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High precision saturation spectroscopy of $^{127}\text{I}_2$ with argon lasers at 5 145 Å and 5 017 Å : I — Main resonances

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Résumé. — On présente un ensemble de résultats sur la spectroscopie hyperfine de l'iode obtenus avec le laser à argon ionisé. Nous décrivons notre spectromètre à absorption ou dispersion saturées ainsi que le comportement de la largeur et du déplacement des résonances avec la pression. A 5 145 Å les écarts de fréquence entre résonances principales des raies 43-0 P(13) et R(15) ont été mesurés avec un écart standard de 200 Hz et représentés par un jeu de constantes hyperfines avec un écart standard de 1,5 kHz. Les constantes trouvées pour P(13) et R(15) sont cohérentes entre elles. Les résultats de Foth et Spieweck sont confirmés pour 58-1 R(98) à 5 145 Å et nous apportons une première détermination des constantes d' et δ' de 62-0 R(26) à 5 017 Å. A travers la variation de ces mêmes constantes au voisinage de la limite de dissociation nous apportons une preuve expérimentale du mélange entre états u et g. La stabilité des lasers à argon asservis sur les résonances de l'iode est illustrée et leurs applications métrologiques sont brièvement discutées.

Abstract. — We present results on the hyperfine spectroscopy of $^{127}\text{I}_2$ obtained with argon lasers. We describe our saturated absorption or dispersion spectrometer and we discuss the pressure dependence of the saturation line shapes. At 5 145 Å we have measured the frequency differences between the main resonances of the 43-0 P(13) and R(15) hyperfine manifolds with a 200 Hz standard deviation and obtained a theoretical fit with a standard deviation of the order of 1.5 kHz. The two sets of hyperfine constants for P(13) and R(15) are consistent. The results of Foth and Spieweck are confirmed for the 58-1 R(98) line at 5 145 Å and we make a first determination of the constants d' and δ' of the 62-0 R(26) line at 5 017 Å. The variation of these constants near the dissociation limit is interpreted as a demonstration of a mixing of u and g states. The stability of argon lasers slaved to iodine peaks is illustrated and their metrological applications are outlined.

1. Introduction. — Our knowledge of the hyperfine interactions in I_2 has been intimately linked to the development of sub-Doppler laser spectroscopy in the visible for the past twelve years. This results from the fact that hyperfine structures in I_2 have an extension comparable to the Doppler half-width (271 MHz); therefore the various hyperfine components overlap each other and only a broadening and an asymmetry of the lines could be detected with the best conventional spectrometers [1]. As soon as sub-Doppler techniques have appeared, these hyperfine structures

have become a favorite playground for laser spectroscopists and we have watched a permanent constructive competition between the various techniques towards higher resolution and accuracy. This interest was further reinforced and motivated by the metrological applications of frequency stabilized lasers using narrow I_2 resonances. Parallel to that experimental effort the increasing accuracy of the measurements has stimulated a permanent improvement of our theoretical understanding of hyperfine interactions in homonuclear diatomic molecules. In turn, a detailed test of the hyperfine Hamiltonian now appears as one of the most exciting and fundamental goals of this branch of spectroscopy. The purpose of this paper is

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to review some of this experimental and theoretical effort as well as to cover in more detail than was done in our previous papers [21, 39-44], the results obtained in our laboratory with argon lasers.

Doppler-broadening can be greatly reduced using either mechanical velocity selection in a molecular beam or optical velocity selection with non-linear spectroscopic methods. In the case of I_2 both approaches have been widely used and permanently challenging each other and one may hope that they will ultimately be combined in the future. The molecular beam approach has been thoroughly explored by S. Ezekiel and his co-workers and in fact the first ever resolved hyperfine components in the visible spectrum of I_2 were recorded with this technique [2] and the argon laser at 5 145 Å in 1967.

As early as 1969 the inverted Lamb-dip technique of Lee and Skolnick [3] was used for $^{127}I_2$ [4] and $^{129}I_2$ [5] with the HeNe laser at 6 328 Å. For the first time 14 of the 21 hyperfine components of a well identified rovibronic transition of I_2 (the R(127) line of the 11-5 band of the $B^3\Pi_{0+u} \leftarrow ^1\Sigma_{0+g}$ electronic transition) were fully resolved with a half-width of 4.5 MHz. A very satisfactory fit of this spectrum was obtained by M. Kroll [6] who introduced two different quadrupole coupling constants for the ground and the excited electronic state and a magnetic hyperfine interaction in the excited state. Also the clustering of lines in alternating triplets and quadruplets in the limit of high J values was first observed and explained giving a very simple clue to the interpretation of these spectra.

In 1971 Hänsch *et al.* [7] were able to record the full manifold of 21 components of the P(117) line of the 21-1 band of the $B \leftarrow X$ transition with the Kr^+ laser at 5 682 Å. For the first time the iodine cell was removed outside the laser resonator and a very sensitive scheme to detect saturated absorption was used : in this method the saturating beam is chopped and the induced amplitude modulation of the probe beam is detected [8]. At 6 328 Å the work of Hanes and Dahlstrom was extended by Hanes *et al.* [9, 10] who used Zeeman broadening of the laser gain profile and a Fox-Smith mode selector to detect and measure the P(33) line of the 6-3 band approximately 700 MHz to the red of the R(127) line (see also [11, 12]). Because of the moderate value of J they could obtain the values of both nuclear quadrupole coupling constants as well as ΔC_i and they showed that the fit was improved by taking into account the 2nd order quadrupole coupling with $\Delta J = \pm 2$.

The years 1971-1972 have been marked by the thesis work of M. Levenson and M. Sorem in Pr. Schawlow's group at Stanford. They performed a systematic study of the hyperfine structures of $^{127}I_2$ and $^{129}I_2$ that they could reach with ion lasers [13-16] from which they could infer the dependence of the hyperfine coupling constants with the vibrational energy of the electronically excited state. Sorem *et al.* introduced the inter-

modulated fluorescence technique [17] with which they were able to detect crossover (3 level) resonances and one $\Delta F = 0$ transition in the (43-0) P(13) manifold [18]. From such measurements it is possible to infer independent values for the nuclear quadrupole coupling constants in both states. An earlier observation of $\Delta F = 0$ resonances had been reported in the (6-3) P(33) line by Latourrette and Eng [19] and both experiments yielded comparable values for eQq .

In 1973 the Canadian group of Hanes *et al.* [20] gave improved measurements at 6 328 Å using the third harmonic of the modulation frequency to discriminate against the broad background. The internal consistency of their measurements for the 7 components d to j of R(127) was 13 kHz (rms deviation). In 1973 also, I_2 and the argon laser have been used to demonstrate a new saturation technique : saturated dispersion spectroscopy, in which it is the change of index associated with saturated absorption which provides the unbalance for the two counter-propagating waves in a Sagnac interferometer [21]. The same year a major challenge was offered to saturation spectroscopy by Ezekiel *et al.* [22] who obtained a 300 kHz full width with their molecular beam for the 42 components of the 43-0 P(13) and R(15) and accurate values for ΔeQq and ΔC_i for these two lines.

From 1974 to 1976 the theoretical fits of the spectra have been greatly improved by introducing higher order terms in the Hamiltonian : essentially the tensor [23] and scalar spin-spin [24, 25] interactions. The R(127) line of the (11-6) band and the P(13) line of the (43-0) band were fitted with standard deviations respectively of 17 and 6 kHz [26]. At this point the evidence of higher order terms such as the magnetic octupole term was still controversial [24-27].

