Optical laser spectroscopy and hyperfine structure investigation of the 10^2S, 11^2S, 8^2D, and 9^2D excited levels in francium

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Optical laser spectroscopy and hyperfine structure investigation of the 10^2S, 11^2S, 8^2D and 9^2D excited levels in francium

E Arnold†, W Borchers‡, H T Duong§, P Juncar‖, J Lermé¶, P Lievens†#, W Neu‡, R Neugart‡, M Pellarin¶, J Pinard§, J L Vialle¶, K Wendt‡ and the ISOLDE Collaboration†

† CERN, CH-1211 Genève 23, Switzerland
‡ Institut für Physik, Universität Mainz, D-6500 Mainz, Federal Republic of Germany
§ Laboratoire Aimé Cotton*, CNRS II, F-91405 Orsay, France
‖ Institut National de Métrologie du CNAM°, F-75141 Paris, France
¶ Laboratoire de Spectrométrie Ionique et Moléculaire°, Université Lyon I, F-69622 Villeurbanne, France

Abstract. We present here an extension to low-lying states of francium (10s, 11s, 8d, 9d) of a previously published high-resolution experiment performed on the ns and nd Rydberg levels. These four levels were investigated at CERN with the on-line mass separator ISOLDE using stepwise laser excitation in collinear geometry. Accurate energy measurements lead to a more reliable determination of the quantum defects of the whole ns and nd series, together with the ionization potential for ^{212}Fr (nuclear spin $I = 5$) which is found to be 32 848.872 (9) cm^{-1}. The measurement of the fine structure splittings for the nd $^2D_{3/2,5/2}$ doublets has been completed at the same time. The main result of this study is the first observation and measurement of hyperfine structures in ^2S and ^2D states. Dipolar hyperfine constants deduced from hyperfine splittings are as follows: $A(10^2S_{1/2}) = 401$ (5) MHz; $A(11^2S_{1/2}) = 225$ (3) MHz; $A(8^2D_{3/2}) = 13.0$ (6) MHz; $A(9^2D_{3/2}) = 7.1$ (7) MHz; $A(8^2D_{5/2}) = -7.2$ (6) MHz and $A(9^2D_{5/2}) = -3.6$ (4) MHz. The negative sign of the $A(n^2D_{3/2})/A(n^2D_{5/2})$ ratios is a clear indication of the large core polarization effects as already pointed out in the case of other heavy alkali elements. A survey of all the available energy terms is also given to summarize the current knowledge of the francium optical spectrum.

1. Introduction

The optical spectrum of the heaviest alkali element francium ($Z = 87$) had remained unknown until 1978, when the D_2 resonance line was observed for the first time (Liberman *et al* 1978). Since then, the energies of the lowest levels (7p $^2P_{1/2,3/2}$ and 8p $^2P_{1/2,3/2}$) of the np series have been measured by laser spectroscopy techniques (Bauche *et al* 1986, Duong *et al* 1987). The ns and nd Rydberg series were also observed and studied for $22 \leqslant n \leqslant 33$ by Andreev *et al* (1987) using optical–optical double resonance and field ionization detection. During the same period, theoretical predictions were published (Dzuba *et al* 1983) which made further experimental investigations much easier.

On leave from the Institute voor Kern-en Stralingsfysika, Leuven University, Leuven, Belgium.
* Laboratoire associé à l'Université Paris-Sud.
° Laboratoire associé au CNRS.

We recently obtained new results concerning lower ns ($n = 12$–22) and nd ($n =$ 10–20) Rydberg levels (Arnold *et al* 1989). Owing to the accuracy of our measurements, we greatly improved the determination of the quantum defects of both series as well as the ionization potential of ^{212}Fr (nuclear spin $I = 5$). Moreover, the high resolution achieved in our collinear laser spectroscopy experiment allowed us to observe for the first time the fine structure splittings $\Delta E(nd)$ of the $nd\,^2D_{3/2,5/2}$ doublets.

