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Very high resolution study of high Rydberg levels of the configurations $4f^{14}$ 6s*n*d of Yb I

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Résumé. — Les niveaux de Rydberg élevés de l'ytterbium ont été étudiés sur un jet d'atomes métastables. Les niveaux de la série $4f^{14}$ 6s*n*d ont été peuplés à partir du niveau métastable $4f^{14}$ 6s 6p $^3P_0$ grâce à la lumière ultraviolette d'un laser à colorant monomode doublé en fréquence et détectés par la méthode d'ionisation par un champ électrique. Les champs critiques d'ionisation F_c des niveaux $4f^{14}$ 6s*n*d $^3D_1$ ($24 \leqslant n \leqslant 57$) ont été mesurés ; ils obéissent à la loi *du col* ($F_c = (16\, n^{*4})^{-1}$). Les structures hyperfines des isotopes impairs ont été analysées ; comme l'interaction hyperfine est du même ordre de grandeur que les interactions électrostatiques et spin-orbite (ou même pour les valeurs de *n* les plus élevées plus importantes que ces dernières), ces structures ont un aspect très particulier. Les structures observées ont été interprétées théoriquement par la méthode paramétrique de Slater-Condon. Les influences respectives de l'électron optique excité (*n*d) et de l'électron optique non excité (6s) ont ainsi pu être étudiées. De plus, l'influence d'un niveau de valence perturbant seulement les composantes des isotopes impairs a été mise en évidence pour le nombre quantique $n = 26$.

Abstract. — High Rydberg levels of ytterbium were studied in a beam of metastable atoms. Levels of the series $4f^{14}$ 6s*n*d were populated from the metastable $4f^{14}$ 6s 6p $^3P_0$ level by means of the U.V. light of a frequency-doubled single-mode dye laser and detected using the field ionization technique. The critical ionization fields F_c of the levels $4f^{14}$ 6s*n*d $^3D_1$ ($24 \leqslant n \leqslant 57$) were measured and found to obey the *saddle point law* ($F_c = (16\, n^{*4})^{-1}$). The hyperfine structures of the odd isotopes were investigated. They are very peculiar due to the fact that the hyperfine interaction is of the same order of magnitude as (or even for the highest *n* values, much more important than) the spin-orbit and electrostatic interactions. A theoretical account of the observed structures using the Slater-Condon parametric method is given. The relative influence of the excited (*n*d) and of the non-excited (6s) optical electron could thus be studied. Furthermore the influence of a valence level perturbing only the odd isotopes components for $n = 26$ was demonstrated.

1. **Introduction.** — During the last few years, the study of high lying Rydberg levels of atoms has become a field of increasing interest in atomic spectroscopy. The spectra of one-electron atoms have been the subject of a very large amount of experimental and theoretical work. Comparatively, rather few very high-resolution studies have been performed on many-electron atoms. Technical as well as theoretical difficulties easily explain this fact. However the study of high Rydberg levels of many-electron atoms is particularly interesting because of the specific characteristics they possess :

(i) their properties are influenced by the presence of the non-excited optical electrons ;

(ii) in the energy range where high Rydberg levels are located there can also exist levels belonging to doubly excited electronic configurations that interact with the usual Rydberg series, thus leading to the so-called perturbed series.

The purpose of this work on the ytterbium atom was to investigate the two foregoing phenomena and more precisely to investigate their influence on the critical ionization fields and on the hyperfine structures of the Rydberg levels.

2. **Energy spectrum of ytterbium I.** — The atomic number of ytterbium is 70. Ytterbium possesses seven stable isotopes with mass numbers ranging from 168 to 176 ; the corresponding natural relative abundances are given in table I. The nuclear spins of ^{171}Yb and of ^{173}Yb are 1/2 and 5/2 respectively.

A part of the level scheme of Yb I is given in figure 1. For some of the levels of Yb I located below the first ionization limit and, in particular, for the Rydberg series converging towards this limit, the 4f shell is

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Table I. — *Isotopic composition of natural ytterbium.*

Mass number	168	170	171	172	173	174	176
Natural abundance (%)	0.14	3.03	14.31	21.82	16.13	31.84	12.73

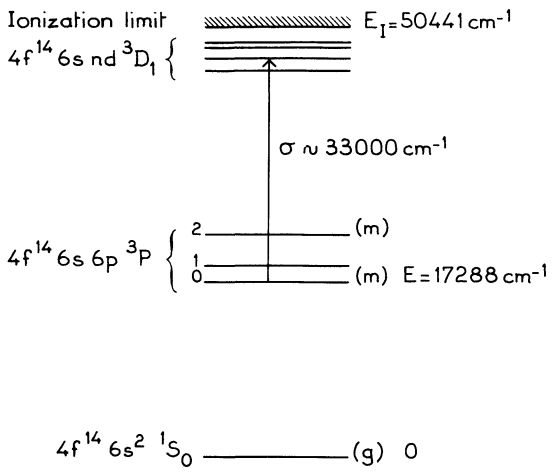

Fig. 1. — Part of the level-scheme of Yb I showing the levels of interest for the present experiment. The metastable $4f^{14}$ 6s 6p $^3P_0$ level is populated inside the atomic beam by means of a discharge. High Rydberg levels belonging to the configurations $4f^{14}$ 6s*n*d are excited from this level by the U.V. light of a frequency-doubled dye-laser. Atoms in the other, higher lying, metastable levels are directly photoionized by the U.V. beam.

closed : these levels can be considered as being those of a two-electron atom. The other levels below the first ionization limit are those of a four-electron spectrum (in fact one hole in the 4f shell and three electrons in other open shells).

