

Study of the iodine absorption spectrum by means of Fourier spectroscopy in the region 12 600-14 000 cm⁻¹

S. Gerstenkorn, P. Luc, J. Sinzelle

► **To cite this version:**

S. Gerstenkorn, P. Luc, J. Sinzelle. Study of the iodine absorption spectrum by means of Fourier spectroscopy in the region 12 600-14 000 cm⁻¹. *Journal de Physique*, 1980, 41 (12), pp.1419-1430. 10.1051/jphys:0198000410120141900 . jpa-00208967

HAL Id: jpa-00208967

<https://hal.archives-ouvertes.fr/jpa-00208967>

Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
 Physics Abstracts
 06.20H — 07.60L

Study of the iodine absorption spectrum by means of Fourier spectroscopy in the region 12 600-14 000 cm^{-1}

S. Gerstenkorn, P. Luc and J. Sinzelle

Laboratoire Aimé Cotton (*), Centre National de la Recherche Scientifique, Bâtiment 505, 91405 Orsay, France

(Reçu le 3 juin 1980, accepté le 25 juillet 1980)

Résumé. — Douze nouvelles bandes du spectre d'absorption de la molécule de l'iode situées dans l'infrarouge proche entre 12 600 et 14 000 cm^{-1} ont été identifiées. Ces bandes appartiennent aux progressions $(0, v'')$, $(1, v'')$ et $(2, v'')$, où $10 \leq v'' \leq 14$; leur étude a permis à la fois de déterminer avec précision les constantes moléculaires $G(v'')$, $B(v'')$ et $D(v'')$ de l'état fondamental $X(^1\Sigma_g^+)$ jusqu'à $v'' = 14$ et d'atteindre les niveaux profonds de l'état excité $B(^3\Pi_{ou}^+)$; en particulier, la distance $T_{0,0}$ entre les états X et B est trouvée égale à $15\,724,586 \pm 0,003 \text{ cm}^{-1}$. Les constantes de distorsion d'ordre élevé D , H et L des états B et X ont été calculées à partir des potentiels RKR grâce à la méthode mise au point par Albritton *et al.* (*J. Mol. Spectrosc.* 46 (1973) 25). L'accord entre les valeurs expérimentales et les valeurs calculées des constantes $D(v'')$ et $D(v')$ est satisfaisant; de même, les intensités relatives observées des bandes sont en bon accord avec les intensités relatives calculées à partir des facteurs de Franck-Condon.

Abstract. — Twelve new absorption bands of the iodine molecular spectrum belonging to the $(0, v'')$, $(1, v'')$ and $(2, v'')$ progressions, where $10 \leq v'' \leq 14$, have been analysed. The data obtained by Fourier spectroscopy measurements between 12 600 and 14 000 cm^{-1} , permit both the extension of the precise determination of the molecular constants $G(v'')$, $B(v'')$ and $D(v'')$ of the ground state $X(^1\Sigma_g^+)$ up to $v'' = 14$ and studies of the low-lying levels of the excited state $B(^3\Pi_{ou}^+)$; in particular the separation between the two states X and B is found to be

$$T_{0,0} = 15\,724.586 \pm 0.003 \text{ cm}^{-1}.$$

Rotational distortion D , H and L constants for the B and X states have been computed from RKR potentials according to the method of Albritton *et al.* (*J. Mol. Spectrosc.* 46 (1973) 25). Good agreement between experimental and calculated $D(v'')$ and $D(v')$ values was found. Franck-Condon Factors (FCF) were calculated and the computed relative intensities are consistent with the observed ones.

1. Introduction. — Recently we have studied the absorption spectrum of the iodine molecule (I_2) by means of Fourier transform spectroscopy in the visible region between 14 000 and 20 000 cm^{-1} . Using molecular constants published in earlier work [1-5], we were able to identify nearly all of the 68 000 recorded lines by analysing 139 bands [6]. The data were published in two atlases [7, 8] and sets of new molecular constants $G(v')$, $B(v')$, $D(v')$ and $H(v')$ valid for $1 \leq v' \leq 62$ describing the excited state $B(^3\Pi_{ou}^+)$ and molecular constants $G(v'')$, $B(v'')$ and $D(v'')$ valid for $0 \leq v'' \leq 9$ describing the ground state $X(^1\Sigma_g^+)$, were also published by one of us [9].

In that research, the band progressions $(0, v'')$ with $0 \leq v'' \leq 9$ were not observed, due to their low Franck-Condon Factors (FCF). For example

the FCF of the $(0, 0)$ band are of the order of 10^{-9} [10]. Consequently, the molecular constants $\sigma'_0(0, 0)$, B'_0 , D'_0 and H'_0 of the $v' = 0$ vibrational state could not be determined previously [9]. In particular the value of the band origin $\sigma'_0(0, 0)$ which is the separation (designated $T_{0,0}$) between the ground state X ($v' = 0$, $J = 0$) and the excited state B ($v' = 0$, $J = 0$) is only known from the extrapolation of the polynomial Dunham expansion coefficients [9]. (The $T_{0,0}(B-X)$ transition was in fact directly observed by Smalley, Wharton and Levy [11], who used a supersonic I_2 free jet inside the laser cavity in an investigation of the I_2 -He Van der Waals complex; but this transition was measured with an uncertainty of 2.5 cm^{-1} (1 Å).)

Consequently, we decided to study the I_2 absorption spectrum in the region 12 000-14 000 cm^{-1} where (v', v'') progressions with $0 \leq v' \leq 2$ and

(*) Laboratoire associé à l'Université Paris-Sud.

$10 \leq v'' \leq 14$ are situated. For these bands the FCF values become relatively important (of the order of $1/20$, see section 4) and by heating the absorption cells to a temperature of about 250°C , the products of the Boltzmann factor and the FCF values were high enough to make these bands observable. The experimental set-up which permits these observations is briefly described in the next section. The reduction and the analysis of the data were performed according to the recommendations of D. L. Albritton, A. L. Schmeltekopf and R. N. Zare [12] and needed the use of *a priori* calculated values of centrifugal distortion constants D , H and L . The computer programs used in our research which enable us to construct potential energy functions based on the Rydberg-Klein-Rees (RKR) procedure [13] and then to calculate either the centrifugal distortion constants D , H , L [14] or the FCF values [15, 10], are slightly modified versions [16] for use on UNIVAC machines of the original versions available from D. L. Albritton and directly usable on CDC machines [17]. In this way, the analysis of the data was straightforward and led among other results, to the determination of the molecular constants of the $v' = 0$ state, in particular to a precise experimental value of the separation distance $T_{0,0}$ between the B and X states. In conclusion, a valuable confirmation of the assignments made in this work is given by the good agreement found between the calculated and observed relative intensities of the analysed bands.

2. Recording of the data. — Figure 1 gives a schematic view of the experimental set-up and a block diagram of the data processing. A 100 W tungsten iodine quartz lamp provided the background. The absorption cell (two meters long) was heated to 250°C , while the iodine pressure was limited to the pressure in two side-arms heated only to 60°C . At this temperature the vapour pressure of iodine is about 5 torr [18], which is twenty times the pressure at room temperature (~ 0.25 torr). With a single pass of 2 m, a pressure of 5 torr is necessary to observe

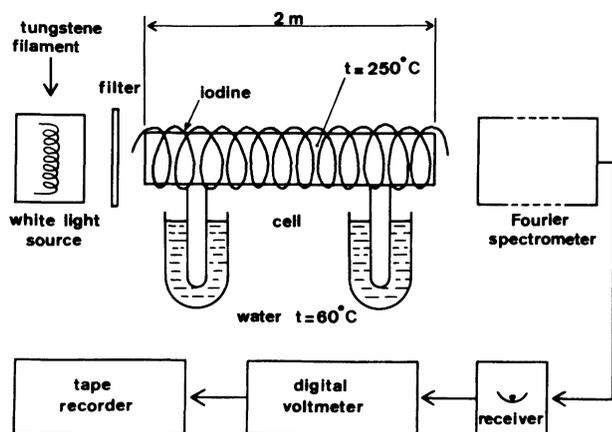


Fig. 1. — Experimental set-up.

the $(0, v'')$ and $(1, v'')$ progressions up to $v'' = 15$. The width of the iodine absorption lines is of the order of 0.025 cm^{-1} (due to the hyperfine structure [19, 20] combined with the Doppler width); the instrumental width of the Fourier spectrometer was therefore made equal to 0.020 cm^{-1} . The interferograms comprise 6×10^5 points; this corresponds to a total path difference of 44 cm, each step being equal to $7/8 \sigma_L$ and σ_L being the wavenumber of the reference line given by a helium-neon laser

$$(\sigma_L = 15\,798.0\text{ cm}^{-1})$$

stabilized on the Lamb dip. Under these conditions it is possible to cover a spectral range extending from $9\,027$ to $18\,054\text{ cm}^{-1}$, without overlapping.