This paper presents the extension of the same experimental study to the case of still lower levels of the same series, namely the 10s, 11s, 8d and 9d levels. These new results, together with the previous ones, induce us to reanalyse these Rydberg series in terms of quantum defects and the ionization limit. Moreover, the experimental resolution is high enough to observe the hyperfine structure of these levels; the corresponding hyperfine constants are deduced. We also compile in this paper all the currently available experimental data concerning the energy levels of francium.

2. Experimental procedure

The present experiment is based on the collinear fast-beam technique (Anton *et al* 1978, Neugart 1987). Details of the experimental procedure as well as the set-up can be found elsewhere (Arnold *et al* 1989, Mueller *et al* 1983). The experiment was carried out at ISOLDE on ^{212}Fr which is the most abundantly produced isotope of this element (Carraz *et al* 1979, Bjørnstad *et al* 1981). The Rydberg levels are populated by a two-step laser excitation process (λ_1, λ_2) via the $7p\,^2P_{3/2}$ intermediate state (see figure 1). More precisely, the $F = \frac{13}{2}$ hyperfine sublevel of the intermediate state is generally selected to avoid optical pumping in the first excitation step, but in some special cases, the $F = \frac{11}{2}$ hyperfine sublevel has to be chosen, as explained below. The detection of the optical resonance on the second stage is performed either by observing the fluorescence emitted at a third wavelength (λ_3) in the decay cascade from the Rydberg level or by detecting the drop in the fluorescence signal at λ_1 due to the optical pumping induced by the second step excitation (Arnold *et al* 1989).

The laser radiations for both excitation steps are provided by commercial frequency-stabilized CW dye lasers (CR-599 or CR-699). The dyes LD 700 and pyridine 2 are
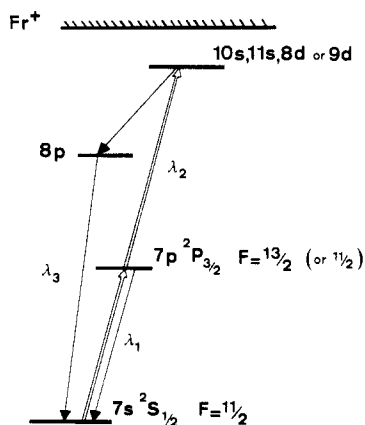

Figure 1. Francium energy levels and transitions involved in the two-step laser excitation experiment.

pumped by Kr^+ and Ar^+ gas lasers, respectively. The determination of the absolute wavenumbers is achieved by means of a commercial wavemeter (Burleigh) and by recording simultaneously the absorption spectrum through an iodine cell (Gerstenkorn and Luc 1978, 1979). For the purpose of an accurate measurement of frequency intervals we also record the fringes of a confocal Fabry-Perot mode analyser, the free spectral range of which was precisely measured prior to the experiment.

3. Experimental results

3.1. Hyperfine structures of the ns states (n = 10, 11)

For the ns states, with the $F = \frac{13}{2}$ hyperfine sublevel of the 7p $^2P_{3/2}$ state chosen as the intermediate level, only one hyperfine component ($F' = I + \frac{1}{2} = \frac{11}{2}$) of the upper state is observed. But it is possible to shift the intermediate level from the $F = \frac{13}{2}$ sublevel to the $F = \frac{11}{2}$ one by slightly changing the francium beam velocity, whereupon both hyperfine components ($F' = \frac{9}{2}, \frac{11}{2}$) of the Rydberg ns state can be observed by rescanning the second laser. Due to the optical pumping then occurring in the first excitation step, the resonances are observed only on the detected fluorescence at λ_3 (see figure 1); the signal is very weak and it requires a long integration time to emerge from the noise. A recording of the hyperfine structure of the 11s level is displayed in figure 2. Similar results are obtained for the 10s level, too. The hyperfine constants $A(ns)$ deduced from the hyperfine splittings are collected in table 1.
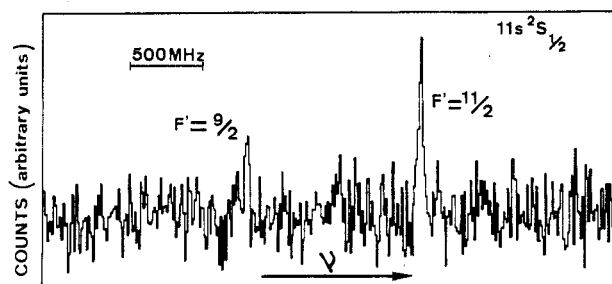