3. **Experimental set-up.** — The experimental set-up we used for studying high Rydberg levels of ytterbium is quite analogous to that described by H. T. Duong, S. Liberman and J. Pinard in their work on rubidium [1]. The atoms of a beam are excited by a frequency-doubled single-mode dye laser [2] (this laser is basically a CW dye laser but it is pumped simultaneously by a CW argon-ion laser and by a pulsed Nd Yag laser) providing U.V. pulses of 50 W peak power and 50 ns duration with a repetition rate of approximately 50 Hz. Atomic — and laser — beams cross at right angle so as to get rid of the Doppler broadening of the lines. By those means, both very high resolution and good efficiency can be achieved.

In fact, due to the rather high value of the ionization energy of ytterbium, the atoms cannot be excited directly from the ground level by the frequency-doubled laser beam as was done in the rubidium experiment [1]. We therefore had to take advantage of the existence of metastable levels (Fig. 1). These levels can be efficiently populated inside the atomic beam itself by means of a discharge produced at the exit aperture of the oven [3]. The energy difference between the Rydberg levels under study and the metastable level $4f^{14}$ 6s 6p $^3P_0$ is about 33 000 cm^{-1}. The corresponding wavelength close to 600 nm, before frequency doubling, is in the spectral range of Rhodamine 6 G dye lasers; single-mode CW dye lasers are particularly easy to operate in this spectral region.

Table II. — *Critical ionization fields in the series* $4f^{14}$ 6s*n*d $^3D_1$ *of* Yb I. *The values of the critical ionization fields* (F_c) *are given as a function of the principal quantum number* (*n*) *or of the effective principal quantum number* (*n**). *The relative uncertainty on the measured* F_c *values is about* 2 %. *The quantity in the last column* ($16\,n^{*4}\,F_c$) *is expressed in atomic units; according to the classical (saddle-point) formula, this quantity should be equal to* 1.

n	n*	F_c (V·cm^{-1})	$16n^{*4}$ F_c (a.u.)
24	21.26 ± 0.02	1550	0.99
25	22.26 ± 0.02	1360	1.04
26	23.26 ± 0.02	1110	1.01
27	24.26 ± 0.02	940	1.01
28	25.26 ± 0.05	810	1.03
29	26.26 ± 0.05	674	1.00
30	27.26 ± 0.05	580	1.00
31	28.26 ± 0.05	502	1.00
32	29.26 ± 0.05	420	1.04
33	30.3 ± 0.1	375	1.03
34	31.3 ± 0.1	339	1.00
35	32.3 ± 0.1	298	1.01
36	33.3 ± 0.1	275	1.04
37	34.3 ± 0.1	240	1.02
38	35.3 ± 0.1	210	1.01
39	36.3 ± 0.1	189	1.01
40	37.3 ± 0.1	172	1.03
41	38.3 ± 0.1	156	1.03
42	39.3 ± 0.1	141	1.04
43	40.3 ± 0.15	127	1.03
44	41.3 ± 0.15	115	1.03
45	42.3 ± 0.15	103.5	1.02
46	43.3 ± 0.15	92	1.00
47	44.3 ± 0.20	82.5	0.98
48	45.3 ± 0.20	75	0.98
49	46.3 ± 0.20	71	1.01
50	47.3 ± 0.25	65	1.01
51	48.3 ± 0.25	59.5	1.00
52	49.3 ± 0.25	56	1.02
53	50.3 ± 0.3	51	1.01
54	51.3 ± 0.3	47	1.01
55	52.3 ± 0.3	44	1.02
56	53.3 ± 0.35	41	1.02
57	54.3 ± 0.35	38	1.02

The excited atoms are detected by the field ionization technique [1, 4]. The positive ions resulting from the field ionization process are accelerated by the ionizing field and collected by the first dynode of an electron multiplier. The pulses provided by the multiplier are counted during the aperture time of a gate, the delay and duration of which are adjusted so that the ions of interest are all counted whereas the parasitic counts are rejected as thoroughly as possible.

The excitation spectrum we have investigated corresponds to the line series : $4f^{14}\ 6s\ 6p\ {}^3P_0$-$4f^{14}\ 6snd\ F$, F being the total angular momentum of the atom (electrons + nucleus).

4. **Critical ionization fields.** — The critical ionization fields of all levels with n ranging from 24 to 57 have been measured. The results are given in table II.

As is well known, in a classical picture the value of the critical ionization field, F_c, corresponding to a level with effective principal quantum number n^* is given in atomic units by the formula : $F_c = 1/16\ n^{*4}$. This limit corresponds to the value of the potential energy at the *saddle point* of the potential energy surface of the atom submitted to a static electric field F.

To check the saddle point formula, the n^* values are needed. For the lowest n values ($24 \leqslant n \leqslant 33$), they were deduced from the measurement of the wavelength of the laser in resonance with the transition under study; for higher n values ($n > 33$) we used n^* values derived from the work of P. Camus, A. Débarre and C. Morillon [5].