The spectral range of interest in this research is below $14\,000\text{ cm}^{-1}$, since the iodine spectrum above $14\,000\text{ cm}^{-1}$ has been recorded previously [9]. In order to eliminate the noise made by unwanted photons corresponding to wavenumbers higher than $14\,000\text{ cm}^{-1}$, the light from the tungsten lamp

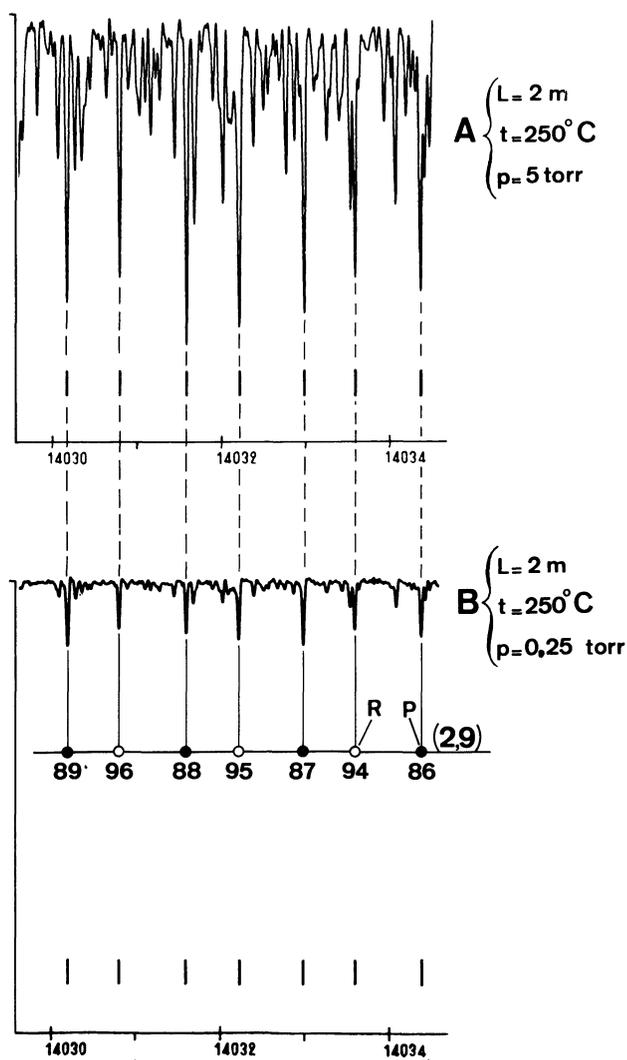


Fig. 2. — Calibration of the iodine absorption spectrum; comparison with previous work [9] showing the gain in absorption.

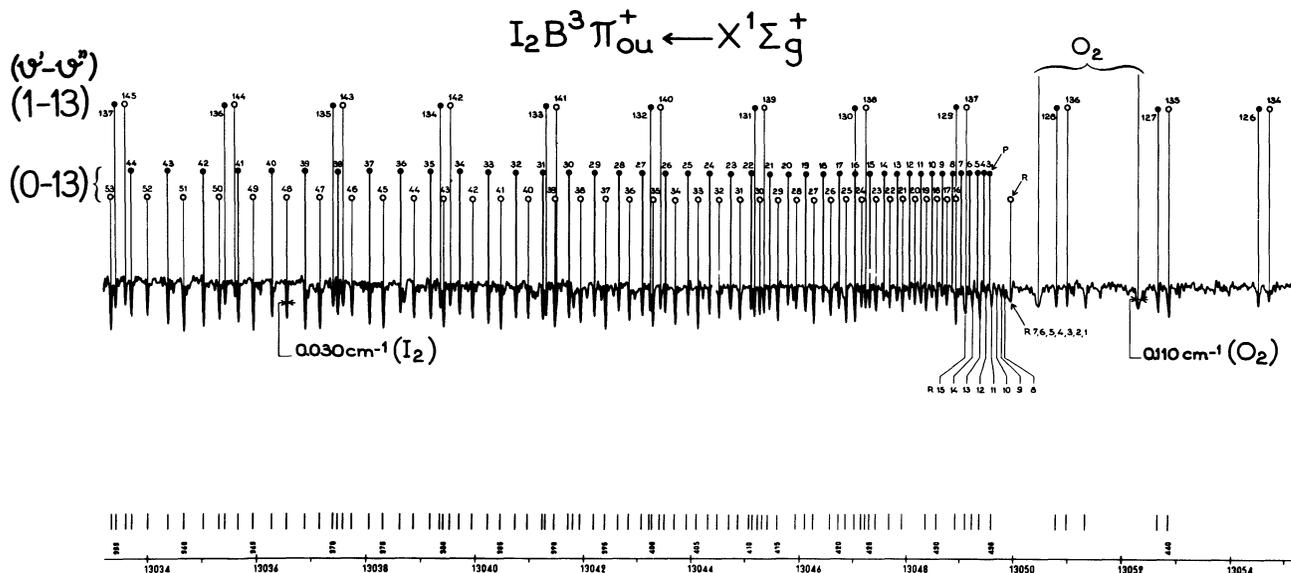


Fig. 3. — Small portion of the recorded spectrum. In this region lines belonging to the atmospheric oxygen band of the magnetic dipole transition ($^1\Sigma_g^+ \leftarrow ^3\Sigma_g^-$) are visible. Note : a) the width of these oxygen lines (0.110 cm^{-1}) compared to the recorded width of the iodine lines (0.030 cm^{-1}) and b) the weak absorption ($\sim 10\%$) of the iodine lines of the (0,13) and (1,13) bands.

passed through filters which limit the background to $14\,600 \text{ cm}^{-1}$. The *superfluous* portion of the spectrum lying between $14\,000$ and $14\,600 \text{ cm}^{-1}$ was used for calibration purposes. The absorption spectrum was calibrated by comparing the recorded wavenumbers of unblended, intense and symmetrical lines situated in the range $14\,000$ - $14\,600 \text{ cm}^{-1}$ with the wavenumbers of the same lines already determined and published in our previous atlas $14\,000$ - $15\,600 \text{ cm}^{-1}$ [8]. Figure 2 illustrates this procedure and shows the gain in absorption when the iodine pressure is increased to 5 torr (part A of figure 2) instead 0.25 torr used in our preceding work (part B of figure 2). Below $12\,600 \text{ cm}^{-1}$ there were no observable absorption lines with high enough signal/noise ratios, probably because the products $N_{v''} \times \text{FCF}$, where $N_{v''}$ is the Boltzmann factor and FCF the Franck-Condon factor, are too small. The level of the noise is about 1.5% of the background given by the tungsten lamp. For lines with an absorption of 10% (which is the case for the 0, v'' progressions, e.g. Fig. 3) the signal/noise ratio is about 6 and drops to 3 for transitions with high J values ($J \sim 125$); thus the uncertainties of the measured wavenumbers become relatively high and are on average between ± 0.002 and $\pm 0.004 \text{ cm}^{-1}$.

The time required for recording an interferogram is approximately 4 h. For reconstituting spectra from interferograms we used programs developed by Delouis [21] and Chauville [22]. All the calculations and traces were made in the Computer at Faculté des Sciences d'Orsay. Figure 3 shows a small part of the recorded spectrum.

3. Results. — 3.1 BAND-BY-BAND ANALYSIS. — In the range $12\,600$ - $14\,000 \text{ cm}^{-1}$, the wavenumbers and

the intensities of about 7 500 lines with a signal-to-noise ratio greater than 3, were measured. From these data 12 bands were analysed. The identification of these bands was achieved with the aid of the extrapolated values of molecular constants deduced from the polynomial expansion expressions previously published (Tables VI and VII of reference [9]). Table I gives the number of assigned lines for each band as well as the minimum and maximum values detected in each R and P branches. The total number of assigned lines is 1 564. Figure 4 shows the analysed bands represented by continuous lines. Bands observed, but too weak to be analysed are represented by points. The wavenumbers corresponding to these points are those of the origins of the bands. (The usefulness of representing the bands as a function of wavenumbers is the following : in laser spectroscopy of iodine, the necessity of identify-

Table I. — Number of assigned lines in the R and P branches in each analysed band.