Figure 2. Hyperfine structure of the 11s level (fluorescence at λ_3). The frequency increases from left to right.

Table 1. Measured values of the A and B hyperfine constants in the 10s, 11s, $8^2D_{3/2,5/2}$ and $9^2D_{3/2,5/2}$ levels of ^{212}Fr.

Level	$A(n^2L_J)$ (MHz)	$B(n^2L_J)$ (MHz)
10s	401 (5)	—
11s	225 (3)	—
$8^2D_{5/2}$	−7.1 (6)	−2 (10)
	−7.2 (6)	assumed = 0
$8^2D_{3/2}$	13.0 (6)	assumed = 0
$9^2D_{5/2}$	−3.6 (4)	assumed = 0
$9^2D_{3/2}$	+7.1 (7)	assumed = 0

3.2. Hyperfine structures of the nd states (n = 8, 9)

The intermediate level of the excitation process is again the $7p\,^2P_{3/2}$, $F = \frac{13}{2}$ level. The hyperfine structures observed for the states $8d\,^2D_{3/2}$ and $8d\,^2D_{5/2}$ are displayed in figure 3. Both detected signals are presented: the fluorescence at λ_3 (figure 3(a)) as well as the optical pumping dip at λ_1 (figure 3(b)). As expected, one observes two components $(F' = \frac{13}{2}, \frac{11}{2})$ of the hyperfine structure for $^2D_{3/2}$ and three $(F' = \frac{15}{2}, \frac{13}{2}, \frac{11}{2})$ for $^2D_{5/2}$. These components only remain to be identified.

Concerning the $^2D_{5/2}$ level, the component which is by far the strongest in the direct fluorescence spectrum (figure 3(a)) certainly corresponds to $F' = \frac{15}{2}$. Since the ^{212}Fr nucleus is known to have a small quadrupole moment (Coc *et al* 1985), the B factor is expected to be small and the order of the components normal (i.e. $F' = \frac{13}{2}$ in the middle of the structure and $F' = \frac{11}{2}$ on the right-hand side). On the other hand, the relative intensities between the two components $(^2P_{3/2};\ F = \frac{13}{2} \to {}^2D_{5/2};\ F' = \frac{13}{2})$ and $(^2P_{3/2};\ F = \frac{13}{2} \to {}^2D_{5/2};\ F' = \frac{11}{2})$ are given by well known angular coefficients (Edmonds 1957): the component $(\frac{13}{2} \to \frac{13}{2})$ is expected to be stronger than the other one $(\frac{13}{2} \to \frac{11}{2})$. This seems to be inconsistent with the assignment given above (see figure 3(b)). However, one has to be careful with this argument. In fact, the two laser beams are linearly polarized with the same direction of polarization for both. It is therefore a π-π two-step excitation. The effect of the Zeeman optical pumping, occurring in the first excitation step, is to concentrate the atomic population in the Zeeman substates $|F, m_F\rangle$ having smaller m_F values and to deplete those with higher m_F values; the populations of the different Zeeman substates involved in the intermediate state of the

