PHYSICAL REVIEW A VOLUME 20, NUMBER 2 AUGUST 1979

Experimental studies of high-lying Rydberg states in atomic rubidium

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(Received 15 May 1978)

This paper summarizes a long series of experiments that have been done on Rydberg states of Rb. The basic experimental technique that has been used is atomic-beam laser spectroscopy which allows both low-resolution and high-resolution studies. Excitation of Rydberg states is provided by single-photon absorption from a suitably frequency-doubled rhodamine 6G tunable laser. Detection is done by field ionization and ion counting. These techniques have allowed us to study the critical ionizing field, which has been found to follow classical, hydrogenic behavior closely. Rydberg states of Rb have been observed from $n = 28$ up to $n > 100$. High-resolution spectroscopic studies have led to measurement of the fine structure for np levels located between $n = 28$ and $n = 60$, as well as the isotope shift of the ground state, $\delta\nu = (172 \pm 15)$ MHz. Anomalies in the intensity ratio of the doublet $5s$-np transitions have been observed and interpreted as relativistic effects. Perturbations by weak and strong dc electric field are reported. In the case of weak electric fields it is possible to evaluate the polarizability. In the case of strong dc electric fields, new phenomena have been observed and analyzed. We also find experimental evidence of selective photoionization in the presence of an appropriate dc electric field, which could have some applications in laser isotope separation. Finally, we give the preliminary results of an experiment on the effect of a strong nonresonant electromagnetic field on high-lying Rydberg states.

I. INTRODUCTION

Extensive experiments have recently been done by several groups to study single-electron atoms in high-lying excited states. In order to perform such experiments it is necessary to solve two important problems. First, one has to choose an efficient way to selectively populate atomic Rydberg states. Second, one has to find a method to detect them. As is well known, the lifetime of these states varies as n^{*3} (n^* being the effective principal quantum number) so that, using classical optical methods, light absorption as well as fluorescence detection become less and less efficient, thus limiting experiments to Rydberg states of $n<32$.[1] Fortunately, two more-sensitive methods have been found. The first one is the so-called space-charge method[2] in which highly excited atoms are ionized by collisions and then detected with thermoionic diode. Such a device may exhibit amplification factors of about 10^5. The $n\,^2D$ Rydberg states of Rb have been studied this way to $n=85$.[3] The same detection technique has been applied to Rydberg-state studies of alkaline earths.[4,5] The second method utilizes electric field ionization of highly excited atoms. In effect, atoms in Rydberg states have their outer electron so weakly bound that they can be ionized in a relatively weak electric field provided it is greater than a threshold value F_c which is called the critical field. The efficiency of such a process is close to 100% thus making this method very attractive although it requires one to work with an atomic beam. Experiments using this detection technique were performed first by Rivière and Sweetman[6] on hydrogen atoms, and more recently by Ducas *et al.*[7] and Fabre *et al.*[8] on sodium atoms.

The problem of excitation of high-lying Rydberg states has been approached in various ways. Most experiments on atomic Rydberg states, including those reported here, have used selective optical excitation by means of pulsed or cw tunable lasers. Some authors have employed nonoptical excitation methods.[6,9] Progress in tunable high-power light sources has led to great flexibility in such excitation techniques, so that it is now possible without too much difficulty to obtain almost any laser wavelength in the range from 200 to 3000 nm. For very high-resolution spectroscopy on these Rydberg states, the useful wavelength range is somewhat less.

Depending both upon the energy of the studied level and its parity, the excitation can be achieved either with a single step,[10] with several steps,[7] or even with two-photon absorption[1] and of course any combination of the latter two methods.[4]

The purpose of the present paper is to describe results of a series of experiments which we have done on the Rydberg states of Rb. In our case Rb atoms were excited with one-photon absorption. Detection was done by the field ionization technique, which means in particular that we used an atomic-beam machine which is naturally well adapted to high-resolution investigation. Section II gives the details of our experimental arrangement. Section III gives the results that we obtained at relatively low resolution concerning systematic study of the critical ionizing field. Section IV deals with high-resolution spectroscopic studies such as fine-structure measurements, intensity anomalies, and isotope shifts. Sections V and VI are devoted to the study of several effects due to interaction with a static electric field. In particular, new photoionization effects in the presence of an electric field are described and a qualitative interpretation is given. Section VII describes an experiment on the interaction of an atom in a Rydberg state with a strong nonresonant electromagnetic field.[11] Section VIII gives some concluding remarks.

II. EXPERIMENTAL ARRANGEMENT

The general scheme of our experimental arrangement has already been published elsewhere.[10] Let us recall that Rb atoms are produced in a temperature of about 120 °C, by using a mixture of Na metal and Rb chloride. This procedure avoids the handling of Rb metal which would oxidize rapidly in air. The Rb atoms propagate through an atomic-beam apparatus, the collimation of which is about 100:1. Neutral atoms are ionized on a rhenium hot wire detector which permits us to count them. Under average conditions, the flux of atoms corresponds roughly to a density of 10^8 atoms/cm^3. The atomic beam passes between two plane electrodes which provide the pulsed ionizing electric field as well as a small dc Stark field if wanted. As can be seen in Fig. 1, the set up is such that ions are deflected at a right angle to the neutral-atom trajectory. Of course the corresponding electrode is formed with a thin grid in order to present good transparency for Rb ions, without disturbing the uniformity of the electric field in the interaction region. Then the ions are guided using an intermediate electrode, until they strike the detector which is an electron multiplier exhibiting a gain of the order of 10^8.

Each ion produces an electric pulse at the output of the detector. Then, during a predetermined period of time (which is of the order of a few seconds) all the pulses are counted in a fast digital boxcar integrator having a time resolution of 5 ns. After passing through a digital converter, the signal is sent to a paper tape recorder. It is to be noticed that the number of ions reaching the detector is about 100 per laser pulse, and that the arrival time of these ions is spread over a few μs (although the laser pulse can be as short as 5 ns).