Bands v', v''	R branch			P branch			$N_P + N_R$
	J_m	J_{Max}	N_R	J_m	J_{Max}	N_P	
0,11	11	144	48	15	136	47	95
0,12	9	127	89	11	138	94	183
0,13	12	126	84	20	124	76	160
0,14	20	135	75	19	129	79	154
1,10	9	134	82	18	126	62	144
1,11	54	168	48	48	160	55	103
1,12	10	148	101	31	140	74	175
1,13	9	151	68	11	144	60	128
1,14	18	126	64	19	117	58	122
2,10	9	157	60	6	149	57	117
2,11	19	87	47	16	77	38	85
2,12	22	132	49	25	129	49	98

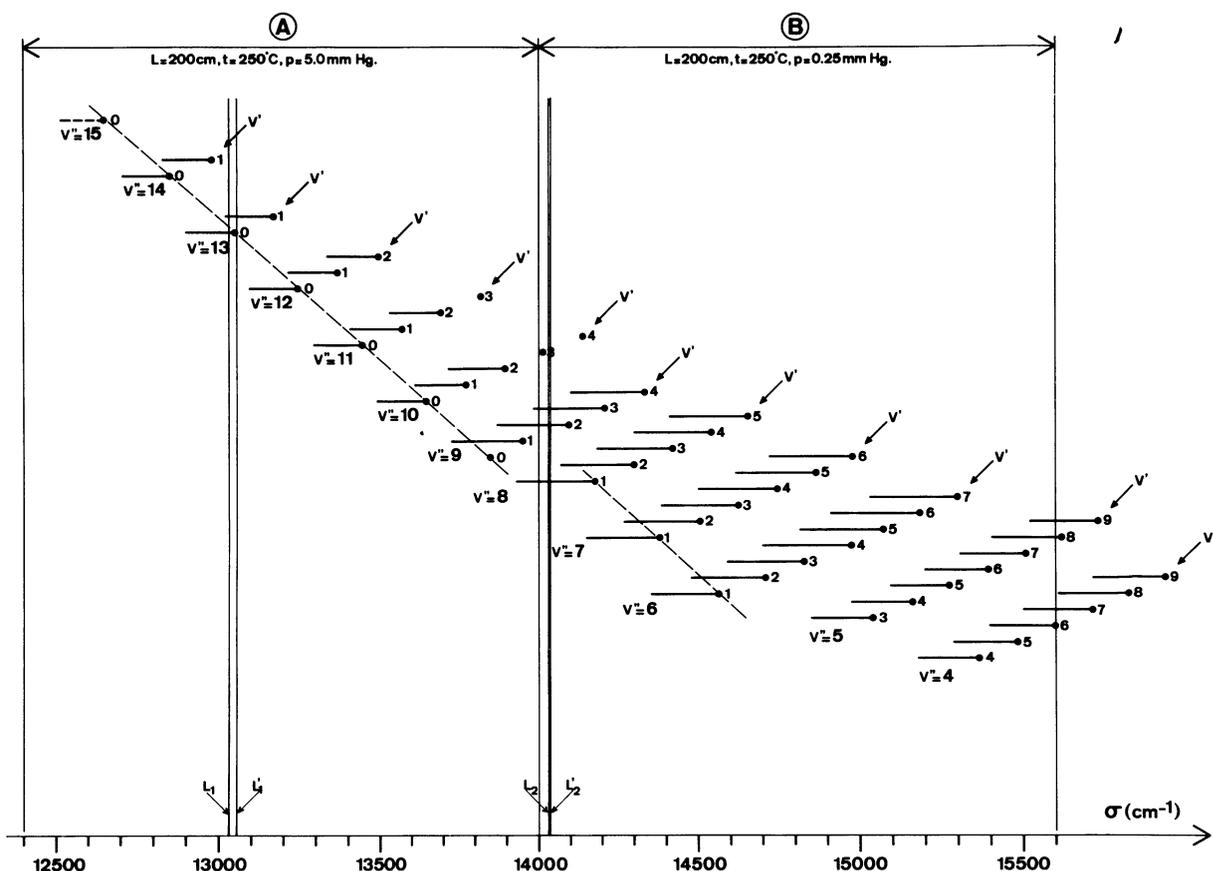
ELECTRONIC TRANSITION $B^3\Pi_{ou}^+ \leftarrow X^1\Sigma_g^+$ OF THE IODINE MOLECULE (I_2)

Fig. 4. — Part A, present work. Part B corresponds to the previous work reference [9]. The pairs of vertical lines L_1, L_1' and L_2, L_2' correspond to the small portion of the iodine spectrum given in figure 3 and figure 2, respectively.

ing transitions not observed in our absorption work is a frequent problem [23, 24]; if the wavenumber of a transition is approximately known, figure 4 shows immediately the possible bands which can be responsible for the observed transition. Then, using the molecular constants characterizing these bands, the assignments remain only a question of straightforward calculation.)

3.2 GLOBAL FIT OF THE DATA. — The ground state of iodine is a $^1\Sigma_{og}^+$ state, and the excited state is a component of a $^3\Pi$ term with very large splitting (Hund's case (c)). The structures of the bands of the transition $B(^3\Pi_{ou}^+) - X(^1\Sigma_{og}^+)$ with $\Delta\Omega = 0$ and $\Omega = 0$ are similar to $^1\Sigma^- - ^1\Sigma^+$ transitions ([25], p. 273) and the observed wavenumbers $\sigma_R(J)$ and $\sigma_P(J)$ obey to the classical relations [25] :

$$\begin{aligned} \sigma_R(J) &= + B_{v'}'(J+1)(J+2) - D_{v'}'(J+1)^2(J+2)^2 + H_{v'}'(J+1)^3(J+2)^3 + L_{v'}'(J+1)^4(J+2)^4 \\ &\quad - B_{v''}''J(J+1) + D_{v''}''J^2(J+1)^2 - H_{v''}''J^3(J+1)^3 + \sigma_0(v', v'') \\ \sigma_P(J) &= + B_{v'}'J(J-1) - D_{v'}'J^2(J-1)^2 + H_{v'}'J^3(J-1)^3 + L_{v'}'J^4(J-1)^4 \\ &\quad - B_{v''}''J(J+1) + D_{v''}''J^2(J+1)^2 - H_{v''}''J^3(J+1)^3 + \sigma_0(v', v'') . \end{aligned}$$

To a first approximation the constants L'' and L' were assumed to be negligible and were made equal to zero. Thus the 12 bands analysed are described by means of 36 molecular constants :

$$\left. \begin{array}{l} 12 \text{ values of } \sigma_0(v', v'') ; \\ 3 \text{ values of } B_{v'}' \\ 3 \text{ values of } D_{v'}' \\ 3 \text{ values of } H_{v'}' \end{array} \right\} \text{ for } 0 \leq v' \leq 2 ;$$

$$\left. \begin{array}{l} 5 \text{ values of } B_{v''}'' \\ 5 \text{ values of } D_{v''}'' \\ 5 \text{ values of } H_{v''}'' \end{array} \right\} \text{ for } 10 \leq v'' \leq 14 .$$

The estimation of the molecular constants involves the solution of a system containing 1 564 equations (corresponding to the 1 564 wavenumbers) of the assigned lines (Table I) and 36 unknowns (which are the molecular constants). This system has been solved,

Table II. — *Extract of the correlation coefficients of the molecular constants. The standard errors (S.E.) are in parentheses on the diagonal.*

	$\sigma_0(0,11)$	B'_0	D'_0	H'_0	$\sigma_0(0,12)$	B''_{10}	D''_{10}	H''_{10}
$\sigma_0(0,11)$	(1.6×10^{-3}) 1							
B'_0	-0.03	(1.6×10^{-6}) 1						
D'_0	-0.06	0.90	(1.5×10^{-10}) 1					
H'_0	-0.07	0.78	0.96	(4×10^{-14}) 1				
$\sigma_0(0,12)$	0.22	-0.057	-0.076	-0.084	(1.6×10^{-3}) 1			
B''_{10}	0.047	0.97	0.86	0.74	0.01	(1.6×10^{-6}) 1		
D''_{10}	0.047	0.85	0.93	0.89	0.05	0.89	(1.5×10^{-10}) 1	
H''_{10}	0.055	0.70	0.85	0.87	0.01	0.78	0.96	(4×10^{-14}) 1

and the resulting standard deviation of the measurement errors was 0.002 9 cm⁻¹, in good agreement with the estimated experimental uncertainties of the measured wavenumbers (between 0.002 and 0.004 cm⁻¹). Unfortunately, the confidence limits of the molecular constants H'' and H' include zero; at a first glance, one concludes that the data of the twelve analysed bands are not adequate to extract meaningful values of H'' and H' . The failure to determine these H'' and H' constants is partially due to unfavourable structure of the data ([12], p. 19), partially to the strong correlations (Table II) between the centrifugal distortion constants of high order (D' , D'' , H' and H'') and partially to the relatively large uncertainties of the measurements (± 0.003 cm⁻¹ on average) compared to the uncertainties of the measurements (± 0.001 cm⁻¹) made in the visible region [9].