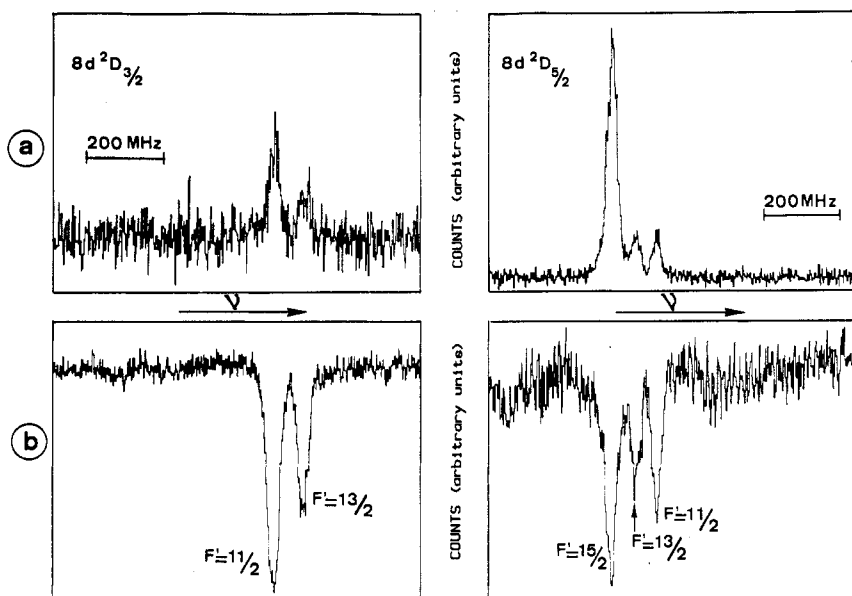**Figure 3.** Hyperfine structure of the $8d\,^2D_{3/2}$ and $8d\,^2D_{5/2}$ levels. (a) Fluorescence signal at λ_3. (b) Optical-pumping dips in the fluorescence light at λ_1. The hyperfine components with $F' \leqslant \frac{9}{2}$ cannot be reached from the $7p\,^2P_{3/2}$ $(F = \frac{13}{2})$ intermediate level. The frequency in each recording increases from left to right.

excitation process are thus strongly unequal. By means of a relatively simple model, we have calculated the influence of this effect on the relative intensities of the two components and find that the relative intensities are inverted, i.e. $(\frac{13}{2} \to \frac{11}{2})$ becomes stronger than $(\frac{13}{2} \to \frac{13}{2})$. This effect then removes the apparent contradiction and the assignment given in the figure 3 is confirmed by the observed relative intensities.

For the same reason, the strongest component in the $^2D_{3/2}$ state corresponds to the $F' = \frac{11}{2}$ sublevel and the smallest one to the $F' = \frac{13}{2}$ sublevel.

From the two hyperfine intervals measured in the 8d $^2D_{5/2}$ level, it is possible to calculate the hyperfine constants $A(8^2D_{5/2})$ and $B(8^2D_{5/2})$. They are given in table 1. As expected, the B value is small and quite compatible with a zero value. Assuming $B = 0$ does not change the A value significantly (see table 1) and has a minor effect on its uncertainty. For the $8^2D_{3/2}$ and $9^2D_{3/2}$ levels, where only one hyperfine interval is measured, as well as for the $9^2D_{5/2}$ level, where the hyperfine splitting is comparable with the experimental resolution, we assume the hyperfine B factor to be zero and calculate the corresponding $A(n\,^2D_J)$ factor. All these results are collected in table 1.

3.3. Energy position of the levels

The hyperfine constants being known, the position of the centre of gravity of the studied Rydberg level is determined with respect to the observed components. As in the preceding paper (Arnold *et al* 1989) we use the iodine absorption spectrum as a frequency calibration and, taking into account the Doppler shift, we calculate the energy position of the Rydberg level relatively to the intermediate level 7p $^2P_{3/2}$, $F = \frac{13}{2}$. The results are listed in table 2 together with the fine structure splittings $\Delta E(n\mathrm{d})$ of the $n\mathrm{d}\,^2D$ doublets for $n = 8$ and $n = 9$. The quoted accuracy is mainly due to the precision in determining the centres of the iodine peaks and to the uncertainty of the iodine wavenumbers.