The following years see a vast experimental effort to extend and improve the techniques both of saturation spectroscopy and of molecular beam spectroscopy. New lines are investigated with gas lasers [28-30] but mainly two new tools have appeared and become operational for iodine spectroscopy : the dye laser [31-32] and the supersonic beam [33]. It is then possible to attempt systematic studies even for low J values. On the theoretical side M. Broyer and J. Vigüé in their thesis works [34-35] in Pr. Lehmann's group give a detailed and complete derivation of a formal hyperfine hamiltonian with an estimate of the order of magnitude of the higher order terms [36] and carry an *ab initio* calculation of hyperfine constants in good agreement with the experiments [37]. In 1980 Ezekiel and his co-workers [38] published a new fit of the P(13) and R(15) hyperfine structures at 5 145 Å with respectively 2.6 and 5.4 kHz for the standard deviations without any octupole term as expected from the very small contribution of this term estimated by Broyer *et al.* [36].

Our own work starts in 1973 with saturated dispersion at 5 145 Å [21]. At that time it was not clear through the results obtained with the He-Ne laser

that really narrow lines could be obtained with I_2 in saturation spectroscopy. Stimulated by the results of Ezekiel with a molecular beam we decided to put the emphasis on a search of high resolution and high accuracy with saturation spectroscopy. In 1975 a full width of the saturation lines equal to 600 kHz is obtained [39] and a saturation spectrum very comparable to the molecular beam spectrum is presented in [40].

The present version of the spectrometer is described in part 2 of this paper. With this apparatus we have tried to get an improved understanding of the line shapes, accurate values for the hyperfine splittings and metrological implications have been studied in detail [41].

The influence of the recoil shift has been analysed in a previous paper [42] and some other aspects of the line shape dependence with pressure are outlined in the present paper.

The I_2 spectra at 5 145 Å and 5 017 Å and accurate nuclear coupling constants have been presented at the 1979 Tours Conference [43] and an account of these results can be found in [44]. These spectra and their fit is the subject matter of sections 3 and 4. For the first time this fit has required the introduction of a spin-rotation interaction in the ground state of I_2 [44]. The value of the spin-rotation constant ($\simeq 3$ kHz) has since been confirmed by a double resonance study of the ground state hyperfine transitions [45]. In this first paper on the hyperfine spectroscopy of I_2 we shall consider essentially the main $\Delta F = \Delta J$ resonances and we shall present detailed results on the crossover resonances in a following paper.

2. The Villetaneuse spectrometer. — The present set-up has evolved from the original Sagnac interferometer that we used to demonstrate saturated dispersion [21] to an adaptative system that can be suitably modified to monitor either saturated absorption or dispersion [40-42] and which has also been used recently to allow for heterodyne saturation spectroscopy [46] (which is a refined version of the saturation chopper method [8]). The schematic diagram of the optical set-up in its current version can be seen on figure 1. The set-up of figure 1 is in fact duplicated and each system is illuminated by a different laser. One of these lasers is a 165 model from Spectra Physics with a BeO tube and the other is the CR-3 model from Coherent Radiation with a graphite tube. Single mode operation is achieved by using internal Fabry-Pérot etalons in the commercial lasers. A good improvement ($\sim$ factor 4) of the short-term frequency stability has been obtained by removing the cavity mirrors onto external mounts. A detailed study of the amplitude and frequency noise characteristics of the lasers can be found in [41]. To be able to use these lasers in high resolution studies we found essential to prestabilize them by slaving their frequency to that of the transmission fringe of external confocal reso-

nators. These resonators have a 300 MHz mode spacing and a finesse of the order of 80. They are built from massive invar ingots and are equipped with a 2.5 cm PZT ceramic with a thermal dilation compensation. The reflected light from the Fabry-Pérot is extracted by a Glan prism combined with a quarter-wave plate which also provides optical isolation. Both the reflected and transmitted beam intensities are monitored and the difference between these two signals is used as the error signal. This difference doubles the available error signal and eliminates the major part of the amplitude noise. The correction signal from the high voltage amplifier is dispatched through a dividing filter to a fast PZT ceramic for high speed corrections (~ 100 kHz) and to a slow one for large amplitude slow drift corrections. In this way, the frequency stability properties of the external resonator are entirely transferred to the laser whose frequency jitter is reduced below 50 kHz. The beams from each of these prestabilized lasers are then used to illuminate an optical ring designed to monitor either the saturated absorption (Fig. 1a) or the saturated dispersion (Fig. 1b) in a 40 cm I_2 cell.

The I_2 pressure is controlled from 0.5 to 100 mtorr with a Peltier element which stabilizes the temperature of a cold finger. A $\lambda/2$ plate inside the ring yields two orthogonal polarizations for the counter-propagating beams and prevents the feedback towards the laser through the input Glan prism. An absorbing plate attenuates the probe beam before the I_2 cell (by a factor ~ 5).

In the saturated absorption version of the apparatus two Glan prisms within the ring extract the saturation and probe beams before the splitter and steer them towards two detectors. By difference between the two corresponding signals it is possible to get rid of the linear absorption part of the signal (Doppler background) and of most of the noise.

The saturated dispersion version is the ring interferometer of figure 1b. Here again a difference signal is produced between the two outputs of the interferometer. Without any tuning element the interferometer would give a signal proportional to the square of the non-linear susceptibility modulus on a dark background [47]. A signal proportional to the non-linear dispersion is produced when the interferometer is tuned with a birefringent plate and the optimum signal is obtained with a quarter-wave plate introducing a $\pi/2$ phase difference between the two perpendicularly polarized counter-propagating beams [21].

The laser frequencies are modulated by varying the length of the external resonators and the saturation signals are obtained by synchronous detection at any desired harmonic of the modulation frequency. One of these devices, locked to an iodine peak is used as a frequency reference. The other one may either be locked in turn to the different peaks whose frequencies are to be measured or be locked, with a tunable frequency offset, with respect to the first laser for line

Fig. 1. — The spectrometer consists of two independent identical optical circuits illuminated by two commercial lasers. One of the two circuits is represented on the figure. The lasers are prestabilized on the side of the transmission/reflection fringe of confocal Fabry-Pérot interferometers. Each laser illuminates an optical ring which can be used to monitor either saturated absorption (Fig. 1a) or saturated dispersion (Fig. 1b).

shape studies (Fig. 2). A quantitative study of the signal-to-noise properties of this spectrometer as well as a detailed description of the servo-loops can be found in [41].

Fig. 2. — Illustration of the frequency offset-locking technique which provides both the tunability and the stability required for line shape studies.