Depending upon the spectral resolution, two series of experiments have been performed on the Rydberg *np* states of Rb. First, experiments have been done at low resolution using a nitrogen-pumped rhodamine 6G dye laser,[10] frequency doubled through an ADA crystal. The resulting uv pulses are in the wave-number range of 1200 cm^{-1} below the Rb ionizing limit 33 691 cm^{-1}, with a spectral linewidth of 0.3 cm^{-1} and peak power of a few hundred watts with a 5-ns duration. Wave-number scanning is achieved by simultaneously rotating the laser grating and adjusting the doubling crystal temperature in order to main-

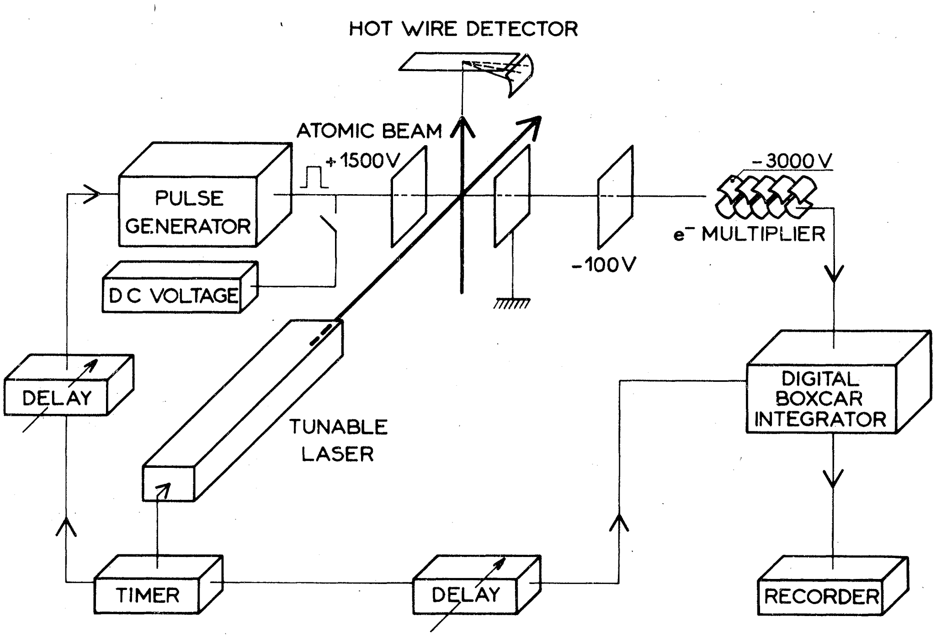

FIG. 1. Experimental setup used for studies of Rydberg states. The tunable laser is either a nitrogen-pumped, frequency-doubled dye laser or a special pulsed single-mode source for high-resolution studies.

tain the phase-matching condition. Second, experiments have been done at higher resolution using an original laser system described elsewhere.[12] Its principle can be thought of as an injection locking laser in which both the master oscillator and the power oscillator are located in the same cavity, the master oscillator being a cw single-mode tunable dye laser, whereas the power oscillator is the same dye laser but excited with a pulsed, frequency-doubled Nd-Yag laser. Such a device delivers light pulses in single-mode operation with a peak power of about 2–3 w during 70 ns. Good conversion efficiency in frequency doubling of this laser light has been achieved using two amplifier stages before the doubling crystal. As can be seen in Fig. 7, the resolution limit of the whole system (atomic beam plus single-mode laser) is 60 MHz, which enables one to easily separate fine and hyperfine components up to $n=65$.

III. CRITICAL IONIZATION FIELD STUDY

A low-resolution spectrum was first obtained on the *np* states. It was possible to detect these states up to $n=78$ as can be seen on the recorded spectrum shown in Fig. 2. Beyond this value the linewidth of the laser was large enough to excite several *np* states at the same time causing the signal to widen so much that it became impossible to distinguish one level from another. As will be shown in Sec. IV higher-resolution techniques have allowed us to reach much higher values of *n*.

Applying a small dc electric field of the order of 10–50 V/cm between the plates produces a Stark mixing of states which causes *ns* levels as well as *nd* levels to appear without seriously disturbing energy-level positions. Figure 3 shows the effect of an electric field of 50 V/cm compared to the zero-field case; *np* levels are clearly shifted. Of course, the direction of polarization of the exciting laser light relative to the orientation of the small permanent dc electric field is important. When one takes into account both fine and hyperfine interaction the selection rules on the magnetic quantum numbers become $\Delta m_s=0$, $\Delta m_l=0$ and $\Delta m_I=0$. Thus *ns* levels as well as *nd* levels can appear if the light polarization is parallel to the electric field (π excitation), whereas only the *nd* levels appear if light polarization is perpendicular to the electric field (σ excitation). These features are shown in Fig. 4. In any case, in low-resolution studies of Rb Rydberg states, fine-structure interaction can be neglected.

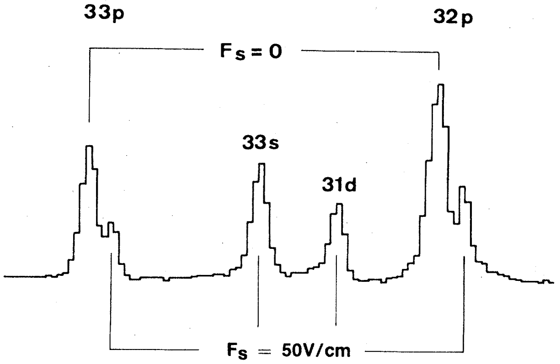

FIG. 3. Effect of a small Stark field on the recorded spectrum. In order to position the perturbed transition, the unperturbed one has been simultaneously recorded.

The most interesting properties to be studied on Rydberg states which do not require high-

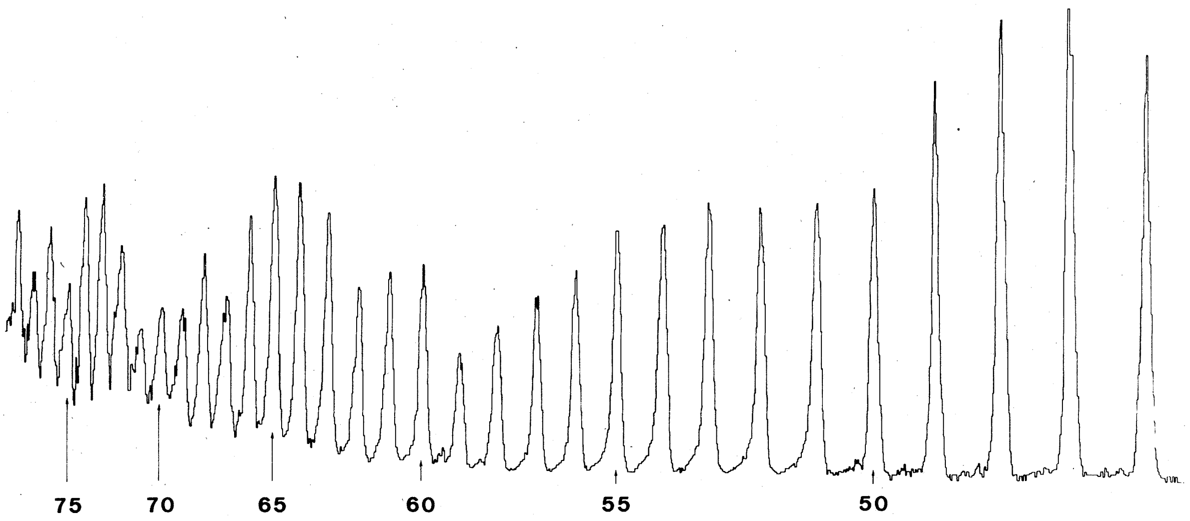

FIG. 2. Typical low-resolution spectrum of Rb Rydberg states between $n=46$ and 78.