Table 2. Energies of studied Rydberg levels in ^{212}Fr relative to the 7p $^2P_{3/2}$; $F = \frac{13}{2}$ intermediate hyperfine sublevel. Fine structure splittings ΔE of the $n\mathrm{d}^2D$ doublets.

	E_n (cm^{-1})			$\Delta E[(n-2)\mathrm{d}]$
n	$n\mathrm{s}\,^2S_{1/2}$	$(n-2)\mathrm{d}\,^2D_{3/2}$	$(n-2)\mathrm{d}\,^2D_{5/2}$	(cm^{-1})
10	14 386.595 (4)	13 676.635 (5)	13 721.351 (5)	44.716 (10)
11	15 794.887 (4)	15 392.475 (5)	15 417.795 (5)	25.321 (10)

4. Discussion of the results

4.1. Energy levels

The experimental results listed in table 2 are combined with those from table 1 of our preceding paper (Arnold *et al* 1989) for a further complete analysis. The hyperfine structures of the ns Rydberg states ($n \geqslant 12$) are calculated from the present experimental values obtained for 10s and 11s, assuming a n_{eff}^{-3} scaling ($n_{\mathrm{eff}} = n - \delta$ is the effective quantum number). The position of the centre of gravity is then determined with respect

to the observed component $F' = \frac{11}{12}$. The analysis procedure being identical to the one reported previously, it is only briefly summarized here, and the notations are kept the same.

For each Rydberg series (i) the energies of the levels are given by the Rydberg–Ritz formula (Edlén 1964).

$$E_n^{(i)} = E_1^{(i)} + \varepsilon_n^{(i)} = E_1^{(i)} - R/(n - \delta_n^{(i)})^2 \tag{1}$$

$E_1^{(i)}$ is the ionization limit, $\varepsilon_n^{(i)}$ is the binding energy of the Rydberg level, $\delta_n^{(i)}$ is the quantum defect and $R = 109\,737.03$ cm^{-1} is the Rydberg constant for ^{212}Fr corrected for the effect of the finite mass of the nucleus.

The quantum defect $\delta_n^{(i)}$ is expressed as an expansion in successive powers of $(\varepsilon_n^{(i)}/R)$ (Ritz quantum defect expansion (Edlén 1964))

$$\delta_n^{(i)} = \delta_0^{(i)} + (\varepsilon_n^{(i)}/R)\delta_1^{(i)} + (\varepsilon_n^{(i)}/R)^2\delta_2^{(i)} + \ldots \tag{2}$$

Since we now have lower energy levels in our experimental data, we attempt to fit our experimental results with formula (1) and an expansion of δ up to the second order. The results obtained for the three Rydberg series ($ns\,^2S_{1/2}$, $nd\,^2D_{3/2}$ and $nd\,^2D_{5/2}$) as well as for the series of the centres of gravity of the $nd\,^2D$ spectral terms are presented in the table 3. For the $ns\,^2S_{1/2}$ series, two fits are performed according to whether or not the $7s\,^2S_{1/2}$ ground state is included in the data set. The last column of the table gives the standard deviations σ between the experimental energies and those calculated from the fitted parameters. Compared to the previous work, we have now introduced lower-lying levels in the fit so that it becomes possible to give an estimate of the δ_2 parameter. The ionization limit of the intermediate state $7p\,^2P_{3/2}$; $F = \frac{13}{2}$ is now found to be $18\,924.850$ (7) cm^{-1}, i.e. 4×10^{-3} cm^{-1} below the preceding value (Arnold *et al* 1989). As a direct consequence, the value of the ionization potential of ^{212}Fr is also lowered by the same amount and we find now $\text{IP}_{212} = 32\,848.872$ (9) cm^{-1}. Since these corrections are less than the error bars, the conclusions of the previous paper remain valid.

Table 3. Optimized sets of parameters (quantum defects and ionization limits) for the studied Rydberg series (see text). CG means centre of gravity.