3. Spectrometer performances, experimental procedures and spectroscopic results. — The resolving power and accuracy of the spectrometer just described can be illustrated by line shape studies. The saturation line shapes of iodine result from many physical processes : inelastic collisions, weak elastic and dephasing collisions, spontaneous emission, predissociation, laser frequency jitter, laser frequency modulation, transit broadening, curvature shift, recoil splitting, saturation broadening, light shifts... All these processes are being investigated and in this paper we limit ourselves to

Fig. 3. — Line shape of a saturated absorption peak (1st harmonic) recorded with the frequency offset-locking technique as a function of pressure.

some aspects of the pressure dependence of the line shape. Figure 3 is a display of this line shape (1st derivative of saturated absorption for various pressures recorded with the frequency-offset locking technique (see Fig. 2)). This line shape can be fairly well represented by the 1st harmonic of a frequency-modulated Lorentzian response [41]. The corresponding half-width extrapolated to vanishing modulation amplitude and vanishing laser power is plotted *versus* pressure on figure 4. The non-linear dependence *versus* pressure is a direct consequence of weak elastic collisions and is in good agreement with theoretical predictions [48-49]. The shift of the line centre can be studied by beating a laser locked to I_2 in a variable pressure cell with a fixed frequency laser. As can be seen on figure 5

Fig. 4. — Half-width (in kilohertz) of an I_2 saturation peak (line a_{17}) *versus* pressure, extrapolated to vanishing power and modulation.

Fig. 5. — Pressure shift of the a_4 saturation peak exhibiting a complex non-linear dependence resulting from the various competing factors discussed in the text. The reference laser is locked to the a_3 resonance of iodine in a fixed pressure cell.

there is also a non-linear dependence of the shift *versus* pressure which results from many factors : weak elastic collisions, recoil doubling with unequal intensities of the two components, wavefront curvature shift, residual electronic offsets. This pressure dependence of the shift is still under investigation to discriminate between the combined influences of the various processes. The magnitude of these shifts makes it compulsory to use a frequency difference procedure to obtain accurate frequency differences between lines : one laser is locked to a reference peak and the second laser is locked successively to the two lines whose frequency difference is to be measured in order to minimize the various shifts that could come from the lack of reproducibility between the two systems. The relative stability of the two lasers is characterized by an Allan variance plot ($\sigma(2, \tau, \tau)$ vs. τ) [50] given in figure 6. Most frequency measurements have been performed with a few seconds counting time for which the Allan variance is of the order of 5×10^{-14} .

Fig. 6. — Allan variance plot $\sigma(2, \tau, \tau)$ versus τ for two argon lasers : I - free-running ; II - slaved to external confocal resonators ; III-a - prestabilized and locked to saturated absorption peaks ; III-b - prestabilized and locked to saturated dispersion peaks.

Fig. 7. — Saturated absorption spectrum of I_2 at 5 145 Å obtained by phase-sensitive detection of the third-harmonic of the modulation frequency. The P(13) and R(15) main resonances ($\Delta F = \Delta J$) are respectively labelled by a and b whereas all crossover resonances are labelled by c. The frequency increases from left to right. The horizontal scale is given by the PZT voltage of the driving Fabry-Pérot and has no very precise one to one correspondence with frequency (see table I for precise frequency differences).

We have used the spectrometer at two argon wave-lengths : 5 145 and 5 017 Å and we have studied the following iodine transitions of the $\text{B} \leftarrow \text{X}$ electronic system :

$\text{P}(13), v'' = 0 \rightarrow v' = 43$

$\text{R}(15), v'' = 0 \rightarrow v' = 43$

$\text{R}(98), v'' = 1 \rightarrow v' = 58$

$\text{R}(26), v'' = 0 \rightarrow v' = 62$

}

at 5 145 Å

at 5 017 Å .

The corresponding spectra are given in figures 7 to 10. These landscapes have been obtained with a single laser slaved to a scanned reference resonator. The horizontal scale is given by the PZT voltage for the driving interferometer and has not a very precise one to one correspondence with frequency.

The frequency differences between lines obtained through beat measurements are given in tables I, VIII, X. The uncertainties on the frequency differences are below 200 Hz (1 σ) for most of the main resonances

of P(13) and R(15), 5 kHz (1σ) for R(98) and R(26) estimated from the statistical reproducibility.

The intensities of the various resonances of these spectra have been measured and compared to theoretical predictions [42-44, 51]. A detailed account of this work will be given in the following paper on crossover resonances.

4. Analysis of the experimental results. — We have extracted the hyperfine constants of the B and X states from the previous data. Our method of analysing the

data by a least-squares fit routine is in principle similar to all the previous works on the subject [6, 7, 9, 16, 18, 22, 23, 25, 26, 31] but the higher accuracy of our measurements requires some care and we are going to present in detail the method and the results.

4.1 THE HYPERFINE HAMILTONIAN. — The two nuclei of $^{127}\text{I}_2$ have a spin $5/2$ and the magnetic dipoles and the electric quadrupoles of these two nuclei interact with the electrons and give rise to the hyperfine structure. From symmetry considerations, one can show that the total spin $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$ can take odd or

Fig. 8. — Saturated dispersion spectrum (second-harmonic) for the same frequency range as figure 7.

Fig. 9. — Third-harmonic saturated absorption spectrum of the 58-1 R(98) manifold at 5 145 Å (see table X for precise frequency differences between peaks).

Fig. 10. — Third-harmonic saturated absorption spectrum of the 62-0 R(26) manifold at 5 017 Å (see table VIII for precise frequency differences).

Table I. — Main line positions in the P(13) and R(15) hyperfine spectrum. All the lines are referred to a_1 for P(13) and b_1 for R(15). In both cases, the first column contains the experimental values and the second column the difference between these observed values and the calculated ones obtained in the best fit. The hyperfine constants derived in these fits are given in table II. All frequencies are in kHz.

P(13)			R(15)		
n	$a_n - a_1$	obs. — calc.	n'	$b_{n'} - b_1$	obs. — calc.
2	71 865.2	1.0	2	69 738.8	0.1
3	131 770.1	— 0.7	3	129 156.1	0.5
4	207 818.8	1.1	5	335 829.4	0.7
5	334 999.1	— 0.1	7	396 443.1	— 0.3
6	372 543.9	— 1.4	10	500 627.9	— 0.2
7	386 775.4	0.5	11	525 208.6	— 1.1
8	470 469.3	— 1.2	12	566 288.0	0.9
9	481 488.4	1.4	13	630 784.3	— 1.0
11	525 732.0	— 0.6	14	658 180.1	— 0.1
12	567 369.8	1.1	15	725 168.2	0.4
13	631 481.6	— 0.2	16	739 395.7	0.1
15	719 166.7	0.5	17	791 675.6	0.0
16	748 526.2	0.2	18	865 525.6	0.7
17	792 702.8	1.0	19	874 843.2	0.6
20	889 401.5	— 0.8	20	892 897.0	0.0
21	949 106.6	— 0.8	21	947 279.9	— 0.8

even values depending on the symmetry of the rotational state. The resulting situation for iodine X and B states is the following :

$I = 1, 3, 5$: ortho states, 21 hyperfine sublevels; this occurs for even J values in the B state and odd J values in the X state.

$I = 0, 2, 4$: para states, 15 hyperfine sublevels; this occurs for odd J values in the B state and even J values in the X state.

The eigenstates are obtained by diagonalization of the hyperfine Hamiltonian that we can write

$$\mathcal{H}_{\text{hfs}} = eqQ\mathcal{H}_Q + C\mathcal{H}_{\text{SR}} + d\mathcal{H}_{\text{TSS}} + \delta\mathcal{H}_{\text{SSS}} + e\mathcal{H}_e + f\mathcal{H}_f + h\mathcal{H}_h + hH\mathcal{H}_{hH}.$$

Table III. — Values of B_0'' and B_{43}' in cm^{-1} published by various authors.