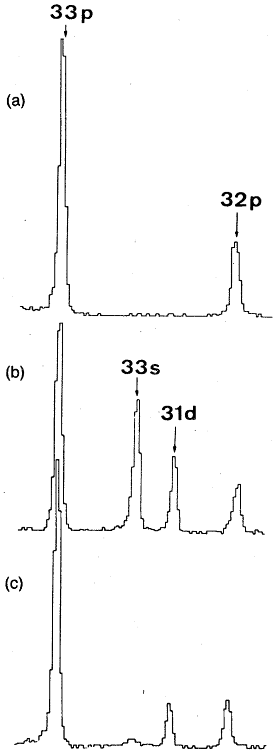

FIG. 4. Effect of the direction of polarization on the Stark pattern: (a) zero-field pattern; (b) light excitation is of the π type; (c) light excitation is of the σ type; in this case, as expected, the s state disappears.

TABLE I. Measured critical ionizing fields F_c are given (in V/cm) for several np, ns, and nd states. In each case the corresponding value of the effective principal quantum number n^* is recalled.

	p states		*s* states		*d* states	
n	n^*	F_c	n^*	F_c	n^*	F_c
30	27.35	568				
32	29.34	412.5			30.63	365
33	30.35	360	29.83	415	31.61	312.5
34	31.35	315	30.83	355	32.62	387.5
35	32.34	280	31.83	320	33.60	255
36	33.34	245	32.81	280	34.61	225
37	34.34	217.5	33.81	242.5	35.60	200
38	35.34	197.5	34.83	217.5	36.60	175
39	36.35	177.5	35.77	195	37.60	167.5
40	37.35	160	36.82	175	38.59	150
41	38.34	147.5	37.80	165	39.59	135
42	39.35	137.5	38.84	145	40.59	122.5
43	40.35	125	39.76	127.5	41.58	115
44	41.35	107.5	40.79	117.5		
45	42.34	100	41.81	107.5		
46	43.34	90	42.81	100		
47	44.34	82.5	43.84	90		
48	45.34	75	44.79	82.5		
49	46.33	70	45.84	75		
50	47.32	63.5	46.82	67.5		
51	48.32	59	47.84	62.5		
55	52.37	47.5				
60	57.31	40				

resolution techniques are field ionization processes, more specifically, critical field measurements. Experimentally, for a given Rydberg level, the ion current versus electric field exhibits a threshold behavior as shown in Fig. 5. It is quite clear from such a curve that the measured value of the critical ionizing field F_c can be well defined, which means that the experimental uncertainty is 2% or less. The measured values obtained for np, ns, and nd levels are given in Table I (of course, in the case of s and d levels, the given value has been corrected for the perturbing effect caused by the small field which is necessary to make them to appear). Figure 6 shows the quantity $F_c\,(2n^*)^4$ (in a.u.) versus n^*. It is well known that in a simple hydrogenic semiclassical picture, F_c varies with n^* as $F_c=(2n^*)^{-4}=\frac{1}{4}E^2$.[13] As can be seen in Fig. 6 this semiclassical law seems to be rather well verified. This result is similar to the one obtained on Cs Rydberg states by Van Raan *et al.*[14] but is slightly different from the results obtained by other groups[7,15] on the Rydberg levels of Na. It should be noted that, with respect to the np levels of Rb, no difference has been detected in the value of F_c as obtained from σ-polarization or π-polarization measurements. These observations are consistent with an adiabatic behavior[22,23] of the interactions in the vicinity of avoided crossings. This assumption is supported by the fact that the slew rate was about 10^9 V/cm s for n values higher than 30 (in addition for a given n value, this slew rate has been decreased to 10^7 V/cm s without showing any significant change in the field ionization threshold measurements).

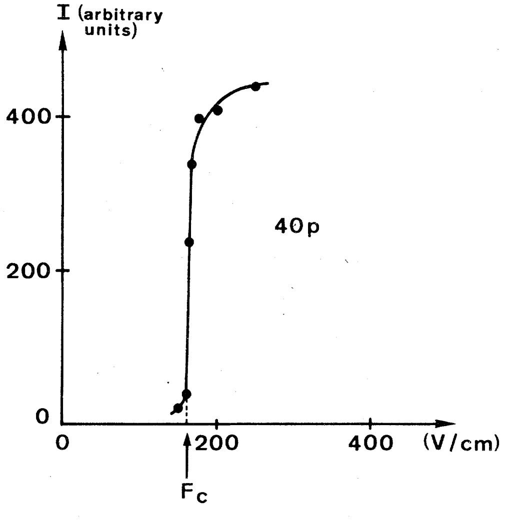

FIG. 5. Ion current on the detector vs the electric field strength for the excitation of the $40p$ state. We define F_c as the field value for which the ions begin to appear.

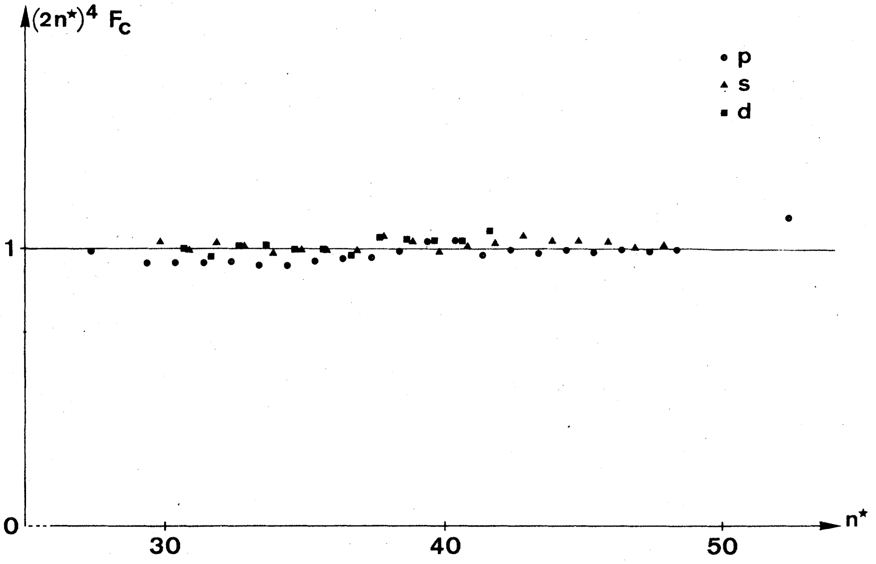

FIG. 6. Variation of the product $F_c\,(2n^*)^4$ vs n^* for s, p, and d states.