According to the saddle point formula, the quantity $\alpha = F_c \times 16\ n^{*4}$ should equal 1 for every level. This was verified by plotting the measured α values *versus* n in figure 2. As can be seen the law is obeyed within the experimental uncertainties for all investigated levels. This is not too surprising since none of these levels turned out to be perturbed. In fact, as we shall see in paragraph 11, the levels $n = 26$ are slightly perturbed but only for the odd isotopes. However, critical field measurements performed on these components do not show any noticeable difference with the values measured on the unperturbed even isotope levels corresponding to the same value of n. But it must be kept in mind that first the perturbation is only weak and second critical field measurements made on the odd isotopes are not very precise due to the weak intensity of the signal (cf. § 5).

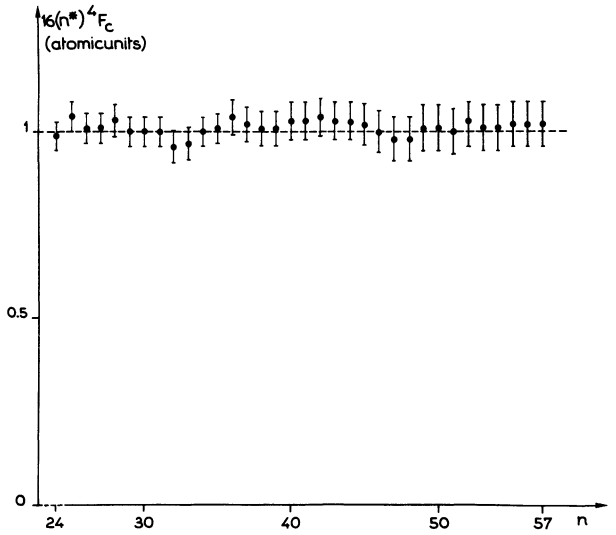

Fig. 2. — Check of the *saddle-point* formula relating the critical ionization field F_c to the effective principal quantum number n^* of the level of interest. For every investigated level, the quantity $16(n^*)^4\ F_c$ which should equal 1 (in atomic units) according to the classical theory has been plotted *versus* n.

5. **Hyperfine structure measurements.** — By scanning continuously the frequency of the laser, one can record the structure of the transition under study. Figure 3 gives typical recordings corresponding to the levels $n = 30$ and $n = 38$.

The most intense components near the centre of each recording are due to the even isotopes; in the direction of increasing wavenumbers, one successively finds ^{170}Yb, ^{172}Yb, ^{174}Yb and ^{176}Yb. The linewidth of a single component is approximately 60 MHz due to the spectral width of the laser light and to the residual Doppler broadening corresponding to the divergence of the atomic beam. The remaining, less intense, components make up the structure of the odd isotopes. The intensity of the weakest recorded component is less than 1 % of the total intensity of the line.

For measuring the distances between the components of the structure, the wavenumber scale of the recordings was calibrated by simultaneously recording the fringes of a spherical Fabry-Pérot interferometer providing frequency markers with an interval of 1.5 GHz (Fig. 3). The position of a given component is obtained by a linear interpolation between the two adjacent reference fringes. The position of all components are referred to the component of the isotope ^{176}Yb.

The uncertainties in the position measurements have two origins : the noise and other fluctuations (of the atomic and laser-beams) and the non-linearity of the scanning of the laser frequency. For the odd isotopes components the uncertainty is estimated to be approximately 3 mK; for the components of the even isotopes which are more intense and less distant from one another, the uncertainty is only 1 mK.

The final results are given in table III and a plot of the structures of all recorded transitions is given on figure 4. The structures of the four even isotopes remain remarkably unchanged as n varies; in contrast, one observes that those of the odd isotopes change considerably as n is increasing; in particular, the structures become much simpler for the highest n values, as will be explained in the next section. One should also notice that the structures change smoothly from a given value of n to the next, except for $n = 26$;

Table III. — *Structures of Rydberg levels belonging to the configurations* $4f^{14}$ 6snd. *The positions of the recorded components referred to the* ^{176}Yb *component are expressed in* GHz. *Each line of the table corresponds to a given value of the principal quantum number n. Each column in the table corresponds to a group of components as it appears in the recording (see Figs.* 3 *and* 4). *The experimental uncertainty is approximately* 0.03 GHz *for the even isotopes components and* 0.1 GHz *for the odd ones.*