Reference	$10^2 B_0'' (\text{cm}^{-1})$	$10^2 B_{43}' (\text{cm}^{-1})$
[52]	3.731 15 (30)	
[53]	3.731 157 1	1.874 131 9
[55]	3.731 29 (7)	1.873 6 (5)
[56]	3.730 6	1.873 87

The validity of this Hamiltonian for iodine B and X states is based on experimental results and theoretical calculations. The quadrupole interaction $eqQ\mathcal{H}_Q$ and the spin-rotation interaction $C\mathcal{H}_{\text{SR}}$ were introduced by Kroll [6]; the tensorial spin-spin interaction $d\mathcal{H}_{\text{TSS}}$ was introduced by Bunker and Hanes [23], the scalar spin-spin interaction $\delta\mathcal{H}_{\text{SSS}}$ by Ezekiel *et al.* [25]. The last four terms have been theoretically introduced in an analysis of small hyperfine terms [36].

This analysis proves also that the magnetic octupole interaction, once introduced [25], is in fact negligible at the present level of accuracy. Finally, it has been recognized early [9] that the terms of the quadrupole interactions, non diagonal in the rotational quantum number, are important; we must therefore use a basis set containing not only the level v, J but also the levels $v, J \pm 2$ and in some cases $v, J \pm 4$. Therefore before diagonalization, we must introduce the rotational Hamiltonian $\mathcal{H}_R$. It is diagonal in the $|JIF\rangle$ basis set and its eigenvalues are given by the usual spectroscopic expansion :

$$\langle JIF | \mathcal{H}_R | JIF \rangle = B_v J(J+1) - D_v [J(J+1)]^2 + H_v [J(J+1)]^3.$$

We have used the values published by Luc and Gerstenkorn [52, 53] for the constants B_v, D_v, H_v . The precision of these values is discussed below.

Table II. — Values of the hyperfine constants deduced from the fits of table I. For each constant, we give the fitted value and the corresponding standard deviation (SD). C_{eqQ} is the correlation coefficient between $eq'Q$ and $eq''Q$. The line SD gives the standard deviation of the fits. All values are in kHz.

	P(13)		R(15)	
	Constant	SD	Constant	SD
$eq'Q$	— 557 717.	164.	— 559 126.	107.
$eq''Q$	— 2 451 682.	164.	— 2 453 086.	107.
ΔeqQ	1 893 965.	2.	1 893 960.	1.
C_{eqQ}	0.999 941		0.999 950 8	
C'	186.880	0.009	187.546	0.006
d'	— 101.604	0.113	— 101.990	0.066
δ'	— 3.116	0.093	— 3.028	0.056
SD	1.07		0.72	

$C'' = d'' = \delta'' = 0$ fixed in the least-squares fit.

The Hamiltonian matrix $\mathcal{H} = \mathcal{H}_R + \mathcal{H}_{\text{hfs}}$ has obviously a block diagonal structure since the total angular momentum F is a good quantum number. We have used this property to reduce the size of the matrices that are numerically diagonalized. For ortho states, the largest submatrix has the following size : 3×3 if we consider only the level J , 8×8 if we consider the levels $J, J \pm 2$, and 11×11 if we include the levels $J \pm 4$.

A feature present in all the studies of the B-X hyperfine structure is bound to the fact that the electric quadrupole term dominates the other terms of the hyperfine Hamiltonian. Therefore as the transitions studied follow the selection rule $\Delta J = \pm 1$ and as J is usually rather large ($J > 10$), the hyperfine eigenstates $|J, F\rangle$ (F is not a good quantum number [16]) are obtained by the diagonalization of very similar Hamiltonians in both states, the only differences being due to the J difference and to the weaker hyperfine terms. This similarity leads to an approximate selection rule $\Delta F = 0$. Another approximate rule is due to the fact that J is usually large and only the transitions $\Delta F = \Delta J$ are strong.

Therefore, a hyperfine spectrum is made of a number of main lines equal to the number of hyperfine sublevels in the excited (or in the ground state). Weaker $\Delta F = 0$ lines are observed either directly [33, 18, 19] or through crossover resonances with the main lines [18, 40] (and present work).

4.2 PRINCIPLE OF THE LEAST-SQUARES FIT. — We have used a non-linear least-squares fit by a method of gradients. The only trick that we have used is that we have calculated the gradients by the first order perturbation theory. Let us consider an eigenstate $|A\rangle$ of energy E . If we need the derivative of E versus an hyperfine constant, eqQ for instance, we may write that a variation of eqQ creates a new Hamiltonian :

$$\mathcal{H}' = \mathcal{H} + d\mathcal{H} \quad \text{with} \quad d\mathcal{H} = \mathcal{H}_Q d(eqQ)$$

with a new eigenvalue $E + dE$. dE is then calculated by considering $d\mathcal{H}$ as a small perturbation and by applying first order perturbation theory. The result is :

$$\frac{\partial E}{\partial eqQ} = \frac{\langle A | \mathcal{H}_Q | A \rangle}{\langle A | A \rangle}.$$

The interest is that this calculation of the derivatives of E needs only a very small computation as the usual diagonalization subroutines give at the same time eigenvalues and eigenstates. All the computations have been made in double precision (18 decimal figures) on the UNIVAC 1110 of Orsay Computer Centre. The litteral expressions have been used for the $3J$, $6J$ and $9J$ symbols appearing in $\mathcal{H}_Q$, $\mathcal{H}_{\text{SR}}$, $\mathcal{H}_{\text{TSS}}$, $\mathcal{H}_{\text{SSS}}$. Appendix A gives some details about these litteral expressions. For the evaluation of $\mathcal{H}_e$, $\mathcal{H}_f$, $\mathcal{H}_h$ and $\mathcal{H}_{\text{hfs}}$, we have used numerical subroutines giving

less precision : this has little importance as these terms are small.

The diagonalization subroutine is stated to give a relative precision of $10^{-18} n^2$ on the eigenvalues of a $n \times n$ matrix. If we consider $n = 11$ and if we take into account that the full spectrum covers the energy range from $J - 4$ to $J + 4$ (about 10^5 to 10^6 MHz) the resulting error is about 10^{-4} Hz, which is surely negligible, even if the accuracy is less good.

A great problem arises from the nature of the hyperfine spectrum. If only main lines are available, the analysis of the data reveals a very high correlation between ground state and excited state corresponding constants ($eq'Q$ and $eq''Q$, C' and C'' , ...). This effect is so strong that it is impossible, in most cases, to fit at the same time excited state and ground state constants. The introduction of weaker $\Delta F = 0$ lines, or of crossovers greatly improves this situation.

4.3 RESULTS FOR THE 43-0 P(13) AND R(15) LINES. — Various analyses of the data have been made ; we are going to describe the results thus obtained.

4.3.1 Analysis without crossovers. — In their principle, these analyses are similar to those of references [25, 26] on the data of reference [25]. The large correlation between upper and lower state corresponding constants precludes the fit of all the parameters, and following the previous works, we have fitted only $eq'Q$, C' , d' , δ' and $eq''Q$. All the other constants are taken equal to zero, although they are not obviously so. The comparison between these results and previous results should be mainly made on the differences $\Delta eqQ = eq'Q - eq''Q$, ΔC , Δd , $\Delta \delta$.