IV. SPECTROSCOPIC STUDIES—FINE STRUCTURE AND ISOTOPE SHIFT

Experiments at higher resolution have been performed in order to study with better accuracy such problems as the fine structure of the Rydberg levels and the isotope shift. A typical recording is shown in Fig. 7. Compared to the resolution limit reached in the previous experiments, the gain is of the order of 150, which permits us to separate each of the eight expected components, taking into account the hyperfine structure of the ground state of the two Rb isotopes as well as the fine structure of the upper *p* state (see Fig. 8). Since hyperfine structure varies as $(n^*)^{-3}$ it is easy to calculate that the hyperfine splitting for *n* values around 30 is of the order of 1 MHz or less, and obviously cannot be resolved in such experiments. Of course, as in the preceding low-resolution experiments, one may observe *ns* and *nd* states using a suitable small Stark mixing. As an example, Fig. 9 shows a recording of the transition $5s \rightarrow 31s$ in which one can note the absence of fine structure as is expected for an *s* state.

High-resolution spectra have been recorded from $n=28$ up to *n* close to 100. However, in the vicinity of $n=80$, it is no longer possible to separate the fine-structure components.

Measured fine-structure splittings are reported in Table II for *p* levels with principal quantum numbers from 28 to 60. These measurements are compared to calculated values obtained from the $n=7p$ level fine-structure splitting, assuming an n^* dependence obeying the $(n^*)^{-3}$ law. Within the limits of our experimental error, the agreement is satisfactory.

Although the fine-structure splitting follows a simple semiclassical law, the intensities do not. We have observed a significant difference between the experimental value of the intensity

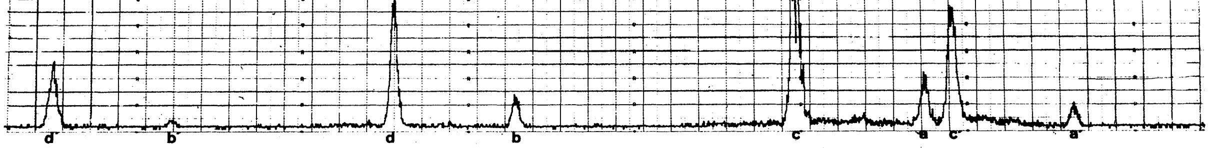

FIG. 7. High-resolution spectrum of $5s \rightarrow 48p$ transition; the resolution is about 60 MHz and the spacing between the reference Fabry-Perot fringes (upper trace) is 1500 MHz. The components *a*, *b*, *c*, *d* refer to ^{85}Rb and *a'*, *b'*, *c'*, *d'* refer to ^{87}Rb.

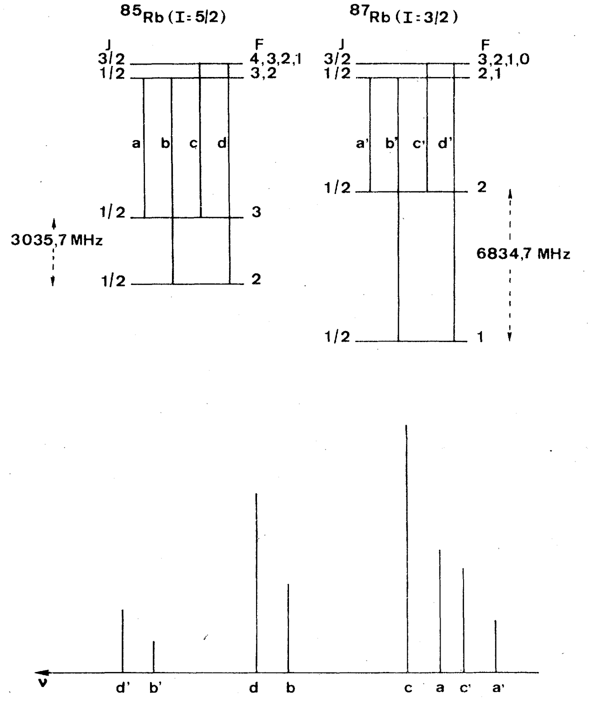

FIG. 8. Diagram showing the relative position of each component and their respective theoretical intensities.

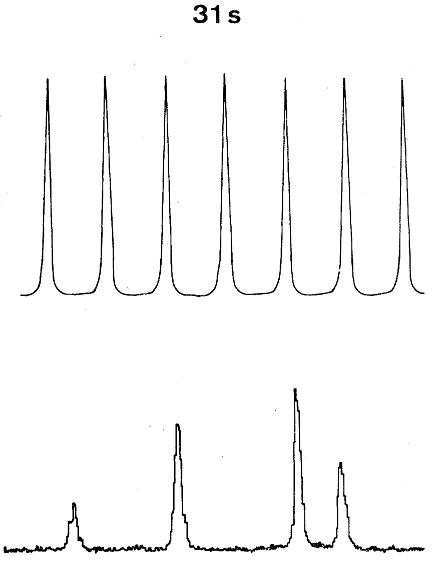

FIG. 9. Recording of the signal corresponding to the transition $5s \rightarrow 31s$ using a small dc Stark field. The upper curve contains reference fringes with a free spectral range of 1.5 GHz.

TABLE II. Fine-structure constants (in MHz) are given for some np states. The fourth column contains our experimental values. The theoretical values in the third column have been calculated from earlier measurements on the $7p$ state under the assumption of an $(n^*)^{-3}$ dependence.[21] The quoted errors are the mean deviations of several measurements.

n	n^*	Calc.	Expt.
28	25.35	5253.4	5275 ± 22
29	26.34	4672.1	4740 ± 60
30	27.35	4178.15	4233 ± 35
35	32.34	2527.18	2534 ± 36
40	37.35	1640.5	1651 ± 30
45	42.34	1126.17	1112 ± 27
50	47.32	804.5	809.5 ± 29
54	51.31	631.3	633.1 ± 17
55	52.37	593.5	602.4 ± 4
56	53.31	564.12	549.7 ± 21
60	57.31	453	460.8 ± 17

ratio of the doublet lines and the well-known theoretical value of 2:1 (for $^2S_{1/2} \rightarrow {}^2P_{3/2}$ and $^2S_{1/2} \rightarrow {}^2P_{1/2}$ transitions). This difference can be clearly seen in Fig. 10, where an actual recording is compared with a diagram of the expected intensities. Using several recordings