But, on an other hand we know the order of magnitude of H'' and H' (for example references [26, 27], for H'' and reference [9], for H'). The contribution of the molecular constants H'' and H' to the wavenumbers of the transitions is proportional to $\simeq (H' - H'') \times J^6$ (Eqs. (1) and (2)). For $v' \leq 2$, H' is of the order of -0.20×10^{-14} cm⁻¹ [9] and for $10 \leq v'' \leq 14$, H'' is of the order of

$$-0.8 \times 10^{-15} \text{ cm}^{-1} \quad [27].$$

For $J = 130$ this contribution is about 0.006 cm⁻¹ which is twice the standard deviation of the global fit, and for $J_{\text{MAX}} = 168$ the contribution reaches 0.024 cm⁻¹. An important fraction, about 10 % of the 1 564 assigned lines, are transitions between rotational levels with J values higher than $J = 130$. From this point of view, at least, H' should be included in the analysis of the observed bands. To a second approximation, thus we put

$$L' = L'' = H'' = 0$$

and solve again the system with 1 564 equations and

31 unknowns. The standard deviation of this global fit is now 0.003 0 cm⁻¹ instead 0.002 9 cm⁻¹ in the previous fit. The difference 0.000 1 cm⁻¹ between the standard deviations of these two global fits is less than twice $\hat{\sigma}_{\text{std}}$, the *standard deviation of the standard deviation* which is equal to 0.000 055 cm⁻¹. Indeed for large degree of freedom and approximately normally distributed measurement errors, $\hat{\sigma}_{\text{std}}$ is equal to the standard deviation of the global fit divided by $(2(n - m))^{1/2}$, where $n = 1 564$ is the number of equations, and $m = 31$ is the number of unknowns ([12], p. 53).

The assumption that the distribution of the errors of measurements is approximately a normal distribution is supported by the analysis of the 1 564 residual values between observed and calculated wavenumbers.

Figure 5 represents the cumulative percentage distribution of the 1 564 residuals. The dashed line represents a cumulative normal distribution (*droite d'Henry* [12], p. 29).

Figure 6 shows the histogram of the $n = 1 564$ residuals. The width of each interval is $l = \hat{\sigma}/5$ with $\hat{\sigma} = 0.003 0$ cm⁻¹ the solid curve is the gaussian curve according to the equation ([12], p. 28) :

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

where μ is taken equal to zero.

Finally plots of the residuals against the rotational quantum number J , from $J = 10$ to $J_{\text{MAX}} = 168$, do not show systematic trends; thus, we may conclude that the errors of measurements are nearly normally distributed and that the analysis of the data can be handled by an unweighted least-squares fit, as we have done: briefly the estimates of the molecular constants are MVLU (minimum-variance linear unbiased) estimates [12].

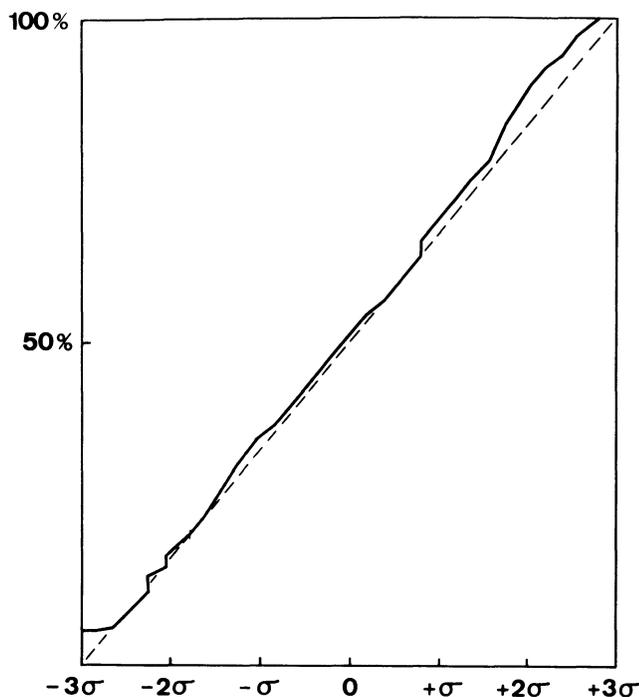


Fig. 5. — Cumulative percentage distribution of the 1564 residuals between observed and calculated lines. The broken line represents a cumulative normal distribution (*droite d'Henry*).

The molecular constants, with their associated standard errors are given in table III. Inspection of the results of table III shows that, while the molecular constants B'' and B' decrease steadily from B''_{10} to B''_{14} and from B'_0 to B'_2 as expected, the D'' and D' values, despite the *correctness* of their values, do not increase regularly with v'' or v' . Moreover, within the set of the three H' constants only H'_1 has a physical meaning : i.e. has the right sign, the expected value, and confidence limits (twice the standard error) outside the zero value

$$(H'_1 = (-0.175 \pm 0.090) \cdot 10^{-14} \text{ cm}^{-1}).$$

Table III. — Molecular constants determined by the global fit of the data with the approximation $H'' = 0$. The standard deviation between measured and calculated wavenumbers is 0.0030 cm^{-1} .

v''	$G(v'') - G(0)$	$10 \cdot B(v'')$	$10^8 \cdot D(v'')$	$10^{15} \cdot H(v'')$
10	2 076.782 4	0.361 333 7	0.482 079	0
11	2 277.429 0	0.360 122 0	0.489 513	0
12	2 476.753 6	0.358 910 6	0.500 389	0
13	2 674.759 3	0.357 666 3	0.500 466	0
14	2 871.431 3	0.356 406 0	0.498 105	0
S.E.	1.5×10^{-3}	1×10^{-6}	4×10^{-11}	
v'	$T_{0,0} + G(v') - G(0)$	$10 B(v')$	$10^8 D(v')$	$10^{14} H(v')$
0	15 724.584 5	0.289 258 2	0.633 803	+ 0.028 (98)
1	15 848.741 3	0.287 732 1	0.638 317	- 0.175 (45)
2	15 971.359 6	0.286 211 8	0.673 862	+ 0.474 (83)
S.E.	1.5×10^{-3}	1×10^{-6}	4×10^{-11}	

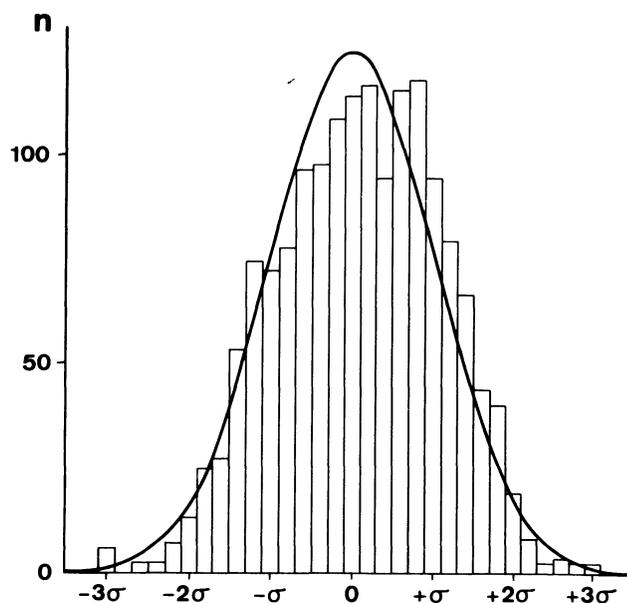


Fig. 6. — Histogram of the 1564 residuals. The solid curve is a normal distribution with $n = 1564$, $l = \hat{\sigma}/5$, $\mu = 0$ and $\hat{\sigma} = 0.0030 \text{ cm}^{-1}$.

The constants, H'_0 and H'_2 , again, are not determined. To overcome these difficulties we have undertaken the calculation of the centrifugal distortion constants D , H , L for the ground and excited states using the perturbation method described by D. L. Albritton, W. J. Harrop, A. L. Schmeltekopf and R. N. Zare [14]. These D , H , L calculated values should be particularly reliable, since we are interested here, only in the lowest vibrational states $v'' \leq 14$ and $v' \leq 2$ of the two X and B electronic states, respectively [14]. Then, we shall make, as usual [3, 5, 12], the values of high order centrifugal constants equal to the calculated values and by means of a least square fit of the data, we hope to be able to determine the molecular constants of the ground vibrational state $v' = 0$ of interest.