The quality of these fits appear clearly in tables I and II. First of all, the standard deviations of these fits are just around 1 kHz : 1.07 kHz for P(13) and 0.72 kHz for R(15). This is considerably smaller than the best standard deviations obtained by Ezekiel [38] : 5.4 kHz for P(13) and 2.6 kHz for R(15). A second point is that ΔeqQ , Δd , $\Delta \delta$ are almost the same for P(13) and R(15). This is a very important test of the quality of our data. The quantity $\Delta C = C' - C''$ is not the same for P(13) and R(15); this is a consequence of the non validity of the assumption $C'' = 0$. This effect will disappear if we remove this assumption. We will do this, with the introduction of the crossovers. In the absence of the crossovers, C' and C'' are extremely correlated and the results of such fits are meaningless.

It is important to note that ΔeqQ is the same for P(13) and R(15) within 10 kHz. This constancy cannot be the result of a parallel variation of $eq'Q$ and $eq''Q$ of 1.4 MHz when going from P(13) to R(15) as it appears by inspection of table II. We feel that $eq'Q$ and $eq''Q$ must be both constant, at least in the 10 kHz range, when going from P(13) to R(15). The apparent variation is an artifact of the present fits and is clearly related to the very high correlation coefficient C_{eqQ} between $eq'Q$ and $eq''Q$; this coefficient is given in table II and is roughly equal to 1.5×10^{-5} .

An important point is that, at the present level of accuracy, we must introduce the $J - 4$ to $J + 4$ basis set. We have compared, for the same values of the constants, the hyperfine splittings calculated with the $J \pm 2$ basis set and the $J \pm 4$ basis set. The largest difference is a few hundred Hertz for P(13). This is in good agreement with the order of magnitude of the effect which is given by $(3/16\ eqQ)^4/(4\ B_v\ J)^3$. The choice of the $J \pm 4$ basis set was done for all the fits involving the P(13) and R(15) and presented here.

Related to this phenomenon is also the sensitivity of the fit to the second order quadrupole coupling and to the rotational constants. To discuss this effect, we use a perturbation theory language, although our program uses a direct diagonalization. The magnitude of the second order quadrupole coupling is given by $(3/16\ eqQ)^2/(4\ B_v\ J)$; as $eq''\ Q \sim 5\ eq'\ Q$ and $B_{v''} \sim 2\ B_v$, this effect is about ten times larger in the X state than in the B state. It amounts to a few Megahertz for the levels discussed here ($J = 12$ to 16). We must note two points :

— An error on the rotational constant B_v induces an error in the calculation of this effect. To keep this error in the 0.5 kHz range, the relative uncertainty must be 10^{-3} for B_v and 10^{-4} for $B_{v''}$. Table III compa-

res the values of $B_{v'}$ and $B_{v''}$ published by various authors [52, 53, 55, 56]. The claimed accuracies and the dispersion of the values seem to indicate that the above condition are fulfilled. All our calculations use the constants B_v, D_v, H_v taken in the tables IV and V of reference [53].

— Owing to the second order coupling, the hyperfine structure is, on the average, shifted from the place of the rotational level with no hyperfine Hamiltonian ; therefore, the observed rotational spacings are « dressed » by the hyperfine Hamiltonian. As a consequence the rotational spacings used in our calculation should be corrected for this dressing effect. Fortunately as the largest second order effect is only a few Megahertz, and as there are some compensating effects, this dressing effect is surely negligible here.

4.3.2 *Analysis with crossovers.* — Only a small number of crossovers have been measured with a good accuracy. They were measured in a search for the evidence of the recoil effect [42]. All the crossovers measured then are forming pairs : one pair is made of the two crossovers of one weak $\Delta F = 0$ line with the two main lines having either a common upper or a common lower level. As we have 4 crossovers for P(13) (and also 4 for R(15)), it means that we have really

Table IV. — *Main line positions (already given in table I) and crossover positions for P(13) and R(15). The (observed — calculated) column refers to the results of the best fits whose constants are given in table V. All frequencies are in kHz.*

P(13)			R(15)		
n	$a_n - a_1$	obs. — calc.	n'	$b_{n'} - b_1$	obs. — calc.
2	71 865.2	1.3	2	69 738.8	0.9
3	131 770.1	— 1.6	3	129 156.1	— 0.6
4	207 818.8	— 1.2	5	335 829.4	0.4
5	334 999.1	— 0.5	7	396 443.1	— 2.1
6	372 543.9	— 0.4	10	500 627.9	— 0.6
7	386 775.4	— 1.6	11	525 208.6	— 1.7
8	470 469.3	— 0.4	12	566 288.0	0.9
9	481 488.4	2.9	13	630 784.3	— 0.9
11	525 732.0	— 2.6	14	658 180.1	— 1.0
12	567 369.8	2.0	15	725 168.2	— 1.2
13	631 481.6	— 0.2	16	739 395.7	1.8
15	719 166.7	— 0.2	17	791 675.6	— 0.3
16	748 526.2	2.2	18	865 525.6	2.3
17	792 702.8	0.0	19	874 843.2	0.9
20	889 401.5	— 1.2	20	892 897.0	— 0.1
21	949 106.6	0.3	21	947 279.9	0.1
m	n	$c_m - a_n$	m'	n'	$c_{m'} - b_{n'}$
6	4	— 24 850.0	82	16	— 21 346.7
6	7	— 203 807.0	82	18	— 147 476.5
8	4	64 629.1	86	16	41 717.9
8	7	— 114 327.8	86	18	— 84 412.0
1	1	— 28 215.2	98	1	924 979.3
3	1	75 693.0	99	1	952 173.9

Table V. — *Values of the hyperfine constants deduced from the fits of table IV. For each constant, we give also the value of the standard deviation. C_{eqQ} is also given, as well as the standard deviation of the fit. All values are in kHz.*

	P(13)		R(15)	
	Constant	SD	Constant	SD
$eq' Q$	— 558 581.	91.	— 558 645.	27.
$eq'' Q$	— 2 452 551.	92.	— 2 452 603.	27.
ΔeqQ	1 893 970.	3.	1 893 958.	2.
C_{eqQ}	0.999 597		0.997 473	
C'	191.488	0.932	189.598	0.082
C''	4.250	0.863	2.159	0.087
ΔC	187.238	0.070	187.439	0.009
d'	— 101.709	0.160	— 101.802	0.115
δ'	— 2.977	0.138	— 3.117	0.098
SD	1.55		1.33	

$d'' = \delta'' = 0$ fixed in the least-squares fits.

only two new informations (namely the frequency of the $\Delta F = 0$ lines) for P(13) (and also for R(15)).

We have introduced these crossovers in our fits and, in order to increase their weights, we have given two measurements for some of them. Of course, we have made the correction for the recoil effect [42] by shifting 2.96 kHz to the red (blue) the crossovers having a common upper (lower) level.

The fits are satisfactory only if we release C'' because this constant has a rather large effect. As the available new information is limited, tentatives to release also d'' and δ'' do not give good results. These fits are described in tables IV and V. The first comment is that their standard deviation remains very good :

1.55 kHz for P(13) and 1.33 kHz for R(15) .

The second important result is that $eq' Q$ and $eq'' Q$ are now almost the same for P(13) and R(15). This agreement is highly satisfactory. Similarly, the values of C' and C'' are in good agreement for P(13) and R(15) the standard deviation on C' and C'' is a lot larger for P(13) than for R(15) because the crossovers introduced have not the same sensitivity to C' and C'' in both cases; more precisely a large correlation appears between $eq' Q$ and C' and between $eq'' Q$ and C'' for P(13) but not for R(15). However the two values of $\Delta C = C' - C''$ are in good agreement.