n	^{173}Yb			^{173}Yb		^{171}Yb		^{176}Yb	^{174}Yb	^{172}Yb	^{170}Yb	^{173}Yb		^{171}Yb
24				6.46	6.26	3.31	2.35	0	-0.32	-0.69	-1.06	-3.60	-4.70	-8.88
25				6.21	6.01	3.11	2.26	0	-0.29	-0.61	-0.93	-3.48	-4.58	-8.78
26		6.25	6.11			2.38	1.05	0	-0.34	-0.66	-1.05	-4.73	-4.90	-10.39
27				5.72		3.15	2.30	0	-0.33	-0.62	-1.01	-3.58	-4.66	-8.77
28		8.63		5.31		2.96	2.28	0	-0.31	-0.62	-1.04	-3.67	-4.60	-8.90
29	9.20	7.67		4.88		2.91	2.29	0	-0.29	-0.55	-0.98	-3.78	-4.57	-8.94
30	8.56	7.19		4.39		2.83	2.29	0	-0.31	-0.65	-1.01	-3.91	-4.64	-9.10
31	7.78	6.65		3.87	3.57	2.69	2.25	0	-0.31	-0.62	-0.99	-3.94	-4.63	-9.17
32	8.19	7.29	6.41	3.18	2.96	2.68	2.25	0	-0.33	-0.63	-1.01	-4.07	-4.65	-9.24
33	7.79	7.08	6.31			2.75	2.36	0	-0.30	-0.64	-0.99	-4.13	-4.66	-9.39
34	7.50	6.87	6.23			2.68	2.33	0	-0.29	-0.63	-1.00	-4.21	-4.75	-9.54
35	7.27	6.70	6.14			2.60	2.25	0	-0.29	-0.62	-1.00	-4.20	-4.69	-9.44
38	6.56	6.20	5.85			2.48	2.24	0	-0.33	-0.70	-1.08	-4.35	-4.72	-9.69
43	6.24	6.03	5.82			2.43	2.28	0	-0.33	-0.63	-1.05	-4.46	-4.73	-10.00
48		6.20	6.02			2.55	2.40	0	-0.35	-0.66	-1.06	-4.72	-4.90	-10.35
53						2.28		0	-0.32	-0.65	-0.99	-4.55		

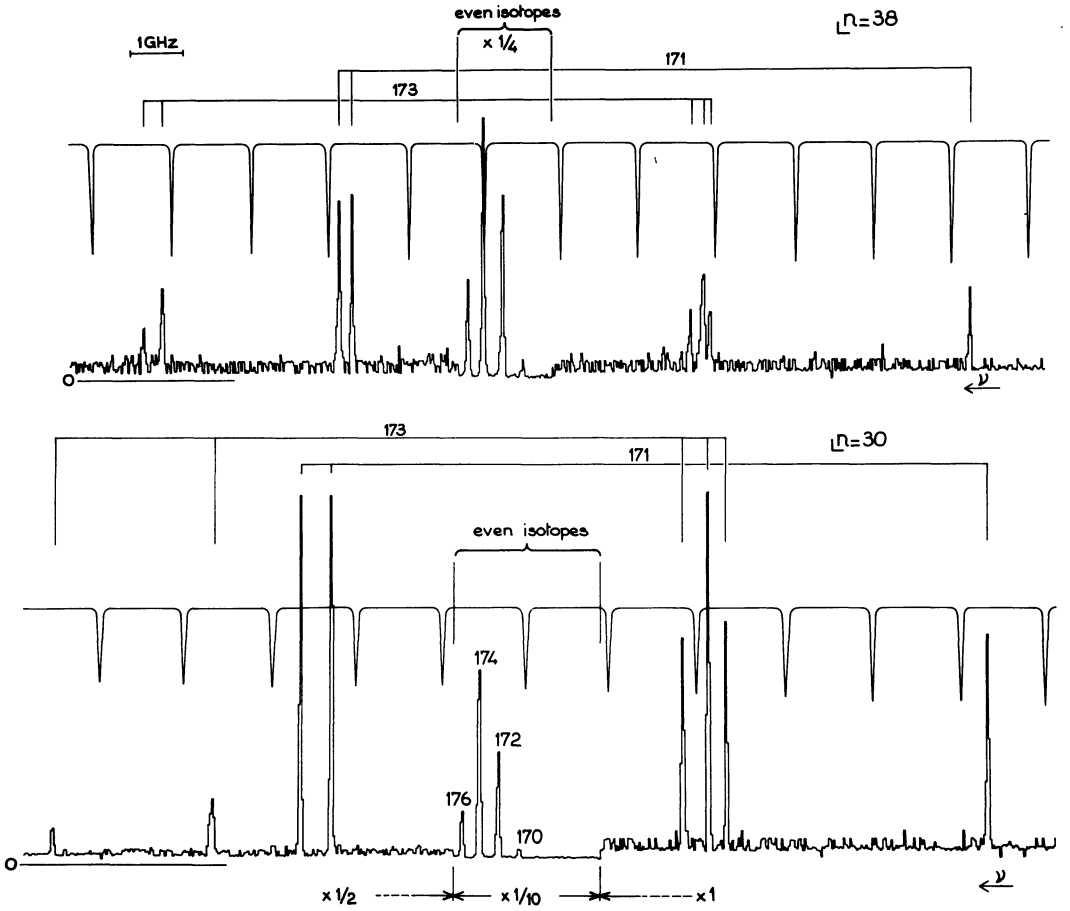

Fig. 3. — Recordings of the structures of the transitions $4f^{14}$ 6s 6p $^3P_0$-$4f^{14}$ 6s 30d and $4f^{14}$ 6s 6p $^3P_0$-$4f^{14}$ 6s 38d *F*. In the region of the even isotopes, the ordinates have been divided by 10 in the first recording, by 5 in the second one. In the former recording the components of the odd isotopes located on the large wavenumbers side with respect to the even ones have also been attenuated by a factor of 2.