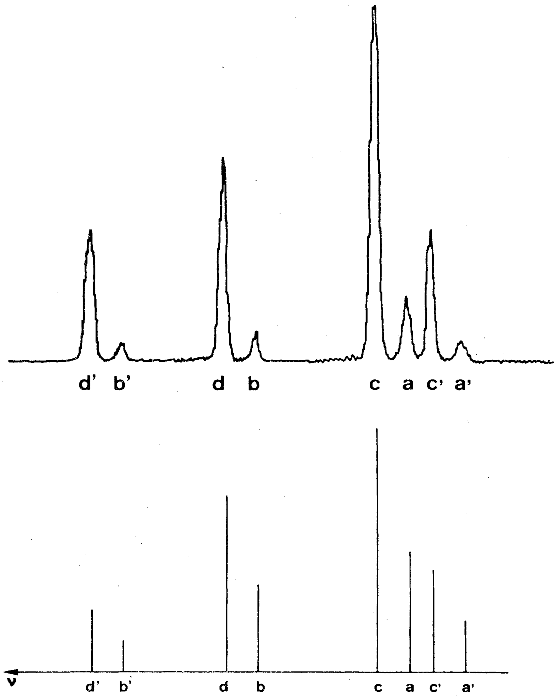

FIG. 10. Comparison between the observed and calculated intensity ratios of the doublet lines. The theoretical value of 2 is far from the measured value of 5.9. As identified in Fig. 8, the lines to be compared are a and c, and b and d as well as $a'c'$ and $b'd'$.

taken under rather different experimental conditions, we obtained a mean value for the intensity ratio of $(5.9 \pm 1.4):1$. In fact, this result corresponds to a minimum value; if saturation phenomena were to be taken into account the real value of the intensity ratio would be still higher. This discrepancy is very similar to the one observed a long time ago on the corresponding lines of Cs, but at much lower n values[16]; it can be explained by relativistic effects, namely, second-order corrections (in α^2) on the large components of the relativistic wave functions. The theoretical calculation gives the value 4.6.[17]

These high-resolution spectra also allow isotope-shift measurements. The isotope shift expresses the effect of the finite nuclear size on the energy of the optical electron. This effect disappears as soon as the electron is free, and one can assume that it is quite negligible for weakly bound electrons such as those in Rydberg states. Thus measuring isotope shift on the $5s$-np transitions involving such high-lying excited states gives directly the isotope shift of the $5s$ ground state. In the case we are dealing with and taking into account the well-known hyperfine splittings of the ground level, it is easy to show that the required isotope shift $\delta\sigma$ is simply related to the relative position of components b (or d) and b' (or d') (see Fig. 8) by the expression

$$\delta\sigma\ (\mathrm{MHz}) = \sigma_{b'} - \sigma_b - 2501.87\,.$$

Isotope-shift measurements from 43 independent cases give the mean value

$$\delta\sigma = 172 \pm 15\ \mathrm{MHz}$$

in good agreement with the measurement of Stoicheff *et al.* under different experimental conditions which gave the value 160 ± 12 MHz.[1] This value is also very close to the normal mass isotope shift that one can calculate exactly, with the result 148.8 MHz for the Rb ground level.

V. STARK EFFECT—POLARIZABILITY

The effects of a weak dc electric field on the Rydberg levels have already been pointed out in Sec. III for low-resolution studies. One can summarize the observed features as follows: first, a small shift of the np levels (Fig. 3), second, a mixing of levels of different parity causing ns and nd levels to appear (Figs. 3 and 4). The field strength is said to be weak as long as the Stark shift is smaller than the fine structure and the mixing causes only the appearance of $l \pm 1$ levels.[13]

In high-resolution experiments the fine structure is well resolved so that it is possible to study the J dependence of the polarizability α of Rb atoms in np Rydberg states. As is well known, in the case we are dealing with, the Stark shift of np levels is essentially quadratic: $\Delta W = -\frac{1}{2}\alpha(JM_J)F^2$. The polarizability is a linear combination of a scalar term $\alpha_{\mathrm{sc}}(J)$ and a tensorial term $\alpha_{\mathrm{ten}}(J)$, as follows[18]:

$$\alpha(JM_J) = \alpha_{\mathrm{sc}}(J) + \alpha_{\mathrm{ten}}(J)\,\frac{3M_J^2 - J(J+1)}{J(2J-1)}\,.$$

Thus for a level $np\,^2P_{1/2}$, $\alpha(\frac{1}{2}, \pm\frac{1}{2}) = \alpha_{\mathrm{sc}}(\frac{1}{2}) + \alpha_{\mathrm{ten}}(\frac{1}{2})$, and the level is shifted by an amount proportional to α. For a level $np\,^2P_{3/2}$, $\alpha(\frac{3}{2}, \pm\frac{3}{2}) = \alpha_{\mathrm{sc}}(\frac{3}{2}) + \alpha_{\mathrm{ten}}(\frac{3}{2})$ and $\alpha(\frac{3}{2}, \pm\frac{1}{2}) = \alpha_{\mathrm{sc}}(\frac{3}{2}) - \alpha_{\mathrm{ten}}(\frac{3}{2})$. Thus in this case the level is not only shifted, but also split into two components whose distance depends upon α_{ten} only. Therefore, experimental measurements of the shifts and splittings allow us to evaluate corresponding scalar and tensorial polarizabilities.

As an example, this experiment has been done on the $30p$ level for which typical recordings are shown in Fig. 11 using a Stark field of $F_s = 30$ V/cm. From such recordings we obtained

$$\Delta W(^2P_{3/2}, \pm\tfrac{3}{2}) = -\tfrac{1}{2}F_S^2(\alpha_{\mathrm{sc}} + \alpha_{\mathrm{ten}}) = -2450\ \mathrm{MHz}\,,$$

$$\Delta W(^2P_{3/2}, \pm\tfrac{1}{2}) = -\tfrac{1}{2}F_S^2(\alpha_{\mathrm{sc}} - \alpha_{\mathrm{ten}}) = -2000\ \mathrm{MHz}\,,$$

which leads to

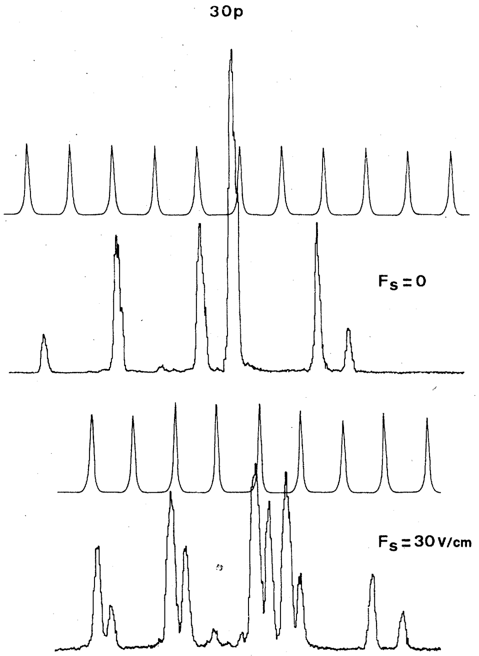

FIG. 11. Stark effect on an s-p transition. Relative to the unperturbed structure (upper trace) the whole perturbed structure is shifted and the components ($5s \rightarrow 30p_{3/2}$) are split corresponding to $|m_J| = 1/2$ and $|m_J| = 3/2$. (In this spectrum the small components b and b' are mixed with the d and c components, respectively).

$$\alpha_{sc}=(4.9\pm0.1)\ \mathrm{MHz}/(\mathrm{V/cm})^2,$$

$$\alpha_{ten}=0.5\pm0.05\ \mathrm{MHz}/(\mathrm{V/cm})^2$$

for the $30p$ level.