These results may be compared to those of Muentner and Yokoseki [45]. These authors have used optically pumped and detected magnetic resonance to measure the hyperfine structure of the $v = 0, J = 13$ level (i.e. the lower level of the 43-0 P(13) transition). They have measured twenty $\Delta F = \pm 1$ lines and interpreted these measurements in terms of $eq'' Q, C'', d'', \delta''$ with a standard deviation of the fit of 0.63 kHz. (We have checked their calculation with our program and all hyperfine frequencies agree within 0.1 kHz.) The values thus obtained for the ground state constants are given in table VI. The agreement with our own values is very good for $eq'' Q$. The agreement is less

Table VI. — *Hyperfine constants and standard deviations obtained by Muentner and Yokoseki [45] for the $X^1 \Sigma_g^+ v'' = 0, J'' = 13$ level.*

	Constant (kHz)	SD (kHz)
$eq'' Q$	— 2 452 583.7	1.6
C''	3.162	0.008
d''	1.58	0.05
δ''	3.66	0.03

good for C'' ; our best determination is obtained on R(15) : $C'' = 2.16$ kHz with a standard deviation of 0.09 kHz, in disagreement with Muentner's value $C'' = 3.162$ kHz (standard deviation of only 8 Hz). However this contradiction could be due to our assumption $d'' = \delta'' = 0$, which is contradicted by the results of Muentner.

We have therefore tried to determine if, by using the ground state constants of Muentner and Yokoseki [45] and by fitting only the excited state constants, we could well represent our data. The result is disappointing. If we try to fit the data of table IV (main lines and crossovers), the standard deviations of the fits are 6.07 kHz for P(13) and 4.7 kHz for R(15). These large standard deviations are mainly due to the crossovers; it is easy to prove, without any calculation, that there is a contradiction between the data contained in the crossovers and the measurement of Muentner *et al.* For instance the distance $c_8 - a_7$, after correction for the recoil effect, given in table IV, should be exactly one half of the hyperfine frequency $I = 5, F'' = 9, I = 5, F'' = 10$ measured by Muentner

$$v_{c_8} - v_{a_7} - \delta/2 \pi = 114\,327.8 \text{ kHz}$$

whereas :

$$v(F'' = 9 - F'' = 10)/2 = 114\,339.5 \text{ kHz} .$$

The difference, 12 kHz, exceeds by a large amount the cumulated uncertainties.

We do not presently know the origin of this puzzling discrepancy which appears with the same order of magnitude in all the cases where we have done the comparison between a frequency of the ground state measured directly by Muentner *et al.* (or deduced from their constants) and the same frequency calculated from the position of a crossover. A systematic study of the crossover resonances is presently underway to investigate the origin of this discrepancy. Preliminary checks indicate that there is an excellent reproducibility of the frequency differences between main lines or between crossovers (only these differences enter into the experimental determinations of the recoil shift) but we found a lack of reproducibility of the frequency differences between main lines and crossovers at the 10 kHz level. Our latest measurements (with reduced offsets) on the c_6 and c_8 crossover resonances confirm the recoil shifts and tend to be in much better agreement with the results of Muentner and Yokoseki. For example :

$$\nu_{c_8} - \nu_{a_7} - \delta/2\pi = 114\,341 \pm 1 \text{ kHz (1 } \sigma)$$

where only statistical reproducibility was considered for the standard deviation. Also it is important to note that there is an unknown correction due to the unequal recoil components for the main peaks which has not been made.

As we could not find a satisfactory fit including both the crossovers and the ground state constants of Muentner, we have made fits of the main line position only. The results of these fits are given in table VII. From the point of view of the standard deviation these fits are slightly less good than those of tables I-II, but they give very coherent values of the excited state constants between P(13) and R(15).

Table VII. — Constants deduced from new fits of the main line positions for the P(13) and R(15) transitions. The ground state constants are taken equal to those of Muentner and Yokoseki (see table VI), and only the excited state constants are fitted. The standard deviations of these new fits appear at the line SD. All values are in kHz.

	P(13)		R(15)	
	Constant	SD	Constant	SD
$eq' Q$	- 558 615.4	3.16	- 558 627.4	1.83
C'	190.322	0.013	190.541	0.007
d'	- 99.976	0.186	- 100.272	0.113
δ'	0.552	0.156	0.574	0.094
ΔeqQ	1 893 968.3	3.16	1 893 956.3	1.83
ΔC	187.160	0.013	187.379	0.007
Δd	- 101.556	0.186	- 101.852	0.113
$\Delta \delta$	- 3.108	0.156	- 3.086	0.094
SD	1.90		1.25	

4.3.3 Conclusion. — We feel that an important progress has been made in the determination of the hyperfine constants in the excited and ground states

of the 43-0 P(13) and R(15) transitions. For the first time, the constants of two transitions present a good coherence. Although a discrepancy has appeared between the results of Muentner and Yokoseki and our earlier measurements of the crossovers we feel that the following values of $eq'' Q$ and C'' are quite sure :

$$eq'' Q = - 2\,452.6 \pm 0.1 \text{ MHz}$$

$$C'' = 3 \pm 1.5 \text{ kHz}.$$

Moreover, the various differences ΔeqQ , ΔC , Δd , $\Delta \delta$ as given in table VII are surely very precisely known.

Some attempts to fit the constants e , f , h , hH were made. Although the values obtained were partly reproducible when going from P(13) to R(15) and from one fit to another (in which for instance ground state constants were either fitted or taken from Muentner [45]), in almost all the cases, the standard deviation on each parameter was comparable to the value of the parameter.

4.4 RESULTS FOR THE OTHER TRANSITIONS STUDIED.

— 4.4.1 Transition 62-0 R(26). — This transition coincides with the 5 017 Å line of the Ar⁺ laser, and was first studied in saturated absorption spectroscopy by Sorem *et al.* [13]. As this transition is weaker than the 43-0 P(13) and R(15), as the laser line is less powerful, and finally as the crossover intensities decrease rapidly with J , the spectrum is made of only 15 main lines (15 because it is a para state transition). The uncertainty on the hyperfine splittings is estimated to 5 kHz.

We have made two different fits of the experimental data. In the first $eq' Q$, C' , d' , δ' and $eq'' Q$ were fitted ; in the second we have used for the level $v'' = 0$, $J'' = 26$ the constants of Muentner determined for the level $v'' = 0$, $J'' = 13$, and only $eq' Q$, C' , d' , δ' were fitted. In both cases, the standard deviation is 17.8 kHz.