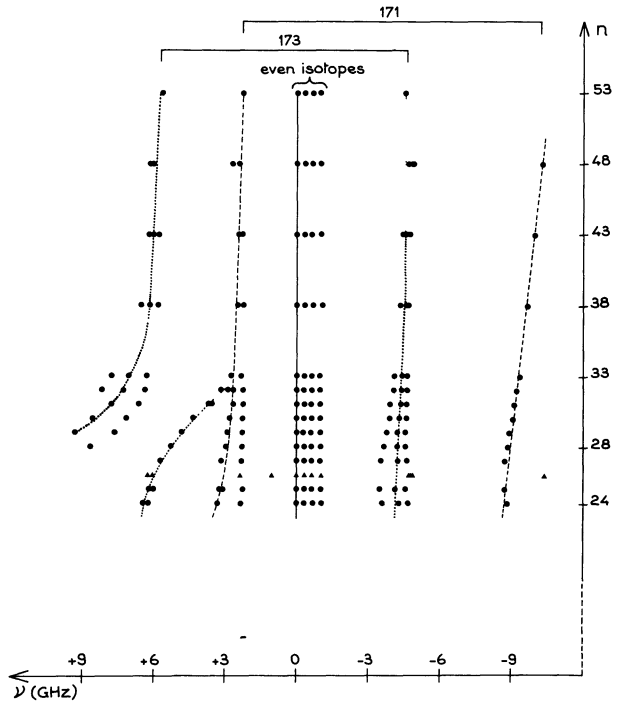

Fig. 4. — Plot of the recorded structures. For the perturbed n-26 level, triangles are used instead of circles for representing the components of the structure.

this is due to the presence of a perturbing level (cf. § 11).

6. **Interactions responsible for the level structure.** — For the considered transitions, $4f^{14}\ 6s\ 6p\ {}^3P_0$-$4f^{14}\ 6snd$, the structure is entirely due to the upper level; the lower level having $J = 0$ is simple even in the case of the odd isotopes.

In order to understand the observed structures, it is first necessary to list the relevant interactions. There are three main perturbing terms in the hamiltonian : (i) the electrostatic interaction between the two optical electrons $G = e^2/r_{12}$, where e is the electron charge and r_{12} the relative distance of the two electrons, (ii) the spin-orbit interaction

$$\Lambda = \sum_{i=1}^{2} \xi(r_i)\, \mathbf{l}_i . \mathbf{s}_i ,$$

where $\mathbf{l}_i$ and $\mathbf{s}_i$ are the orbital and spin angular momenta of electron i and $\xi(r_i)$ a scalar function of the distance r_i of electron i from the origin, (iii) the magnetic hyperfine interaction (Fermi contact term) which can be accounted for by the effective operator $H_m = a_s\, \mathbf{I}.\mathbf{s}_s$, where a_s is a constant (hyperfine splitting factor of the 6s electron), $\mathbf{I}$ the nuclear spin and $\mathbf{s}_s$ the spin angular momentum of the 6s electron.

Other interactions, e.g. the magnetic dipole and electric quadrupole hyperfine interactions associated with the nd electron as well as the spin-spin and spin-other-orbit interactions are supposedly negligible.

For each of the important operators, only one radial integral plays a role in the level structure of the configuration $4f^{14}\ 6snd$: the Slater integral $G_2(6s, nd)$ for operator G, the spin-orbit interval factor of the nd electron, ζ_{nd}, for operator Λ and the constant a_s for operator H_m.

The radial function of the nd electron is involved in the first two parameters, G_2 and ζ_{nd}, but not, of course, in the third one, a_s. In a hydrogenic picture, it is well known that ζ_{nd} varies as $(n^*)^{-3}$ with increasing n; it can be shown that G_2 also obeys the same law. In contrast, the parameter a_s only depends on the wavefunction of the 6s electron, more precisely a_s is proportional to the probability density of this electron at the nucleus. For the values of n that have been investigated, the probability density of the nd electron near the nucleus is very small; as a consequence the screening effect produced by the nd electron on the 6s electron is negligible; therefore with very good accuracy a_s has the same value for all investigated high Rydberg levels and also for the ground level $4f^{14}\ 6s\ {}^2S_{1/2}$ of Yb II.

7. **Qualitative interpretation of the structures of the highest levels.** — The previous considerations enable the structures encountered for the highest n values to be understood. For these cases the interactions G and Λ can be neglected as a first approximation. For each odd isotope, the configuration $4f^{14}\ 6snd$ is thus split into two levels whose interval should be equal to $a_s \times (I + 1/2)$ as the ground configuration $4f^{14}\ 6s$ of Yb II, whose hyperfine structure was measured by Chaiko [6]. These values are compared in table IV with the corresponding values that we have measured in the configurations $4f^{14}\ 6s\ 48d$ and $4f^{14}\ 6s\ 53d$. For each isotope, the values are rather close to one another, thus giving a strong support to the proposed interpretation.

Table IV. — *Comparison of the structures of the Rydberg levels* $4f^{14}\ 6s\ 53d$ *and* $4f^{14}\ 6s\ 48d$ *with the hyperfine structure of the ground level* $4f^{14}\ 6s\ {}^2S_{1/2}$ *of* Yb II. *All values are given in* GHz.