3.3 CALCULATION OF THE DISTORTION CONSTANTS

D, H, L. — 3.3.1 *Energy potential of the ground state.* — From the data published by P. Luc [9], we know precise $G(v'')$ and $B(v'')$ values for $0 \leq v'' \leq 9$; from the global fit of the data given in table III we have a set of preliminary values of $G(v'')$ and $B(v'')$ valid for $10 \leq v'' \leq 14$. However, precise calculation of the distortion constants for v'' values up to $v'' = 14$ requires wavefunctions of somewhat higher vibrational levels than $v'' = 14$ [14]. Recently, J. Vergès studying fluorescence series of the iodine molecule by means of the Ar⁺ laser line 19 433.683 1 cm⁻¹ and Fourier spectroscopy techniques, has observed fluorescence doublets from $v'' = 43$ up to $v'' = 14$ [28]. Using some of the data obtained by J. Vergès, from $v'' = 14$ to $v'' = 25$ (which was sufficient for our purposes) precise $G(v'')$ and $B(v'')$ values valid for $0 \leq v'' \leq 25$ were finally available. The Dunham expansion coefficients Y_{10} and Y_{11} derived from these $G(v'')$ and $B(v'')$ values are given in table IV.

The rotationless potential for the ground state using these Y_{10} and Y_{11} coefficients and the RKR procedure was calculated using the above mentioned programs [16, 17]. The eigen values $E_{v''0}$ compare very well to the corresponding values of $Y_{00} + G(v'')$, differing by 0.001 cm⁻¹ at the lower vibrational levels and up to 0.010 cm⁻¹ at the upper level $v'' = 24$. Similarly good agreement is found between $\langle B(r) \rangle_{v''}$ and $B_{v''}$ values, the differences varying from 0.3×10^{-7} to 10^{-7} cm⁻¹ from the lower level $v'' = 0$ to the upper level $v'' = 24$. The wavefunctions of this poten-

tial are used to calculate the D'', H'', L'' values for the twenty first vibrational level of the ground state.

The Dunham expansion coefficients Y_{12} and Y_{13} valid (for $0 \leq v'' \leq 19$) are also given in table IV.

Remark I. — Instead of using the Y_{10} and Y_{11} Dunham coefficients given in this section, it is also possible to use the Dunham coefficients determined by J. Tellinghuisen *et al.* [27] reanalysing the D(I₂)-X system. The calculated D'', H'' and L'' values with the Dunham coefficients Y_{10} and Y_{11} taken from table VII of reference [27] are in very good agreement with our calculated values (see Table V) but differ slightly from the adopted values of D'' and H'' published by these authors (Table VII, [27]).

Remark II. — For $J = 150$ and for $v'' = 14$ the contribution of L'' is only 0.000 07 cm⁻¹ which is completely negligible. This is not the case for H'' : for $v'' = 10$ and $J = 150$, the contribution is of the order of 0.007 cm⁻¹, which is about twice the average experimental uncertainty. Therefore, even when the experimental data are not adequate to allow precise determination of the H'' constants, nevertheless calculated values of H'' should be included in the analysis of the observed bands.

3.3.2 *Energy potential of the excited state.* — Taking account both of the preliminary $G'(0)$ and $B'(0)$ values deduced from the global fit of the data belonging to the 12 600-14 000 cm⁻¹ range as explained in section 3.2, table III, and the values of $G(v')$ and $B(v')$, for $1 \leq v' \leq 62$, deduced from the global

Table IV. — Dunham expansion coefficients Y_{10}, Y_{11}, Y_{12} and Y_{13} of the ground state $X(1\Sigma_g^+)$. (The Y_{12} and Y_{13} coefficients are necessary for the FCF calculation at $J \simeq 70$, see section 4.)

Experimental values valid for $0 \leq v'' \leq 25$ (cm ⁻¹)		Calculated values valid for $0 \leq v'' \leq 19$ (cm ⁻¹)	
$G(v'') = \Sigma Y_{10}(v + \frac{1}{2})^2$	$B(v'') = \Sigma Y_{11}(v + \frac{1}{2})^4$	$D(v'') = \Sigma Y_{12}(v + \frac{1}{2})^2$	$H(v'') = \Sigma Y_{13}(v + \frac{1}{2})^4$
214.521 9(ω_e)	+ 0.037 368 67(B_e)	+ 0.453 583 $\times 10^{-8}$ (D_e)	- 0.513 35 $\times 10^{-15}$ (H_e)
- 0.608 766 8	- 1.139 875 7 $\times 10^{-4}$	+ 0.230 371 $\times 10^{-10}$	- 0.899 87 $\times 10^{-17}$
- 0.114 162 1 $\times 10^{-2}$	- 2.724 471 2 $\times 10^{-7}$	+ 0.645 335 $\times 10^{-12}$	- 0.257 19 $\times 10^{-17}$
- 0.124 722 1 $\times 10^{-4}$	- 5.426 966 7 $\times 10^{-9}$	- 0.208 826 $\times 10^{-13}$	+ 0.915 36 $\times 10^{-19}$
		+ 0.847 084 $\times 10^{-15}$	- 0.122 32 $\times 10^{-20}$

Table V. — Calculated $D(v'')$, $H(v'')$ and $L(v'')$ values. a) From Y_{10} and Y_{11} coefficients of table IV. b) From Y_{10} and Y_{11} coefficients given by J. Tellinghuisen *et al.* (Table VI, ref. [27]). c) Adopted values published by J. Tellinghuisen *et al.* (Table VII, ref. [27]).

v''	$10^8 \times D_{v''}$			$10^{15} \times H_{v''}$			$10^{21} \times L_{v''}$	
	a)	b)	c)	a)	b)	c)	a)	b)
10	0.483 6	0.483 5	0.482	- 0.781	- 0.802	- 0.73	- 0.620	- 0.601
11	0.487 1	0.487 0	0.485	- 0.817	- 0.840	- 0.75	- 0.406	- 0.390
12	0.490 7	0.490 4	0.488	- 0.854	- 0.877	- 0.78	- 0.738	- 0.731
13	0.494 6	0.494 2	0.492	- 0.897	- 0.920	- 0.81	- 0.440	- 0.448
14	0.498 4	0.497 9	0.495	- 0.938	- 0.956	- 0.84	- 0.877	- 0.896

fit of the data of the visible range (Table V of reference [9]), we obtain the Y_{10} and Y_{11} Dunham coefficients valid for $0 \leq v' \leq 62$ given in table VI.

Using the same procedure as for the ground state, the rotationless potential of the excited state was determined. Again the eigen values $E_{v',0}$ compare very well with the corresponding $Y_{00} + G'(0)$ values, differing by 0.0003 cm^{-1} at the lower vibrational level $v' = 0$ and up to 0.007 cm^{-1} for $v' = 24$. The $B_{v'}$ values are reproduced with an accuracy of 10^{-7} on average.

D' , H' and L' values were calculated by means of the wave functions of this potential and the corresponding Dunham expansion coefficients Y_{12} , Y_{13} are given in table VI.

Remark. — The contribution of the molecular constant L' is to a first approximation proportional to $\sim J^8 \times L'$. For $J = 150$ and $v' = 0$ this contribution is approximately 0.0007 cm^{-1} , but increases very rapidly with J , and for $J = 168$ the highest rotational level detected in the range $12\,600$ – $14\,000 \text{ cm}^{-1}$ (see Table I), the contribution is about 0.003 cm^{-1} which is of the same order as the uncertainties of the experimental measurements. For $v' = 10$ and for J values greater than 150 the contribution of L' is more than 0.010 cm^{-1} and therefore L'_v should be included in the analysis of the iodine absorption spectrum observed in the visible range [9].

3.4 DETERMINATION OF THE MOLECULAR CONSTANTS OF THE VIBRATIONAL STATE $v' = 0$. — The values of the constants D'' , H'' , D' , H' and L' were made equal to the values calculated in the preceding section, except that the D'_0 constant was left free. Thus, we have a system of 1 564 equations and 21 unknowns (the 12 values of $\sigma_0(v', v'')$, 5 values of B'' , 3 values of B' and the D'_0 value). The result of the global fit

of this system is given in table VII. The standard deviation 0.00336 cm^{-1} found in this case is 12% higher than the standard deviation obtained when all 31 parameters are left free (0.0030 cm^{-1}), but remains comparable to the experimental uncertainties ($0.003 \pm 0.001 \text{ cm}^{-1}$ on average). The estimation of the standard errors of the fixed molecular constants D' , D'' , H' , H'' are of course, no longer given by the covariance coefficients of the global fit of the data. Therefore it seems reasonable to consider that the standard errors of the molecular constants given in table VII are those obtained in the case where all the constants were left free (1.5×10^{-3} , 10^{-6} , $4 \times 10^{-11} \text{ cm}^{-1}$ respectively for the $G(v) - G(0)$, B_v and D_v values) (Table III). This assumption is supported by the fact that the values of the molecular constants obtained in different ways, namely from :

(i) the input values of $G(v')$, $G(v'')$, $B(v')$, $B(v'')$ given by the Dunham expansion coefficients of table IV and table VI ;

(ii) the recalculated values of $G(v')$, $G(v'')$, $B(v')$, $B(v'')$ and the calculated values of $D(v'')$ and $D(v')$ from the potential energy functions ;

(iii) the *experimental values* deduced from the global fit, tables III and VII ;

(iv) the values of the molecular constants of the vibrational levels $v' = 1$ and $v' = 2$ determined by the global fit of the data belonging to the visible range and given in brackets in table VII, agree all within one or two standard errors.