Table VIII. — Observed main line positions in the 62-0 R(26) transition and (observed — calculated) values for the two fits described in the text. All values are in kHz.

n	$a_n - a_1$	First fit obs. — calc.	2nd fit obs. — calc.
2	166 252	24	22
3	265 929	- 12	- 21
4	295 323	- 1	8
5	317 930	- 2	2
6	364 482	- 18	- 21
7	397 181	- 22	- 20
8	474 032	20	26
9	523 535	10	6
10	560 022	- 7	- 7
11	637 042	- 18	- 14
12	660 260	- 10	- 5
13	739 960	10	7
14	769 732	2	- 4
15	842 250	16	16

Table IX. — *Values of the hyperfine constants for the 62-0 R(26) transition. The results of the two fits are given, and the previous results of Sorem et al. [13] are given also for comparison.*

	First fit		Second fit		Results of Sorem <i>et al.</i> [13]	
	Constant	SD	Constant	SD	Constant	SD
<i>eq' Q</i> (MHz)	— 550.568	17.468	— 569.132	0.035	—	—
<i>eq'' Q</i> (MHz)	— 2 434.020	17.469	— 2 452.583 7 (*)			
<i>C'</i> (kHz)	935.811	0.140	938.739	0.078		
<i>d'</i> (kHz)	— 410.994	2.05	— 410.709	2.05		
<i>δ'</i> (kHz)	562.387	2.26	565.976	2.26		
<i>ΔeqQ</i> (MHz)	1 883.456	0.035	1 883.452	0.035	1 878.	10.
<i>ΔC</i> (kHz)	935.811	0.14	935.577	0.078	944.	60.
<i>SD</i> (kHz)	17.8		17.8			

$C'' = d'' = \delta'' = 0.$

(*) *eq'' Q*, *C''*, *d''*, *δ''* from reference [45], see table VI.

The results of these fits are given in tables VIII and IX. We give also, for comparison, the constants obtained by Sorem *et al.* [13].

We may comment on the results of these two fits :

- first of all, the two constants *d'* and *δ'* have large values (about half a Megahertz). These large values will be discussed below ;
- the values of *ΔeqQ* and *ΔC* are in good agreement with the previous values [13], but they are a lot more precise ;
- obviously, in the first fit, *eq'' Q* and *eq' Q* are both adjusted and highly correlated (correlation coefficient $C_{eqQ} = 0.999\,998$) and therefore their uncertainties are large (standard deviation = 17.5 MHz) but the true values are well inside this error bar. *ΔeqQ* is very well determined by both fits ; only the second one should give a reliable value of *eq' Q* ;
- we have used indifferently a $J \pm 2$ or a $J \pm 4$ basis set ; the value of *J* is sufficiently high so that the effect of quadrupole coupling to fourth order is negligible, at the present level of accuracy ;
- the introduction of the constants *e*, *f*, *h*, and *hH* has not improved the standard deviation of the fits, and here also, these new constants were determined with an error comparable to their value.

4.4.2 *Transition 58-1 R(98).* — This transition is coincident with the Ar⁺ laser 5 145 Å line [57, 58, 29] and has been recently studied in saturated absorption spectroscopy by Foth and Spieweck [30]. As this line is rather weak, and as the *J* value is large, only main lines are observed. Moreover the accuracy of hyperfine splittings is estimated not to be better than 5 kHz in our study of the line.

We have used our computer program to fit our data, and also the data of reference [30]. Our determination of the hyperfine constants are in good agreement with those determined by Foth *et al.* in both cases. The most striking result is that, in *v* = 58 as in *v* = 62, the values of *C'*, *d'*, *δ'* are very large. We give in table XI the constants deduced from the fits of our data. In the first fit, *C''*, *d''*, *δ''* were held fixed at zero, and *eq' Q*,

Table X. — *Observed main line positions in the 58-1 R(98) transition and (observed — calculated) values for the two fits described in the text. As the *a*₁₀ and *a*₁₁ lines are very close, their position is surely not very accurate and these values were not included in the fits.*

<i>n</i>	<i>a_n — a₆</i> (kHz)	obs. — calc. kHz	obs. — calc. kHz
—	—	—	—
1	— 413 487	18	21
2	— 359 554	1	— 23
3	— 194 520	4	8
4	— 159 158	— 13	— 38
5	— 105 771	— 10	— 20
6	0		
7	172 197	— 32	— 19
8	200 476	— 2	— 4
9	225 982	6	8
10	253 087	not fitted	not fitted
11	254 138	— —	— —
12	314 133	— 27	— 36
13	426 693	19	13
14	481 574	10	10
15	510 245	11	— 5
		fit n° 1	fit n° 2

Table XI. — *Values of the hyperfine constants for the 58-1 R(98) transition. The results of the two fits are given. The agreement with the previous results of Foth and Spieweck is good.*

	First fit		Second fit (*)	
	—	—	—	—
<i>eq' Q</i> (MHz)	— 419.447	62.0	— 572.464	0.078
<i>eq'' Q</i> (MHz)	— 2 299.614	62.0	— 2 452.583 7	
<i>C'</i> (kHz)	829.234	0.038	832.322	0.039
<i>d'</i> (kHz)	— 501.63	3.22	— 500.46	3.84
<i>δ'</i> (kHz)	357.89	3.17	360.54	3.75
<i>ΔeqQ</i> (MHz)	1 880.167	0.078	1 880.120	0.078
<i>ΔC</i> (kHz)	829.324	0.038	829.160	0.039
<i>SD</i> (kHz)	20.5		24.6	

(*) *eq'' Q*, *C''*, *d''*, *δ''* taken from reference [45], see table VI.

C' , d' , δ' , and $eq''Q$ were adjusted. The standard deviation is 24 kHz, and the very high correlation between $eq'Q$ and $eq''Q$ ($C_{eqQ} = 0.999\,999\,4$) explains the large standard deviation on these constants and their rather inaccurate values. In the second fit, the ground state constants were taken equal to those of reference [45], although the present ground state $v'' = 1$, $J = 98$ is not the level considered in this reference which is $v'' = 0$, $J'' = 13$. This means that the $eq''Q$ may be inexact by a few MHz [59], but the value of ΔeqQ is very precise. The other differences ΔC , Δd , $\Delta \delta$ are not very different from one fit to the next.

There are some differences between the present results and the analysis of Foth and Spieweck [30] :

i) Our standard deviation is larger than theirs because we used a different definition :

$$SD = (\sum (v_{\text{obs}} - v_{\text{calc}})^2 / N)^{1/2}$$

N = number of fitted frequencies — number of fitted parameters.

ii) We do not fit the « zero » frequency in the spectrum (cf. their table I).

iii) Their correlation coefficient $C_{eqQ} = 0.999\,943\,5$ does not seem close enough to 1, for such a high J value [26]. Using our program and their data, we get $C_{eqQ} = 0.999\,999\,5$. This is also in agreement with the fact that a reasonable value of $eq''Q$ (say $eq''Q = -2\,452$ MHz) is inside an error bar of 3 standard deviations for our fit, and not for the fit of Foth *et al.*

4.5 COMMENT ON THE SPECTROSCOPIC RESULTS. —

We have now very precise values of various hyperfine constants as a function of the vibrational level of the B state. We shall now comment briefly on these values.

4.5.1 Quadrupole coupling constant. — The eqQ values are now very well known. A detailed study of the variation as a function of the vibrational level in the B and X state of iodine has appeared [59]. We will say here that this study explains quantitatively the values of eqQ near the dissociation limit and qualitatively the vibrational dependences.

4.5.2 The C' , d' , δ' constants. — These three constants vary very rapidly near the dissociation limit; this very rapid variation is illustrated by figure 11, which represents these constants as a function of the vibrational energy.