Series	δ_0	δ_1	δ_2	E_1 (cm^{-1})	Error σ (cm^{-1})
$ns\,^2S_{1/2}$	5.07073 (7)	−0.276 (4)	0.28 (6)	18 924.852 (6)	2.1×10^{-3}
$ns\,^2S_{1/2}$ including 7s	5.07063 (4)	−0.282 (2)	0.191 (4)	18 924.847 (7)	3.7×10^{-3}
$nd\,^2D_{3/2}$	3.42375 (6)	−0.089 (3)	−0.30 (4)	18 924.850 (6)	2.6×10^{-3}
$nd\,^2D_{5/2}$	3.40277 (6)	−0.115 (3)	−0.23 (5)	18 924.850 (6)	2.8×10^{-3}
$nd\,^2D$ (CG)	3.41118 (5)	−0.105 (3)	−0.26 (4)	18 924.850 (5)	2.1×10^{-3}

4.2. Fine structures of the $nd\,^2D$ terms

The fine structure splittings $\Delta E(nd)$ are now measured for thirteen levels ($n = 8$–20). The order of the components $D_{3/2}$ and $D_{5/2}$ remains normal for low-lying states as already observed in Cs; the inverted order observed in the case of Na disappears

when going up the alkali group. Several alternative formulae have been proposed in the literature to reproduce the variation of the fine structure splitting ΔE along the Rydberg series (Pendrill 1983, Sansonetti and Lorenzen 1984). As already done in similar studies on other elements (MacAdam and Wing 1976, Fabre *et al* 1975, Harvey and Stoicheff 1977), we have attempted to reproduce these splittings by the empirical law:

$$\Delta E(n\mathrm{d}) = An_{\mathrm{eff}}^{-3} + Bn_{\mathrm{eff}}^{-5} \tag{3}$$

$n_{\mathrm{eff}} = n - \delta$ is the effective quantum number calculated for the centre of gravity of the $n\mathrm{d}\,^2\mathrm{D}_{3/2,5/2}$ doublet; A and B are two adjustable parameters determined by a least-squares fit procedure. We also fitted the experimental data with an empirical formula having three independent parameters

$$\Delta E(n\mathrm{d}) = An_{\mathrm{eff}}^{-3} + Bn_{\mathrm{eff}}^{-5} + Cn_{\mathrm{eff}}^{-7}. \tag{4}$$

The optimized values of the parameters in both cases are summarized in table 4. By comparing the respective standard deviations σ, one can conclude that the fit obtained with formula (4) is only slightly better than the one obtained with formula (3). Both formulae (3) and (4), extrapolated to lower 6d and 7d levels, give fine-structure splittings in agreement with the qualitative theoretical estimates of Dzuba *et al* (1983). It would therefore be interesting to measure these quantities precisely in the future.

Table 4. Optimized parameters for empirical formulae describing the fine structure splittings $\Delta E(n\mathrm{d})$.

Empirical formula	A (cm^{-1})	B (10^3 cm^{-1})	C (10^3 cm^{-1})	σ (cm^{-1})
(3)	4 619 (8)	−6.53 (18)	—	7×10^{-3}
(4)	4 605 (10)	−5.48 (62)	−16 (10)	3.6×10^{-3}

4.3. Hyperfine constants

Theoretical works on the hyperfine structure of Fr have been published by several authors (Desclaux 1972, Vajed-Samii *et al* 1982, Heully and Martensson-Pendrill 1983, Dzuba *et al* 1983). In most cases these theoretical calculations essentially turn on the ground-state hyperfine structure. Theoretical predictions on the hyperfine structures in the Fr *n*s and *n*d excited states are less abundant (Desclaux 1972, Dzuba *et al* 1983).

The experimental value of the ground-state hyperfine splitting has been published elsewhere (Coc *et al* 1985). The agreement with the theoretical estimates is good.