Finally, the estimates of the molecular constants and their confidence limits (twice the standard errors) of the ground vibrational level $v' = 0$ of the excited state are the followings :

Table VI. — Dunham expansion coefficients Y_{10} , Y_{11} , Y_{12} and Y_{13} of the excited state $B(^3\Pi_{ou}^+)$. (The Y_{12} and Y_{13} coefficients are necessary for the FCF calculation at $J = 70$, see text section 4.)

Experimental values valid for $0 \leq v' \leq 62$		Calculated values valid for $0 \leq v' \leq 19$	
$T_e + G_{v'}$ (cm^{-1})	$B_{v'}$ (cm^{-1})	$D_{v'}$ (cm^{-1})	$H_{v'}$ (cm^{-1})
$T_{0,0} = 15\,724.584\,0$	$0.028\,999\,893(B_0)$	$+ 0.617\,768 \times 10^{-8}(D_0)$	$- 0.233\,34 \times 10^{-14}(H_0)$
$+ 125.676\,2(\omega_e)$	$- 0.148\,759\,25 \times 10^{-3}$	$+ 0.107\,022 \times 10^{-9}$	$- 0.932\,13 \times 10^{-16}$
$- 0.755\,110$	$- 0.146\,011\,76 \times 10^{-5}$	$+ 0.293\,780 \times 10^{-11}$	$- 0.310\,91 \times 10^{-16}$
$- 0.266\,230\,75 \times 10^{-2}$	$+ 0.531\,185\,08 \times 10^{-7}$	$+ 0.387\,618 \times 10^{-13}$	$+ 0.199\,27 \times 10^{-17}$
$- 0.536\,002\,85 \times 10^{-4}$	$- 0.710\,415\,12 \times 10^{-8}$	$+ 0.189\,781 \times 10^{-14}$	$- 0.720\,84 \times 10^{-19}$
$+ 0.186\,046\,21 \times 10^{-5}$	$+ 0.219\,212\,95 \times 10^{-9}$		
$- 0.408\,236\,27 \times 10^{-7}$	$+ 0.216\,765\,28 \times 10^{-10}$		
$+ 0.176\,114\,92 \times 10^{-9}$	$- 0.275\,974\,77 \times 10^{-11}$		
$+ 0.160\,905\,57 \times 10^{-10}$	$+ 0.145\,023\,42 \times 10^{-12}$		
$- 0.290\,851\,20 \times 10^{-12}$	$- 0.444\,895\,17 \times 10^{-14}$		
$+ 0.146\,630\,20 \times 10^{-14}$	$+ 0.849\,540\,29 \times 10^{-16}$		
	$- 0.995\,971\,15 \times 10^{-18}$		
	$+ 0.657\,286\,80 \times 10^{-20}$		
	$- 0.187\,129\,68 \times 10^{-22}$		

Table VII. — *Molecular constants determined by the global fit of the data ; the values of the molecular constants marked with an asterisk are those calculated by means of the wavefunctions of the potential energy functions [14]. The standard deviation between measured and calculated wavenumbers is 0.003 36 cm⁻¹ in this case. The values of the molecular constants given in brackets were obtained independently from the analysis of the data belonging to the visible region [9]. The number of digits given in this table is larger than one standard error digit ; this permits the recalculation of the wavenumbers of the lines without loss of precision due to the use of overrounded molecular constants ([12], p. 52).*

v''	$G(v'') - G(0)$	$10 \cdot B(v'')$	$10^8 \cdot D(v'')^*$	$10^{15} \cdot H(v'')^*$	$10^{21} \cdot L(v'')$
10	2 076.782 4	0.361 346 7	0.483 609	- 0.780 8	0
11	2 277.429 6	0.360 127 8	0.487 178	- 0.817 0	0
12	2 476.759 5	0.358 900 8	0.490 717	- 0.854 3	0
13	2 674.763 8	0.357 663 1	0.494 564	- 0.897 0	0
14	2 871.432 9	0.356 413 9	0.498 379	- 0.937 5	0
v'	$T_{0,0} + (G(v') - G(0))$	$10 \cdot B(v')$	$10^8 \cdot D(v')$	$10^{14} \cdot H(v')^*$	$10^{20} \cdot L(v')^*$
0	15 724.586 0	0.289 252 5	0.623 423 0.623 152*	- 0.234 6	- 0.300 2
1	15 848.741 1 [15 848.742 0]	0.287 733 8 [0.287 739 1]	0.634 539* [0.633 502]	- 0.255 4 [- 0.288 4]	- 0.338 8
2	15 971.362 1 [15 971.361 8]	0.286 192 4 [0.286 197 5]	0.646 458* [0.647 986]	- 0.277 8 [- 0.244 6]	- 0.382 9

$$T_{0,0} = (15\,724.586 \pm 0.003) \text{ cm}^{-1}$$

$$B'_0 = 0.028\,925\,2(20) \text{ cm}^{-1}$$

$$D'_0 = 0.623\,3(80) \text{ cm}^{-1}$$

$$(H'_0 = -0.234\,6 \times 10^{-14} \text{ cm}^{-1} \text{ calculated}).$$

It should be noted that D'_0 was left free in the last global fit. The D'_0 value found $0.623\,3 \times 10^{-8} \text{ cm}^{-1}$ is in very good agreement with the calculated value : $0.623\,15 \times 10^{-8} \text{ cm}^{-1}$ (Table VII). Likewise the adopted value of $T_{0,0}$ is also in agreement with the extrapolated value

$$15\,724.583\,8 \text{ cm}^{-1} = (15\,724.589\,4 - 0.005\,6) \text{ cm}^{-1}$$

based on the data of the visible range [9]. The subtraction of $0.005\,6 \text{ cm}^{-1}$ is made for calibration purposes, as explained in reference [29]. This rather long discussion on the standard deviations of the successive global fits and the proposed standard errors of the molecular constants of table VII is principally motivated by the sentence found in reference [12], p. 58 : *A devil known is at least better than a devil unknown, even though it cannot be exorcised.*

4. Intensity measurements. — The observed intensities of the bands in the $12\,600\text{-}14\,000 \text{ cm}^{-1}$ range are weak ; in other words the absorption is linear and it is possible to determine the relative intensities of these bands without the knowledge of *absorption coefficients*. Agreement between experimental and calculated relative intensities, should be a valuable confirmation of the band assignments, which are until now, based solely on wavenumber measurements.

The efficiency of this method [15] depends on the precision of the intensity measurements and on the ability to achieve reliable calculation of FCF. This latter requirement was able to be fulfilled thanks to Dr J. T. Hougen [16] who made available to us reliable RKR potential and FCF programs directly usable on our UNIVAC 1100 machine.