	Hyperfine splitting (GHz)	
	^{171}Yb	^{173}Yb
Ground level of Yb II	12.7	10.5
Configuration $4f^{14}6s53d$ of Yb I		10.2
Configuration $4f^{14}6s48d$ of Yb I	12.8	10.9

8. **Theoretical interpretation of the experimental results by the parametric method.** — To give a quantitative theoretical account of all the measurements we have made use of the semi-empirical Slater-Condon parametric method.

It must be first recalled that the hyperfine operator H_m does not commute with the total angular momentum **J** of the electrons. As, furthermore H_m is not small compared to G and A, none of the usual coupling schemes (e.g. Russell-Saunders, *jj* and also $J - I$ for the coupling between electrons and nucleus) corresponds to the physical situation; for the odd isotopes, even J is not a *good* quantum number.

Except for the highest n values (see § 7), none of the three perturbing hamiltonians G, A and H_m can be considered as much more important than the other two; we have therefore to consider the entire configuration $4f^{14}$ 6s*n*d as the *unperturbed level* and to handle the total perturbation $H' = H_m + G + A$ as a whole.

To apply the parametric method, the matrix of the hamiltonian H' is built using the basis set $|\, 4f^{14}\ 6snd(SLJ, I)\ FM_F \rangle$. By diagonalizing this matrix, one obtains the perturbed energy levels that depends on parameters ζ_d, G_2, $a_s(171)$, $a_s(173)$ and one additional constant ($ADD(171)$ or $ADD(173)$) for each odd isotope. Physically each of the last two constants determines the position of the structure of one odd isotope with respect to the corresponding level of ^{176}Yb taken as reference.

The parameters are fitted to the experimental values by comparing the theoretical and experimental values of the energy. In fact, only G_2(6s, *n*d), ζ_{nd}, $ADD(171)$ and $ADD(173)$ were free; the two parameters $a_s(171)$ and $a_s(173)$ were fixed to the values they assume in the ground level of Yb II, respectively 12.7 GHz and 3.51 GHz. In the fitting procedure, the levels of the two odd isotopes were treated simultaneously so as to avoid that the parameters G_2 and ζ_{nd} which have no isotopic dependence take different values for the two isotopes.

9. **Results.** — For all investigated levels, except $n = 26$ and $n = 48$, a satisfactory agreement between experiment and theory has been achieved since the mean square difference between experimental and theoretical values of the energy levels is approximately equal to the experimental uncertainty.

We first comment on the special cases. For $n = 48$, the fitting procedure did not converge : this may be due to the fact that the values of G_2 and ζ_{nd} are not large enough in comparison to the experimental uncertainties. The case of $n = 26$ which is perturbed will be discussed in paragraph 11. For $n = 53$, the observed structure can be interpreted by putting $G_2 = \zeta_d = 0$ (cf. § 6).

The final values of the parameters G_2 and ζ_{nd} obtained for all the other investigated n values are listed in table V. These values are plotted *versus n* in figure 5. As can be seen they follow rather accurately an $(n^*)^{-3}$ law, in agreement with theory (cf. § 6). However, a sudden decrease of the values of ζ_d and G_2 is observed at $n = 33$; this is obviously related to the qualitative change in the recorded structures (in particular the components for ^{173}Yb located on the large wavenumbers side) which can be noticed in

Table V. — *Values of the parameters G_2 and ζ_d for the configurations* $4f^{14}$ 6s*n*d *as a function of the principal quantum number n. These values are given in* GHz.

n	G_2	ζ_d
24	3.78	5.75
25	4.35	4.86
27	4.28	4.40
28	4.23	3.92
29	3.56	3.47
30	3.21	3.23
31	2.65	2.86
32	2.39	2.55
33	2.55	1.58
34	2.22	1.60
35	2.56	0.93
38	1.95	0.57
43	0.89	0.37

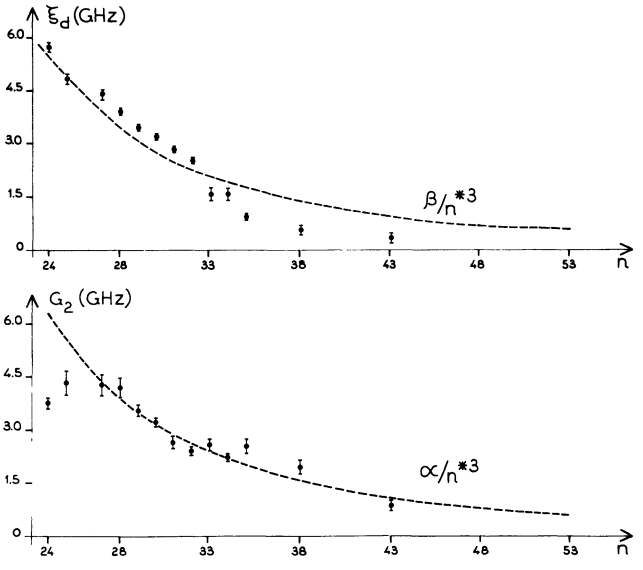

Fig. 5. — Evolution with n of the parameters G_2 and ζ_d. In a hydrogenic scheme, the parameters G_2 and ζ_d should vary like $(n^*)^{-3}$. To check this, we have drawn on each diagram (dotted line) the graph of the function $(n^*)^{-3}$ multiplied by the factor α (resp. β) which provides the best agreement with the values obtained for G_2 (resp. ζ_d).

figure 4 for the same value of n but no explanation of this phenomenon could be found.