The hyperfine constants $A(ns)$ are now available for $n = 7, 10, 11$. These values can be compared with the predictions of the Fermi–Segré formula (Kopfermann 1958, Arimondo *et al* 1977). In particular one expects that the hyperfine constant $A(ns)$ would approximately vary along the Rydberg series as the quantity $K = n_{\mathrm{eff}}^{-3}(1 - \mathrm{d}\delta/\mathrm{d}n)$. Starting from formula (2) including terms up to the second order, one gets $1 - \mathrm{d}\delta/\mathrm{d}n = (1 + 2\delta_1 n_{\mathrm{eff}}^{-3} - 4\delta_2 n_{\mathrm{eff}}^{-5})^{-1}$. The quantity K can then be calculated using the values of n_{eff} deduced from the binding energies, and the values of the parameters δ_1 and δ_2 listed in the second row of table 3. The results are presented in table 5. The hyperfine constant remains proportional to the quantity K within ±2%; this deviation is comparable with

Table 5. Compared evolutions, along the ns series, of the hyperfine constant $A(n$s$)$ and of the quantity $K = n_{\text{eff}}^{-3}(1 - \mathrm{d}\delta/\mathrm{d}n)$ (see text).

Level	$A(n$s$)$ (MHz)	$K = n_{\text{eff}}^{-3}(1 - \mathrm{d}\delta/\mathrm{d}n)$	$A/(10^3 K)$ (MHz)
7s	9 064.2 (2)[a]	0.188 18 (36)	48.17 (10)
10s	401 (5)	8.452×10^{-3}	47.44 (60)
11s	225 (3)	4.831×10^{-3}	46.58 (63)

[a] Coc *et al* (1985).

Table 6. The measured energy levels of ^{212}Fr. Energies are given in cm^{-1} and relative to the ground state.

Level	Energy (cm^{-1})	Level	Energy (cm^{-1})
7s	0	15s	31 735.182 (6)[c]
$7p_{1/2}$	12 237.409 (2)[a]	$14d_{3/2}$	31 867.682 (6)[c]
$7p_{3/2}$	13 923.998 (2)[a]	$14d_{5/2}$	31 871.514 (6)[c]
$8p_{1/2}$	23 112.960 (5)[b]	16s	31 929.789 (6)[c]
$8p_{3/2}$	23 658.306 (4)[b]	$15d_{3/2}$	32 029.909 (6)[c]
$8d_{3/2}$	27 600.657 (7)	$15d_{5/2}$	32 032.821 (22)[c]
$8d_{5/2}$	27 645.373 (7)	17s	32 077.492 (6)[c]
10s	28 310.617 (6)	$16d_{3/2}$	32 154.979 (6)[c]
$9d_{3/2}$	29 316.497 (7)	$16d_{5/2}$	32 157.274 (6)[c]
$9d_{5/2}$	29 341.817 (7)	18s	32 192.251 (6)[c]
11s	29 718.909 (6)	$17d_{3/2}$	32 253.449 (6)[c]
$10d_{3/2}$	30 309.962 (6)[c]	$17d_{5/2}$	32 255.275 (6)[c]
$10d_{5/2}$	30 325.605 (6)[c]	19s	32 283.180 (6)[c]
12s	30 559.504 (6)[c]	$18d_{3/2}$	32 332.354 (6)[c]
$11d_{3/2}$	30 936.325 (6)[c]	$18d_{5/2}$	32 333.827 (6)[c]
$11d_{5/2}$	30 946.643 (6)[c]	20s	32 356.444 (6)[c]
13s	31 101.539 (6)[c]	$19d_{3/2}$	32 396.552 (6)[c]
$12d_{3/2}$	31 356.506 (6)[c]	$19d_{5/2}$	32 397.761 (6)[c]
$12d_{5/2}$	31 363.655 (6)[c]	21s	32 416.340 (6)[c]
14s	31 471.465 (6)[c]	$20d_{3/2}$	32 449.483 (6)[c]
$13d_{3/2}$	31 652.000 (6)[c]	$20d_{5/2}$	32 450.488 (6)[c]
$13d_{5/2}$	31 657.155 (6)[c]	22s	32 465.937 (6)[c]
		Ionization limit	32 848.872 (9)

[a] Bauche *et al* (1986).
[b] Duong *et al* (1987).
[c] Arnold *et al* (1989).

the experimental uncertainties. However, this good agreement is probably somewhat fortuitous: Rosen and Lindgren (1972, 1973) have shown that some other quantities involved in the Fermi–Segré formula, namely the effective nuclear charge Z_i and the relativistic correction factor $F_{r,J}$, also slightly vary with n.