Table VIII gives the computed values of the FCF for the three progressions (0, v''), (1, v'') and (2, v'') where $8 \leq v'' \leq 15$. The intensity $I_{\text{abs}}(v', v'', J'')$ of an absorbed line is given by the classical relation :

$$I_{\text{abs}} \sim \frac{8 \Pi^3}{3 hc} \sigma_{v'', J''} \left(\frac{g'}{g''} \right) \left[\frac{S_{J', J''}}{2 J'' + 1} \right] \times \\ \times N_{v'', J''} | \langle v'(J') | \mu_e(R) | v''(J'') \rangle |^2$$

where $\sigma_{v'', J''}$ is the wavenumber of the line, $S_{J', J''}$ the Hönl-London rotational line strength [30], g' and g'' are the electronic degeneracies, $N_{v'', J''}$ the population of the (v'' , J'') level proportional to the Boltzmann factor. The last factor can be represented by the product of an average electronic transition strength $|\mu_e|^2$ and a Franck-Condon Factor

$$| \langle v''(J'') | v'(J') \rangle |^2 \quad [31].$$

If we assume that the average electronic transition strength remains constant for all the recorded bands in the $12\,600\text{-}14\,000 \text{ cm}^{-1}$ region, then the ratio of the intensities of two lines only depends on three quantities, namely $\sigma_{v'', J''}$, $N_{v'', J''}$ and the FCF values. In our experiment, the absorption cell was heated to $250 \text{ }^\circ\text{C}$; in this case the maximum intensity of the

Table VIII. — Franck-Condon factors and R centroid values, Boltzmann factors for $N_{v''}$ ($J = 70$) and values of the wavenumbers $\sigma_{(v',v'')}$ corresponding to $\sim J = 70$, where the intensity of the observed bands is maximum.

v''	v'			$10^4 N(v'', 70)$	$\sigma_{(v',v'')}$ for $J = 70$ (cm^{-1})	
	0	1	2		$v' = 0$	$v' = 1$
8	0.347 7-2 2.922 3	0.174 0-1 2.914 7	0.413 4-1 2.907 2	0.457 3	14 020	14 143
9	0.814 6-2 2.934 7	0.330 1-1 2.926 9	0.607 0-1 2.919 2	0.269 2	13 817	13 941
10	0.167 4-1 2.947 3	0.531 1-1 2.939 3	0.709 4-1 2.931 4	0.159 0	13 616	13 739
11	0.304 4-1 2.960 1	0.723 3-1 2.951 8	0.632 4-1 2.943 6	0.094 3	13 416	13 539
12	0.493 7-1 2.973 0	0.825 8-1 2.964 5	0.386 1-1 2.955 8	0.056 1	13 217	13 340
13	0.718 5-1 2.986 2	0.771 5-1 2.977 3	0.112 1-1 2.967 4	0.033 4	13 019	13 143
14	0.943 1-1 2.999 5	0.558 4-1 2.990 2	0.311 8-1 3.026 5	0.020 0	12 823	12 947
15	0.112 1 3.013 1	0.272 1-1 3.003 1	0.133 8-1 2.997 8	0.012 0	12 629	not observed

iodine bands occurs at $J \simeq 70$. For a given band, the variations of the calculated FCF values in the range $J = 65$ to $J = 75$, are less than 0.5% and the Boltzmann factors are also, within 0.7% reasonably constant; similarly the differences between the FCF values at the P and R branches are completely negligible (less than 0.000 3), and the values given in table VIII correspond to an hypothetical Q branch for $J' = J'' = 70$. To summarize we may assume that the calculated ratios of the FCF for $J = 70$ remain valid in the range $J = 65$ to $J = 75$ to an accuracy better than 1%. Consequently, we have sampled unblended lines with J values between 65 and 75 of the P and R branches and we have taken the mean value of the measured intensities as a measure of the intensity of a band. The uncertainties of these mean values are of the order of $\pm 5\%$ on average for the $(1, v'')$ progression (Fig. 7) and reach $\pm 10\%$ for the $(0, v'')$ progression (Fig. 8). (The lines situated in the range $J = 65$ to $J = 75$ and belonging to the $(2, v'')$ progression are blended with lines of the atmospheric oxygen band (${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$) also observed in our spectrum; therefore no comparison between calculated and observed intensities was made for this progression.)

Figures 9a and 9b show the comparison between experimental and calculated quantities. Note that for the two progressions studied $(0, v'')$ and $(1, v'')$, we have taken the intensity of the same band $I_{(1,9)}$, arbitrarily, as unity. Despite the fact that the relative intensities of the $(0, v'')$ progression are of a poor precision ($\pm 10\%$), the general trend of the mea-

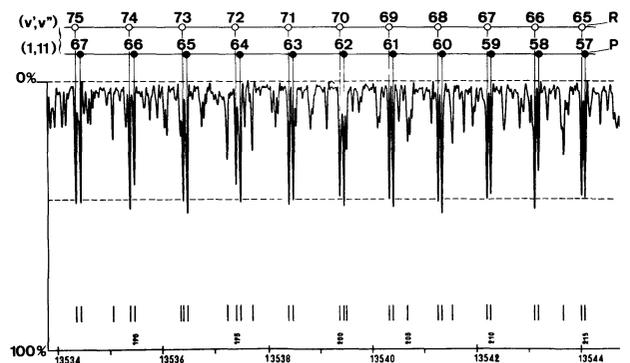


Fig. 7. — Intensities of the recorded lines around $J = 70$ belonging to the $(1,11)$ band.

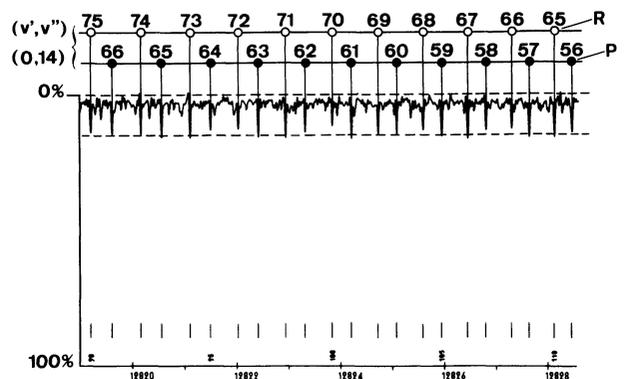


Fig. 8. — Intensities of the recorded lines around $J = 70$ belonging to the $(0,14)$ band.

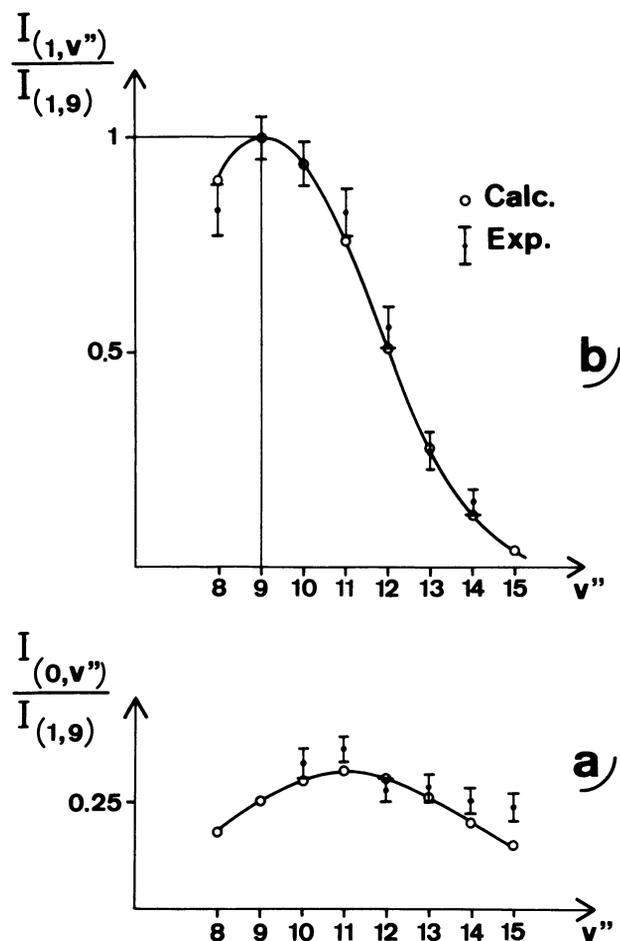


Fig. 9. — Comparison between observed and calculated relative intensities of the analysed band of the $(0, v'')$ (Fig. 9a) and the $(1, v'')$ progressions (Fig. 9b).

sured intensities follows the calculated ones. The intensity measurements of the $(1, v'')$ are more reliable ($\pm 5\%$) and the comparison given in figure 9b is, as could be expected, more convincing.

Briefly, the compatibility between the observed intensities and the assignments made in this work is well confirmed by the overall agreement between the measured and calculated relative intensities. On the other hand, this result shows also that even in absorption, relative Fourier spectroscopy intensity measurements are easy to make and meaningful, provided that the absorption is small enough to remain linear.

5. Discussion. — One of the aims of the study of the iodine absorption spectrum is the determination of sets of molecular constants sufficiently precise and reliable for it to be possible to assign, without ambiguity, any transition of this spectrum, even those not detected in our absorption work. *Without ambiguity*, means here that the uncertainties of the calculated wavenumbers of these transitions, do not exceed about a third of the width of the iodine lines.

