 831.8712	.8714	.8710	− 0.2	+ 0.2
R76(40-0)	(h)	19 194.6090	.6085	.6084	+ 0.5	+ 0.6
P108(49-1)	(i)	.691	.6911	.6884	− 0.1	+ 2.6
R98(58-1)	(j)	19 429.730	.7270	.7140	+ 3.0	+ 16.0
P13(43-0)	(j, k)	.8087	.8094	.8094	− 0.7	− 0.7
R15(43-0)	(j, k)	.8182	.8186	.8185	− 0.4	− 0.3
P12(61-0)	(l, m)	19 925.9160	.9164	.9163	− 0.4	− 0.3
R49(67-0)	(l)	.9410	.9453	.9449	− 4.3	− 3.9
R39(64-0)	(l)	.9532	.9531	.9531	+ 0.1	+ 0.1
R26(62-0)	(l)	19 926.0009	.9997	.9997	+ 1.2	+ 1.2
P56(73-0)	(l)	.0172	.0337	.0192	− 16.5	− 2.0
R54(70-0)	(l)	.0359	.0421	.0389	− 6.2	− 3.0
R55(71-0)	(l)	.0490	.0550	.0488	− 6.0	− 0.2
R51(68-0)	(l)	.1724	.1762	.1754	− 3.8	− 3.0

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existence of state with $\Omega = -1$. For the rotational level $E(v = 78, J = 10)$ the correction should be $\Delta B J(J + 1) \sim 0.003\ cm^{-1}$ which is of the order of the experimental uncertainties in this region ; but for $J = 22$, the last vibrational level observed in the (78, 0) band (see Table I), the correction reaches a value of about 0.015 cm^{-1} which is no more negligible at the degree of precision of our measurements ; but this correction remains comparable (in sign and magnitude) with the contributions of the M_v constants. It follows that together with the use of empirical B_v values, the relative high value of the scaling factor k can be attributed to the necessity of absorbing partially the depression of the rotational levels caused by the Coriolis effect.

At the same time, the success and the limitation of the iterative procedure illustrated on figure 4 can

be explained in this manner : after each iteration the CDC_s remain practically unchanged ; the adjustments (differences between computed and « distortion-free » wavenumbers) are mainly absorbed by the vibrational and rotational constants $G(v)$ and $B(v)$. For compact representation, the only requirement which remains to be satisfied is that the $G(v)$ and $B(v)$ constants resulting after a given iteration process should be representable by Dunham expansion series. Of course, this cannot be achieved without some loss on the final overall standard errors $\hat{\sigma}$; but on the other hand it is easy to understand why in general two iterations are sufficient to reach convergence. Some other systematic errors can be introduced by the use of an incorrect scaling factor k which would mainly yield biased values of the rotational constants $B(v)$. This cannot be avoided if we choose, for the sake of simplicity, to represent the

higher neglected CDC_s N_v, O_v ... by a unique scaling factor k for all v' levels, while actually the scaling factor is rather band dependent. Thus, the final overall standard error $\hat{\sigma} = 0.002$ cm^{-1} is model dependent, at least, in two ways : first, the introduction of an empirical scaling factor in the fits, and second, which is more important, the use of Dunham's expansion series for the representation of the vibrational and rotational effective constants.

The price we pay in order to fulfil the last « model dependent condition » can be estimated from the difference between the overall standard errors $\sigma_2 = 0.0017$ cm^{-1} obtained after the first iteration (where $G(v)$ and $B(v)$ remain free) and the final overall standard error $\hat{\sigma} = 0.002$ cm^{-1} where the $G(v)$ and $B(v)$ values are those deduced from the Dunham expansion series. Likewise the slight increase of the standard errors with v' (Fig. 9) has the same origin. The $G(v)$ and $B(v)$ values obtained after the first iteration are less faithfully represented by the Dunham expansion series as v' increases. Fortunately, the standard deviations $\hat{\sigma} = 0.002$ cm^{-1} remain comparable to the uncertainties of the measurements on the vertex positions (~ 0.0016 cm^{-1} Table II), thanks to the simultaneous decrease of the J values observed in each band (Fig. 5).