Concerning the hyperfine constants of the nd states $A(n^2D_J)$, the most striking point is the change of sign between $A(n^2D_{3/2})$ and $A(n^2D_{5/2})$, the first one being positive while the second is negative. This effect has already been observed in the nd states of rubidium and caesium (Liao *et al* 1974, Svanberg and Tsekeris 1975, Arimondo

et al 1977). It originates from the dominant weight of the contact term contribution, due to the core polarization, in the dipole hyperfine constant $A(n^2D_J)$. This term, indeed, is of equal magnitude and opposite sign depending on whether J equals $\frac{3}{2}$ or $\frac{5}{2}$. This behaviour is clearly established for the 8d and 9d states only, but, as in the case of Cs and Rb, it probably occurs also for the other nd states and in particular for the 6d and 7d ones. Concerning the $6^2D_{5/2}$ state, it is interesting to point out that Dzuba *et al* (1984) have obtained a negative value for the dipole hyperfine constant $A(6^2D_{5/2})$ by a relativistic many-body calculation. The calculations of Desclaux (1972) are also in agreement with the observed ordering of the hyperfine sublevels.

5. Conclusions

Knowledge of the francium optical spectrum has been improved considerably since 1978, and it is now instructive to summarize all the spectroscopic results obtained during this period. Figure 4 presents the energy levels of francium. The levels observed experimentally are indicated with full lines, the others with dotted lines. In addition, the energies of the francium excited levels presently known are given in table 6, the ground level being taken as the zero energy point. The results of Andreev *et al* (1987) concerning ns and nd Rydberg states ($n \geqslant 22$) are not included in the table, because these values are less accurate than those which can now be calculated from the quantum defects and the ionization limit (table 3). The experimental observation of the excited
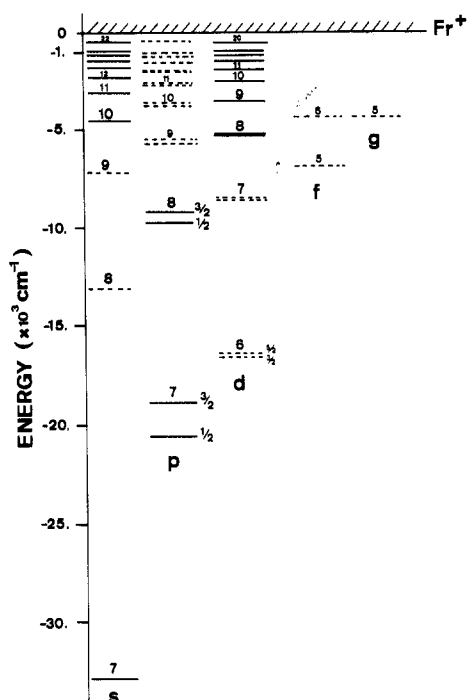

Figure 4. Chart of the francium energy levels. (The full lines indicate the levels measured up to the present time and the broken lines the still unknown levels).

levels with high-l values (nf, ng series) still seems difficult. Further developments will therefore probably concentrate on the np Rydberg states for which the quantum defects are not precisely known; this will require a single-step UV excitation. On the other hand, it would be interesting to perform the hyperfine spectroscopy of the lowest unknown levels 8s and 6d of the ns and nd series. In the case of the 6d level it would be important to confirm the anomalous behaviour of the dipolar hyperfine constants, which we have observed in the 8d and 9d levels. From the excitation energies shown in figure 4, it is obvious that the present method cannot be applied for this purpose.

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