For a given n, the values obtained for $G_2(6s, nd)$ and ζ_{nd} are approximately equal. This is at first rather surprising because Hartree-Fock calculations of the ratio ζ_{nd}/G_2 (which should be independent of n^*, as noticed above) performed in the configuration $4f^{14}$ 6s 6d yield the value 0.15. But, on the one hand, the configuration $4f^{14}$ 6s 6d may be not excited enough to fit in the normal characteristics of the Rydberg series and, on the other hand, for the n values we consider, the distance between two successive 6snd configurations is not much larger than the range occupied by each configuration (for instance, the distance between configurations 6s 38d and 6s 39d is 5 cm^{-1}, the overall width of each structure being 0.6 cm^{-1}) so that configuration interaction effects may be appreciable. It is therefore most probable that the values of the parameters are *effective* values taking into account at least partially the effect of such interactions. It would be more appropriate to treat together all configurations 6snd using the Multichannel Quantum-Defect Theory. Unfortunately the application of the MQDT method to hyperfine sublevels is not straightforward.

10. **Fine structure of the configurations $4f^{14}$ 6snd.** — Once the values of the parameters G_2 and ζ_{nd} have been obtained for a given n, one can compute the relative energies of the four levels $^1D_2$, $^3D_1$, $^3D_2$ and $^3D_3$ *without hyperfine structure* by putting $a_s = 0$ in the energy matrix, diagonalizing it and taking its eigenvalues. The energies so obtained are plotted in figure 6 with respect to the energy of the level $^3D_1$ taken as origin.

Our measurements allow us to obtain the complete level structure resulting from the electrostatic and spin-orbit interactions for all investigated $4f^{14}$ 6snd

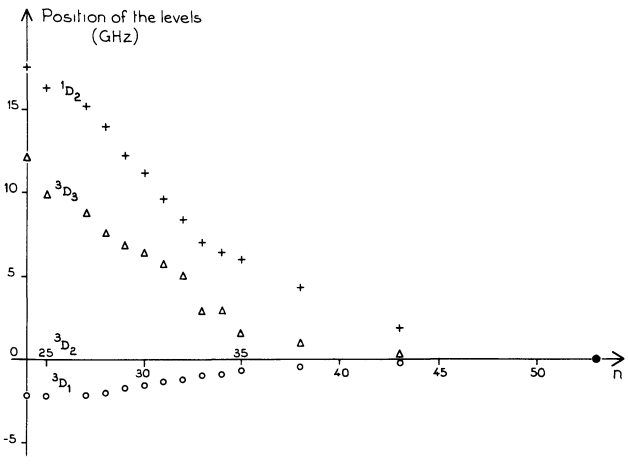

Fig. 6. — Level scheme of the configurations $4f^{14}$ 6snd. The relative positions of the four levels of each investigated configuration $4f^{14}$ 6snd (without hyperfine structure) have been obtained as a result of the parametric analysis of the recorded structures (cf. § 10). These positions are plotted *versus* n (the level $^3D_2$ is taken as a reference).

configurations, in spite of the electric dipole radiation selection rules that prevent the levels $^3D_2$, $^3D_3$ and $^1D_2$ being excited from the $^3P_0$ level. This is possible because, due to the hyperfine structure operator, the eigenstates of several *hyperfine* levels of the odd isotopes contain a significant admixture of a state corresponding to $^3D_1$.

Nevertheless, as the preceding results rely on theoretical assumptions (interactions have been neglected), it would be worthwhile to have a direct experimental check of the preceding results by exciting the even isotopes levels $^1D_2$, $^3D_2$ and $^3D_3$ and measuring their energies. In order to perform those measurements, it would be possible to choose one of the two metastable levels having $J = 2$ (Fig. 1) as lower level instead of the 6s 6p $^3P_0$ level.

11. **Perturbation of the configuration $4f^{14}$ 6s 26d.** — As was mentioned before (cf. § 9), it was not possible to give a theoretical interpretation of the structure of the configuration $4f^{14}$ 6s 26d. As can clearly be seen on the plot of figure 4, this structure does not follow the normal evolution with n. This is due to the presence of a perturbing level with $J = 2$ belonging to the configuration $4f^{13}$ 5d 6s 6p [7] and located about 5 cm^{-1} above the configuration $4f^{14}$ 6s 26d. The even isotopes levels whose eigenstates are purely $J = 1$ states are not influenced by this perturber, but the odd ones can be perturbed because their eigenstates contain admixtures of $^3D_2$ or $^1D_2$ states. As expected, the odd levels are shifted (with respect to the *unshifted* even levels) towards lower frequencies as a consequence of the repulsion of the perturbing level. No further analysis of the phenomenon was attempted. As far as we know this is the first reported evidence of the influence of a perturbing level on the hyperfine structure of a high Rydberg level.

12. **Isotope shifts.** — The shifts of the even isotopes are given in table III. Those of the odd isotopes can be deduced from the theoretical study of the structures (cf. § 8) as explained in paragraph 10. By definition, the energy of the $^3D_1$ level *without hyperfine structure* obtained for each isotope, gives the shift of that isotope. The shifts of both odd isotopes referred to ^{176}Yb are given in table VI.