Other « compact » representations of the CDC constants using Near Dissociation Expansion (NDE) functions have been proposed by J. P. Tromp and R. J. Le Roy [44]. These representations also need the use of the traditional methods [19, 39] but have the ability to provide reliable predictions for vibrational levels lying above the highest one observed. Since in the iodine (B-X) I_2 system above $v' = 80$, the last vibrational level considered in this work, clear band structures are no longer easily observable [21], because of the existence of both hyperfine structures which are of the same order of magnitude as the rotational structure and mixing between u and g states [34], « compact » representation of the (B-X) I_2 system was achieved using only the traditional method (Dunham series-RKR potentials and computed CDC_s [19]).

It follows that in this last representation the vibrational and rotational constants of the B state are « effective » constants rather than « true » molecular ones, because the quantum eigenvalues of the IPA potential do not represent with enough accuracy the observed $G(v)$ and $B(v)$ values at least in the medium region $40 < v' < 60$, as recalled above. It was not possible to obtain an accurate « compact » representation based on a pure quantum-chain « IPA potential-computed CDC_s ».

But the reason why the potential of the B state cannot be represented within experimental uncertainties throughout its whole depth (from $v' = 0$ to $v' = 80$) by a pure quantum potential was not clear to us, until the very recent work of J. P. Pique et al. who have shown (Refs. [34a] and [34b], Annexe III, p. 289) that the B state should be slightly perturbed by

the 1'g state (around $v' \sim 58$ and $v' \sim 78$) through hyperfine interactions occurring between the BO_u^+ and 1'g states. In other words, IPA calculations seem to act as a good « perturbation detector » ([24, 25] see Fig. 10) and finally it follows now that, in a natural way, only effective G_v' and B_v' values can be used for the « compact » representation of the whole (B-X) I_2 system. Again, the advantage of the iterative process used in this work is perceptible since in our fits vibrational and rotational constants remain free, while using IPA potentials they are no more. Therefore, in presence of weak perturbations, for the « compact » representation the traditional method, which is more flexible, has to be used.

6. Conclusion.

The (B-X) I_2 system of iodine constitutes now one of the few diatomic molecular systems which is accurately known. It has been analysed entirely by means of the simple oscillator model in the framework of the Born-Oppenheimer approximation which seems to be adequate for the analysis of the data field situated below the dissociation limit (Fig. 3). Above this limit, for high v' and J' values the Born-Oppenheimer approximation may be insufficient : with this restriction in mind, the whole observed (B-X) I_2 system can be recalculated, within experimental uncertainties, provided that the vibrational and rotational constants are known; in other words the recalculation of the wavenumbers of the 100 000 recorded lines in the iodine Atlases needed the knowledge of only 45 Dunham expansion coefficients describing both the X state (up to $v' = 19$) and the B state (up to $v' = 80$), (plus one empirical scaling factor defining the effective M_v constants). As a result of this work a series of atlases representing the iodine absorption spectrum ranging from 11 000 to 20 040 cm^{-1} serve, universally, at present time, as standard reference for calibration purposes mainly in Laser spectroscopy.

This achievement is the best proof of the high quality of the F.T.S. measurements as well as an excellent illustration of the high degree of confidence reached in modern diatomic theory [9, 19, 23, 24, 37-42]. However, the tremendous « compact » representation of the (B-X) I_2 system was obtained assuming that « effective » vibrational and rotational constants are sufficient to describe the B state; indeed, it was not possible to compute a quantum potential of the B state through its whole depth using the IPA method [23, 24]. Thus, some amount of work remains in order to put directly in evidence the genuine perturbation induced by the 1'g state; and according to the work of J. P. Pique et al. some weak absorption lines belonging to the X → 1'g system should be observed in the 19 800 cm^{-1} region where the vibrational levels around $v' \sim 58$ are situated.

Acknowledgments.

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