The large values of these constants are due to a mixing of the $B^3\Pi_{0+u}$ state with other electronic states [16, 36]. The divergent character of C' has been qualitatively [16] and quantitatively [37] related to a perturbation by two $1u$ states having the same dissociation limit. Reference [36] has shown that the constants d' and δ' are due to the perturbation of the B state by the states of the following symmetries : $1u$, 0^-u , and also $1g$, 0^-g . The divergent character of d' and δ' can be related to the presence of one 0^-u , two $1u$,

Fig. 11. — Variation of C , d , δ as a function of the vibrational energy for the levels of the B state studied here ($v = 43, 58$ and 62 ; the C value is also given for $v = 40$ [16]). The interpolating curves are just tentative plots; obviously for C and d these plots are irregular when going from $v = 58$ to $v = 62$; this proves that the simple theory which relates C , d , δ only to the vibrational energy is not sufficient.

two $1g$, one 0^-g states having the same dissociation limit [60]. All those states are antibonding at short internuclear distances, but may be slightly bound at long internuclear distances due to Van der Waals and quadrupole interactions. This means that the energy denominators appearing in second order perturbation formulas are probably negative for all these states. Therefore we may use table IV of reference [36]. It appears then that, if only u states were mixed to the B state, δ should be negative and d positive or negative depending on the relative effect of the $1u$ and 0^-u states. This is not verified and the fact that δ is positive and d is negative ($d \simeq -\delta$) for the levels $v = 58$ and 62 seems to indicate that the main effect should be due to a 0^-g state.

We see that the measurement of these quantities is a direct proof of the u - g mixing of the B state of iodine near its dissociation limit. The effect of u - g perturbation is often neglected in homonuclear diatomic molecule as it is due only to the hyperfine Hamiltonian. We think that we have given here one of the first experimental evidences.

To go further in the evaluation is clearly very difficult. Evidently the contribution of all the 6 perturbing electronic states should be evaluated using the method established in [37], but the simplifying assumption used then on the energy denominators is not sufficient here and the potential curves of these 6 states should be calculated precisely.

It is difficult to explain why d decreases in modulus when going from $v = 58$ to $v = 62$. This may be due to the very large J value ($J = 98$) of the level $v = 58$. Owing to the rotational energy, the level $v = 58$, $J = 98$ is closer to the dissociation limit than the level $v = 62$, $J = 27$. This may also be an effect of some

competition between the contribution of the six electronic states, or even a local perturbation if some of these states have bound rovibrational levels.

5. Conclusion. — We feel that we have made a significant progress with respect to previous determinations of hyperfine constants of iodine for the P(13) and R(15) lines : the fact that the two independent sets of hyperfine constants are consistent together and the small number of these constants suggest that the theoretical fit has not a purely effective character. (In other words we expect that the various terms of the hamiltonian correspond to physical effects and do not simply provide a phenomenological representation of an isolated hyperfine spectrum.) It will be difficult to go much further without taking into account the details of the line shape : recoil structure, differential shifts of the various hyperfine components, partial overlap of neighbouring resonances...

On the other hand we expect to make further progress through the comparison of the ground level splittings from the crossover resonances frequencies and from magnetic resonance data and this part of the program is still underway.

For the 58-1 R(98) line at 5 145 Å we essentially confirm the results of Foth and Spieweck [30] but for the 62-0 R(26) line at 5 017 Å we bring a substantially improved knowledge of the spectrum and the first determination of the two hyperfine spin-spin coupling constants d' and δ' . The variation of these constants near the dissociation limit can be considered as a first experimental demonstration of the mixing of the $B^3\Pi_{0+u}$ state with g electronic states having the same dissociation limit.

A very detailed knowledge of these spectra is essential for the metrological applications of argon lasers slaved to iodine peaks. Already, the argon laser/iodine system appears as one of the best optical fre-

quency and (wave) length standards in the visible. Very accurate wavelength measurements have been performed at the PTB (Physikalische-Technische Bundesanstalt, Braunschweig), at the BIPM (Bureau International des Poids et Mesures) and at the INM (Institut National de Métrologie, Paris) for the hyperfine component a_3 of the P(13) spectrum [63] yielding

$$\lambda_{a_3} = 514.673\,467\text{ nm } (\pm 4 \times 10^{-9} \lambda).$$

International frequency comparisons have been started between the PTB and our laboratory demonstrating a reproducibility of 10^{-11} [64]. In June 1979, the CCMD (Comité Consultatif pour la Définition du Mètre) has estimated that the Ar^+/I_2 system slaved to the a_3 resonance could be considered as a reference wavelength for length measurements [65].

Besides stability and reproducibility an important quality for a frequency standard is absolute accuracy. From our knowledge of the various shifts (unresolved recoil splitting, wavefront curvature shift, pressure shifts, electronic offsets...) the absolute accuracy for the Ar^+/I_2 frequency standard can be estimated to be of the order of 5 kilohertz. We should be able to reduce this number in the future as we progress in our knowledge of the line shape. Among other factors we need to know the pressure and power dependence of the recoil peaks ratio which can be inferred from the study of crossover resonance intensities.

Finally we have already calculated the intensity of all the resonances in the P(13)/R(15) spectrum including crossover resonances and weak $\Delta F = 0$ lines. The catalog of these intensities will be published in the forthcoming paper on crossovers but is already available upon request. An important conclusion that can be drawn from this study is the fact that the a_3 resonance is well isolated from any adjacent resonance and appears as a very good choice for a reference line.

Appendix A. — The expressions for the various Hamiltonians have been taken from references [9] and [36].

For $\mathcal{H}_Q$, we have noticed that formula (A. 1) of reference [9] when developed, using the 3 J and 6 J literal expressions of Edmunds [4] can be given a simpler form than equation (A. 4). We get the following expression which is numerically equivalent to this equation :

$$\langle JIF | \mathcal{H}_Q | JIF \rangle = - \frac{(3X(X-1) - 4I(I+1)J(J+1))}{8I_1(2I_1-1)(2J-1)(2J+3)} \cdot \frac{3(I(I+1)-1) - 4I_1(I_1+1)}{(2I-1)(2I+3)}$$

with $X = J(J+1) + I(I+1) - F(F+1)$, and I_1 is the individual nuclear spin ($I_1 = 5/2$ for $^{127}\text{I}_2$).

For $\mathcal{H}_{\text{SR}}$, $\mathcal{H}_{\text{SSS}}$ the expressions are very simple. The only difficulty comes from $\mathcal{H}_{\text{TSS}}$. Its expression given by [36] involves the following 9 J symbol

$$\left\{ \begin{array}{ccc} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I & I'' & 2 \end{array} \right\}.$$

We have found the expressions for the two non-zero such symbols in Mizushima [62]. However one was false and we have recalculated it. We give here these two expressions :

$$\left\{ \begin{array}{ccc} S & S & 1 \\ S & S & 1 \\ I & I & 2 \end{array} \right\} = \frac{1}{\sqrt{120}} \sqrt{\frac{I(I+1)}{(2I-1)(2I+1)(2I+3)}} \cdot \frac{4S(S+1) + I(I+1)}{S(S+1)(2S+1)}$$

$$\left\{ \begin{array}{ccc} S & S & 1 \\ S & S & 1 \\ I & I-2 & 2 \end{array} \right\} = -\frac{1}{\sqrt{5}} \sqrt{\frac{[(2S+1)^2 - (I-1)^2][(2S+1)^2 - I^2](I-1)I}{(2I-3)(2I-1)(2I+1)}} \cdot \frac{1}{2S(2S+1)(2S+2)}$$

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