The general behavior and evolution of Rb Rydberg states under a dc electric field whose strength is varied from weak values up to strong values which may be close to critical field values has been studied experimentally as well as theoretically. Results are reported in the following paper in this issue.[19]

VI. PHOTOIONIZATION IN THE PRESENCE OF A STRONG ELECTRIC FIELD

One can also consider the case in which the dc Stark field is higher than the characteristic critical ionizing field of a level (when excited in zero dc field). We have studied such a case and have observed original features which we will describe in what follows. In any case these results are to be considered as preliminary for both the experimental part and its interpretation. In the presence of a dc electric field F in the z direction, the ionizing energy E_{ion} is lowered by an amount[13] $E_c(F)=2(F)^{1/2}$ (Fig. 12). Thus, if a Rb atom, in the presence of such a field, absorbs a photon of frequency ν higher than $h^{-1}\times[E_{ion}-E_c(F)]$, it ionizes. If one scans the frequency ν, the photoionizing continuum is explored and, as for hydrogenlike atoms in zero field, no discrete structure of this continuum is expected. In order to check this point, an experiment was carried out[20] with natural Rb in the region of the $50p$ levels and with a dc field of ~80 V/cm (which is about 10 V/cm above the corresponding critical field). Surprisingly, we observed many discrete and very narrow lines in such an intricate spectrum that, in order to simplify, we decided to repeat the experiment

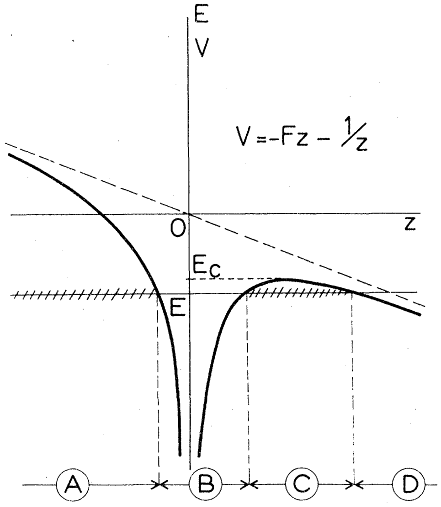

FIG. 12. Potential energy of the outer electron created by the atom core and a uniform dc electric field in the z direction. An electron with total energy E above E_c is no longer bound, whereas an electron with total energy E lower than E_c can escape the atom only through the potential barrier in the region C.

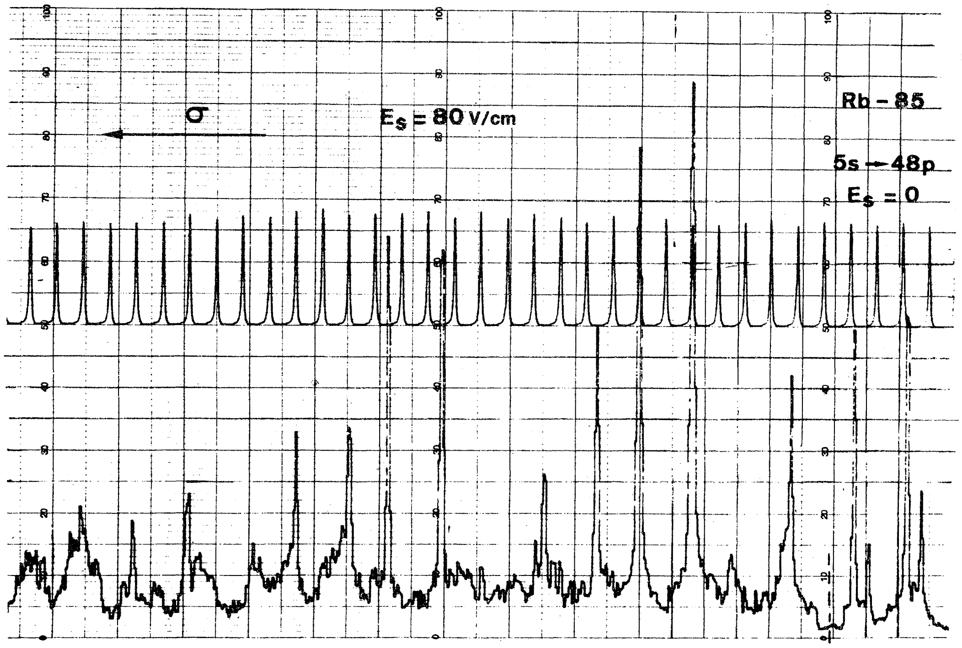

FIG. 13. High-resolution spectrum of the pseudocontinuum created by a dc electric field. The transition $5s \longleftrightarrow 48p$ (^{85}Rb) has been recorded without dc electric field (right part of the spectrum marked with the vertical dotted line) to give a reference frequency for the spectrum. (The electric gain is divided by 4 in this portion.)

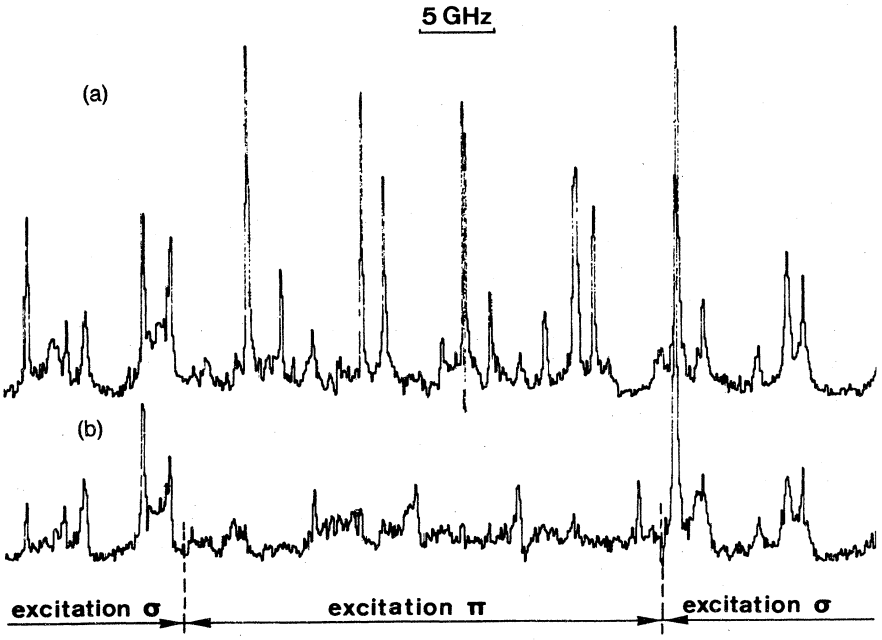

FIG. 14. Effect of the direction of polarization on the pseudocontinuum spectrum. σ [trace (a)] and π [middle part of trace (b)] excitation give rise to completely different spectra.