In other words, the recorded width of the iodine lines being about 0.030 cm^{-1} on average, a result of the presence of hyperfine structure, the uncertainties have to be, for example, less than one third of the width or $\pm 0.010\text{ cm}^{-1}$. This can be achieved by using the molecular constants deduced from the Fourier spectroscopy data, provided that the two following conditions are strictly observed : first, the molecular constants used both for the ground state X and for the excited state B must necessarily be extracted from table III or VII of this work and from tables IV and V of reference [9]. These constants obtained simultaneously by the global fit of the data are connected by the inherent correlations between these constants [12]. It would be a mistake to mix in molecular constants from different origins than those based on the Fourier spectroscopy measurements. Secondly, extension coefficients to higher v'' values than 14 or to higher J values than those given in table I, must be avoided. If it is absolutely necessary to identify rotational levels with high J values, the sets of molecular constants given in table VII should be *better* to use, than those given in table III, since we have introduced in table VII the high order centrifugal distortion constants H'' , H' and even L' . But in any case the agreement between calculated and measured wavenumbers in the range 12 600-14 000 cm^{-1} will be about twice worse than the agreement found in the visible range 14 000-20 000 cm^{-1} . This loss in precision is mainly due to the low and rapidly decreasing values of the Boltzmann factor : from $v'' = 10$ to $v'' = 14$ the population of the levels $N_{v'', J''}$ drops down by about one order of magnitude. But other reasons can be invoked : for example, pressure shifts due to the relatively high pressure of iodine in the absorption cell (5 torr), and above all, fluctuations of the population of the levels belonging to the *hot bands*. These fluctuations due to temperature fluctuations of the cell heated to 250 °C, introduce additional local noise of the same kind as the fluctuations of light source in Fourier spectroscopy [32]. Improvement of the determination of the molecular constants deduced from the study of the 12 600-14 000 cm^{-1} region should be, in principle, possible by mixing the wavenumber measurements made in the 12 600-14 000 cm^{-1} region with those made in the 14 000-20 000 cm^{-1} region and by fitting all these data together. Because of the different quality of measurements in these two regions, it will be necessary to have recourse to weighted least-squares fits, and also to resolve again a system with more than 15 000 equations and about 380 unknowns ! This amount of work was considered unnecessary, since we were principally interested in the determination of the molecular constants of the vibrational state $v' = 0$. The data of the region 12 600-14 000 cm^{-1} were thus handled separately : the excellent agreement between the molecular constants of the $v' = 1$ and $v' = 2$ vibrational states deter-

minated independently in this study and in the earlier study of the visible region between 14 000 and 20 000 cm^{-1} , as shown in table VII is the best justification of our procedure.

6. Conclusion. — As a result of the study of the iodine absorption spectrum in the range 12 600-14 000 cm^{-1} , the molecular constants $G(v')$, $B(v')$, $D(v')$ and $H(v')$ of the excited state are known from $v' = 0$ to $v' = 62$.

In course of this work, H'' and L' values were computed from the wavefunctions of the X and B states, respectively; it follows that the approximation $H'' = L' = 0$, made in the earlier analysis [9], is, due to the accuracy of the Fourier spectroscopy measurements in the visible, no longer acceptable. The whole spectrum of the 14 000-20 000 cm^{-1} region must be recalculated with the introduction of the H'' and L' constants. This task will be undertaken, after completing the missing Fourier spectroscopy data on the iodine spectrum near the dissociation limit ($v' > 62$) between 19 950 and 20 043 cm^{-1} .

For the precise determination of the molecular

constants of the ground state X ($0 \leq v' \leq 113$), this work shows also the limit reached by the conventional studies of the absorption spectrum of iodine, which should be around $v'' = 19$, even if a much longer absorption path is used; indeed below 12 440 cm^{-1} , the dissociation limit of the ground state X($^1\Sigma_g^+$), the bands of the system B(I_2)-X overlap the bands of the system A(I_2)-X [33]. Fortunately, extensive studies of fluorescence series, by means of Fourier spectroscopy techniques, provide precise data for the determination of the molecular constants of the ground state up to the dissociation limit [34].

Acknowledgments. — The authors acknowledge with gratitude the help of Dr. J. Hougen of the National Bureau of Standards (Washington) both for making available to us the RKR, FCF and DHL programs and for illuminating advice how to use them. We are also indebted to Dr. M. Smadja (E.N.S.T.A.) for his assistance in programming problems, and we thank Prof. D. A. Jackson for kindly reading this manuscript and giving us valuable comments.

References

- [1] STEINFELD, J. I., ZARE, R. N., JONES, L., LESK, M. and KLEMPERER, W., *J. Chem. Phys.* **42** (1965) 25.
- [2] LE ROY, R. J., *J. Chem. Phys.* **52** (1970) 2683.
- [3] BROWN, J. D., BURNS, G. and LE ROY, R. J., *Can. J. Phys.* **51** (1973) 1664.
- [4] BARROW, R. F. and YEE, K. K., *J.C.S. Faraday II* **69** (1973) 684.
- [5] WEI, J. and TELLINGHUISEN, J., *J. Mol. Spectrosc.* **50** (1974) 317.
- [6] GERSTENKORN, S. and LUC, P., *J. Mol. Spectrosc.* **77** (1979) 310.
- [7] GERSTENKORN, S. and LUC, P., *Atlas du spectre d'absorption de la molécule de l'iode 14 800-20 000 cm^{-1}* (Editions du C.N.R.S.) 1978.
- [8] GERSTENKORN, S. and LUC, P., *Atlas du spectre d'absorption de la molécule de l'iode 14 000-15 600 cm^{-1}* (Laboratoire Aimé Cotton, C.N.R.S. II) 1978.
- [9] LUC, P., *J. Mol. Spectrosc.* **80** (1980) 41.
- [10] TELLINGHUISEN, J., *J. Quant. Spectrosc. Radiat. Transfer* **19** (1978) 149.
- [11] SMALLEY, E., WHARTON, L. and LEVY, D., *Chem. Phys. Lett.* **51** (1977) 392.
- [12] ALBRITTON, D. L., SCHMELTEKOPF, A. L. and ZARE, R. N., *Molecular spectroscopy, Modern Research*, Edited by K. Narahari Rao (Academic Press, New York) 1976, vol. II, p. 1-67.
- [13] RYDBERG, R., *Z. Phys.* **73** (1931) 376; **80** (1933) 514. KLEIN, O., *Z. Phys.* **76** (1932) 226. REES, A. L. G., *Proc. Phys. Soc.* **59** (1947) 948.
- [14] ALBRITTON, D. L., HARROP, W. J., SCHMELTEKOPF, A. L. and ZARE, R. N., *J. Mol. Spectrosc.* **46** (1973) 25.
- [15] ZARE, R. N., *J. Chem. Phys.* **40** (1964) 1934.
- [16] HOUGEN, J., Private communication.
- [17] ALBRITTON, D. L., Private communication.
- [18] NESMEYANOV, A. N., *Vapor pressure of the chemical elements*, Edited by R. Gary (Elsevier Publishing Company, Amsterdam) 1963.
- [19] KROLL, M. and INNES, K. K., *J. Mol. Spectrosc.* **36** (1970) 295.
- [20] VIGNÉ, J., BROYER, M. and LEHMANN, J. C., *J. Phys. B : Atom. Molec. Phys.* **10** (1977) L 379.
- [21] DELOUIS, H., Thèse, Orsay (France) (1973).
- [22] GERSTENKORN, S., LUC, P., PERRIN, A. and CHAUVILLE, J., *J. Astron. Astrophys.* **58** (1977) 255.
- [23] BRILLET, A., CEREZ, P., MAN, N., LUQUET, P., Private communication and to be published.
- [24] CHURASSY, S., GRENET, G., GAILLARD, M. L. and BACIS, R., *Opt. Commun.* **30** (1979) 41.
- [25] HERZBERG, G., *Spectra of Diatomic Molecules* (Van Nostrand, New York) 1970.
- [26] YEE, K. K., *J. C. S. Faraday II* **72** (1976) 2113.
- [27] TELLINGHUISEN, J., MCKEEVER, M. R. and SUR, A., *J. Mol. Spectrosc.* **82** (1980) 225.
- [28] VERGÈS, J., Private communication.
- [29] GERSTENKORN, S. and LUC, P., *Revue Phys. Appl.* **14** (1979) 791.
- [30] HOUGEN, J., *The calculation of Rotational Energy levels and Rotational Line Intensities in Diatomic Molecules*, Monograph n° 115 (N.B.S.) Washington (1970).
- [31] FRASER, P. A., *Com. J. Phys.* **32** (1954) 516.
- [32] GERSTENKORN, S. and LUC, P., *Nouv. Rev. Opt.* **7** (1976) 148.
- [33] ASHBY, R. A., *Com. J. Phys.* **57** (1979) 698.
- [34] VERGÈS, J., BACIS, R., CHURASSY, S. and MARTIN, F., *35th Symposium on Molecular Spectroscopy*, Columbus, U.S.A., 1980.