As can be seen the shift of a given isotope does not depend on n, at least within the experimental uncertainties. This is not surprising because the field effect as well as the mass effect must have approximately constant values for all investigated transitions. The field effect is determined by the probability density at the nucleus of the electrons that should remain constant for all n values (cf. § 5); the normal mass effect (Bohr effect) proportional to the wavenumber of the considered lines varies only by 0.01 mK (0.3 MHz), for an isotopic pair whose mass numbers difference is 2, when n varies from 24 to 53; it is more difficult to draw conclusions concerning the specific mass shifts

Table VI. — *Isotope shifts of the odd isotopes of ytterbium. In this table are given the positions the levels* $4f^{14}$ 6s*nd* $^3D_1$ *of the odd isotopes of* Yb *would occupy if the hyperfine structure were zero; these values are obtained as explained in paragraph* 10. *They are expressed in* GHz *and referred to the corresponding component of* ^{176}Yb. *The uncertainty is about* 0.1 GHz.

n	^{171}Yb $^3D_1$	^{173}Yb $^3D_1$
24	-0.82	-0.57
25	-0.95	-0.49
26	-	-
27	-0.89	-0.56
28	-0.98	-0.54
29	-0.89	-0.47
30	-0.91	-0.52
31	-0.90	-0.48
32	-0.88	-0.51
33	-0.84	-0.46
34	-0.89	-0.50
35	-0.90	-0.45
38	-0.93	-0.45
43	-0.88	-0.41

but on a theoretical basis this effect is expected to be small and almost constant for all concerned transitions [8].

It is therefore justified to take for each isotope the average values of the shifts of all transitions (Table VII). In table VII can also be found the so-called residual shift obtained by subtracting the normal mass effect from the total measured shift. Considering that the isotope shifts so obtained are dominated by the field shift, it is interesting to check if their values can be interpreted in terms of the empirical screening factors well known in the analysis of the field shift [8]. The field shift of each investigated transition is proportional to the difference of the 6s electron probability densities at the nucleus for the upper and lower levels; it therefore directly reflects the screening effect of the 6p electron in the level $4f^{14}$ 6s 6p $^3P_1$ since the *n*d electron has a negligible screening effect. It is known from the analysis of the field isotope shifts in a large variety of atoms that the presence of a *n*p electron decreases the probability density at the nucleus of a *n*s electron of about 10 %. If the residual shifts in table VII were entirely due to field effects, they should thus be equal to 1/10 of the field effect of a 6s electron that is to say to − 0.10 times the field effect of the resonance lines $4f^{14}$ 6s-$4f^{14}$ 6p of Yb II. The shifts of a transition of this type were measured by Chaiko [6] and the values can be found in table VII. As can be seen, the ratio of the residual shifts of the Rydberg lines and of the resonance line of Yb II is in fact − 0.22 instead of − 0.1. This disagreement should not be taken too seriously since we have neglected the specific mass shifts in the Rydberg as well as in the resonance Yb II line, and also because the 10 % screening factor is only an approximate empirical value; it is satisfactory that the signs and orders of magnitude are in agreement.

13. **Conclusion.** — The values of the critical ionization fields we obtained in this work only lead to the expected results that the classical saddle point law is valid also in the case of many electron atoms. In fact as was discussed above, the series we investigated is only slightly and indirectly perturbed; the problem of the influence of a perturber on the critical ionization fields remains therefore an open one.

The analysis of the structures is much more fruitful. It gives the possibility of describing the evolution of the hyperfine structures of high Rydberg levels and of studying the relative influence of the excited (*n*d) and of the non-excited (6s) optical electrons on these structures. Furthermore, the influence of a level perturbing only the odd isotopes *via* the hyperfine interaction has been observed for the first time.

Table VII. — *Average values of the isotope shifts of the transitions* $4f^{14}$ 6s*n*d-$4f^{14}$ 6s 6p *of* Yb I. *In the first line of the table are the average values of the measured position of each isotope referred to* ^{176}Yb *and in the second line the corresponding residual shifts. For comparison, the residual shifts of the line* λ = 369 nm *of* Yb II *are given in the third line and, in the last line, the ratios for the residual shifts of the Rydberg lines and of the* Yb II *line. All shifts are given in* GHz.

	176	174	173	172	171	170
	—	—	—	—	—	—
Measured shift of Rydberg lines	0	− 0.32	− 0.49	− 0.64	− 0.90	− 1.02
Residual shift of Rydberg lines	0	− 0.28	− 0.44	− 0.56	− 0.80	− 0.91
Residual shift for Yb II λ = 369 nm	0	+ 1.24	+ 2.00	+ 2.53	+ 3.68	+ 4.20
Ratio Rydberg/Yb II resonance line	–	− 0.23	− 0.22	− 0.22	− 0.22	− 0.22

For the highest investigated n values, we were able to reach the limit where all interactions responsible for the structure except the hyperfine interaction are negligible. It would be worthwhile to study the structures for lower n values in order to reach another limiting situation where, as is the more usual case, the hyperfine interaction becomes smaller than the other interactions ; in this way the evolution of the observed structure between the two limiting coupling schemes could be followed completely.

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