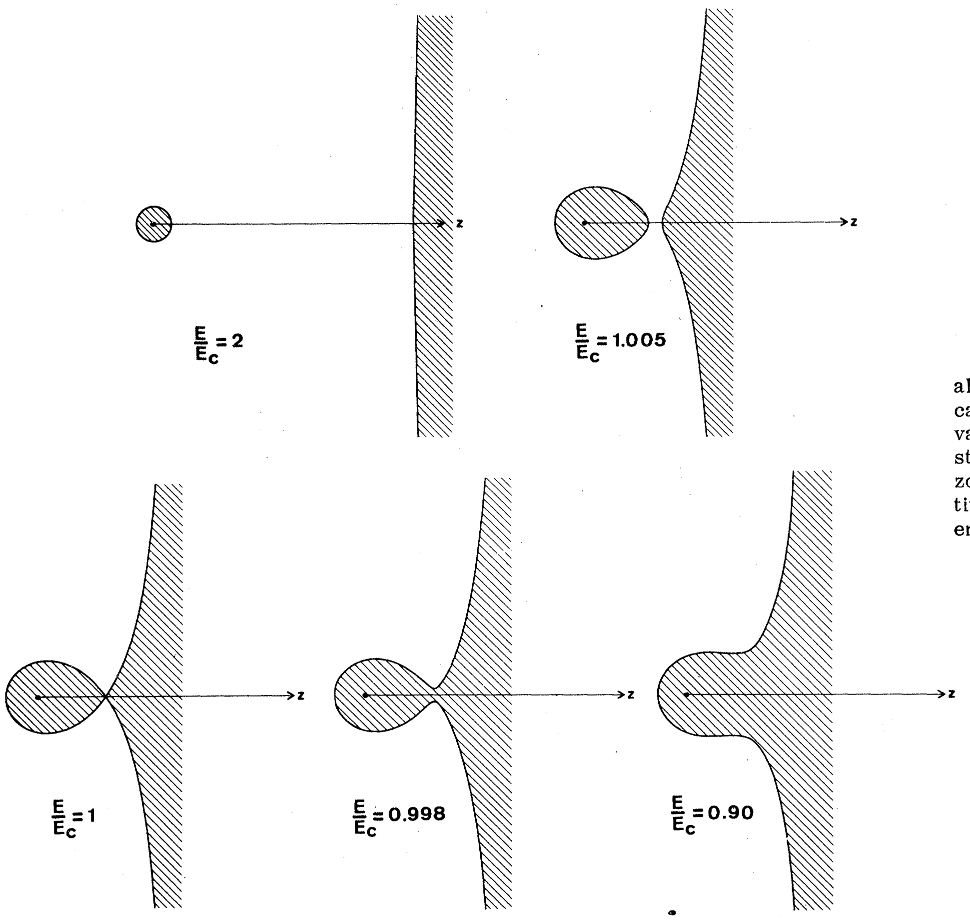

FIG. 15. Two-dimensional representation of the location of the electron for various dc electric field strengths. (The shaded zones correspond to positive values of the kinetic energy.)

with monoisotopic Rb. The result is shown in the recording of Fig. 13, in which narrow resonances are superimposed on a slightly modulated background signal. Compared to the zero field resonances, the observed peaks are not significantly widened. As seen previously, the polarizability of Rb atoms in high-lying excited states is very large. Thus the position of the observed resonances is very sensitive to the electric field; a variation of the field strength of less than 1% strongly modifies the recorded spectrum. The recording shown in Fig. 13 has been obtained with σ-polarized exciting light (linear polarization perpendicular to the electric field), which means that starting from the $5s\,^2S_{1/2}$ ($m_l=0$) ground state, only sublevels with $|m_l|=1$ can be excited. An experiment has also been done using π excitation (linear polarization parallel to the dc electric field) giving rise in this case only to sublevels with $m_l=0$. The result of this experiment is shown in Fig. 14 along with the results for the case of σ excitation. One can notice that with π excitation narrow resonances disappear completely; all that remains is a continuum of photoionization in which one may find small signals whose structure is still to be studied. To our knowledge, such a phenomenon has not been reported previously. Its complete interpretation would require long and difficult calculations. Nevertheless rather simple theoretical considerations may allow one to gain some qualitative insight. Figure 12 is a one-dimensional representation of the potential energy of the electron orbiting around the atomic core $V=-1/r-Fz$ (in a.u.), in which the x and y coordinates are zero. The intersection of this curve with a straight line corresponding to the energy E of the electron divides the z space into four zones in which the kinetic energy of the electron is alternatively negative (hatch marks) and positive (solid line zone). One may say equivalently, and in a very classical way, that the probability of finding the electron in the hatched zone is zero, and nonzero everywhere else. Quantum mechanically, the electron is bound inside the atomic trough (region B) and it has a nonzero probability of crossing over the potential barrier (region C) towards region D via tunneling processes. If the energy of the electron is higher than the potential barrier, the electron is no longer bound, and the atom spontaneously ionizes. In fact, for a given energy E the spatial location of the electron is a three-dimensional surface determined by the equation $E=-1/r-Fz$ which has cylindrical symmetry around the z axis. A plane intersection of such a surface, containing the z axis is shown for several E values in Fig. 15. Looking at this figure it is easy to understand that the probability for the electron to escape the atom, in the case $E>E_c$, depends upon the probability of the electron being near to the z axis. In particular, for states with $m=0$ (the magnetic quantum number is a good quantum number in any case), which are reached using π excitation, the properties of spherical harmonics cause this probability to be a maximum on the z axis. This means that in this case the atom ionizes almost immediately. On the other hand, for states with $m=1$ (or $m>1$) reached using σ excitation, this probability is zero on the z axis so that, in some way, the electron can be considered as bound. This gives a qualitative explanation of the observed sharp resonances in the σ-excited spectrum.

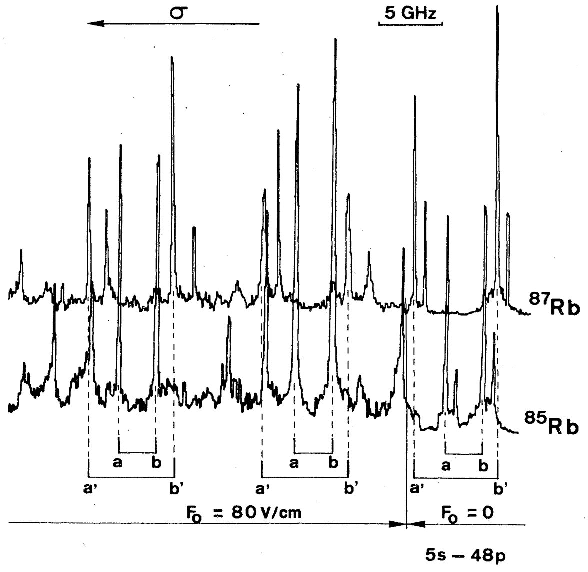

FIG. 16. Recorded spectra of photoionization in the presence of an electric field higher than the critical field, for the two isotopes ^{85}Rb and ^{87}Rb. This figure shows the isotope selectivity of this ionization process.

An interesting property of these resonances is that they permit one to discriminate the spectrum of one isotope from the other, as is clearly shown in Fig. 16. It is possible, therefore to ionize a single isotopic species. One can think of this process as a continuous optical pumping into an ionized state. This could be a new technique of particular importance in laser isotope separation.

VII. EFFECT OF A STRONG, NONRESONANT ELECTROMAGNETIC FIELD

Avan *et al.*[11] have studied theoretically the shifts of Rydberg states produced by an intense high-frequency irradiation. They pointed out that if highly excited atoms interact with an intense laser beam having a frequency ν_L much larger than either the spacing between Rydberg states or the ionizing energy, then all Rydberg states in first approximation are shifted by an amount E_v given by $E_v = e^2F_L^2/2m\omega_L^2$ where F_L is the amplitude of the laser electric field. It is easy to estimate that the expected shift for a laser intensity of 1 $\mathrm{MW/cm^2}$ at 1 μm would be 30 MHz which is actually detectable with our high-resolution arrangement. This experiment has been done by illuminating the atoms with the major part of the intensity delivered at 1.06 μm by the Nd-Yag laser, the other part being utilized as described previously to get the tunable uv laser light exciting the Rb atoms. A boxcar integrator joined to a mechanical chopper permits one to record simultaneously the perturbed and the nonperturbed transitions. Figure 17 shows such a recording obtained with the most intense component of the structure of $5s \rightarrow 48p$ transition. A shift of about 20 MHz towards high frequency is clearly seen between envelope (a) (without ir irradiation) and envelope (b) (with intense ir irradiation) a result consistent with the theory. However, to account for this measured value, it is necessary to add all possible contributions and in particular the ordinary light shift of the ground state via its coupling with the $5p$ resonant level (about 13 000 $\mathrm{cm^{-1}}$), which varies as $e^2F_L^2\langle r\rangle^2/4(\omega_L - \omega_0)$, ω_0 being the energy of the atomic transition and $\langle r\rangle$ the mean value of the atomic-dipole length.[11] The latter shift is estimated to be of the same order of magnitude as the expected effect, so that in this preliminary experiment only qualitative agreement can be deduced.

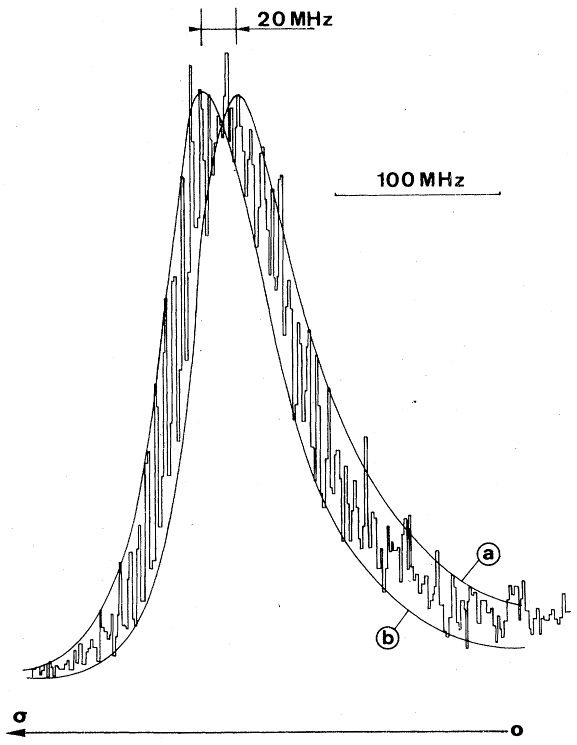

FIG. 17. Recording of a line showing the perturbation of a Rydberg state by an intense ir radiation. This spectrum has been taken by turning the ir field on and off as the laser scans across the line. (a) without ir irradiation; (b) with ir irradiation.

VIII. CONCLUDING REMARKS

We have given experimental results concerning properties of the high-lying excited states of Rb atoms, both in the absence of any external field and in the presence of an external electric field or an intense electromagnetic field. In almost all cases, the observed phenomena can be understood in a simple semiclassical way, but a more sophisticated analysis is required for a full interpretation. Our measured values of the critical ionizing field in Rb, for instance, are in good agreement with the semiclassical law but they differ from similar results obtained by other groups with Na atoms. Concerning the anomalies of intensity that we recorded in the fine-structure patterns, higher-order relativistic effects can account for a certain amount of the observed discrepancy, but further calculations are needed to completely explain this phenomenon.

In the presence of a dc electric field, such an effect as the selective photoionization that we discovered with Rb, although it seems to be classically easy to interpret, should be studied in much greater detail both experimentally and theoretically in order to make sure that it corresponds to a general behavior which could be extended to atoms having many electron configurations. Finally, concerning the effect of an intense, nonresonant laser irradiation, we have shown the appearance of a shift, but the use of longer wavelengths, such as those delivered by CO or $\mathrm{CO_2}$ lasers, would facilitate the observations by increasing the shift which varies as λ^2.

ACKNOWLEDGMENT

The authors are very much indebted to Professor P. Jacquinot and Professor S. Feneuille for their constant interest in these experiments and many fruitful discussions. They gratefully acknowledge Professor C. Cohen-Tannoudji and Professor J. Dupont-Roc for helping them to conceive and interpret the experiment about the effect of a strong nonresonant electromagnetic field on Rydberg states. They thank very much Professor R. W. Stanley for carefully reading their manuscript.

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[1] Y. Kato and B. P. Stoicheff, J. Opt. Soc. Am. Lett. 66, 490 (1976).

[2] D. Popescu, C. B. Collins, B. W. Johnson, and I. Popescu, Phys. Rev. A 9, 1182 (1974).

[3] K. C. Harvey and B. P. Stoicheff, Phys. Rev. Lett. 38, 537 (1977).

[4] P. Camus and C. Morillon, J. Phys. B 10, L133 (1977).

[5] P. Esherick, J. A. Armstrong, R. W. Dreyfus, and J. J. Wynne, Phys. Rev. Lett. 36, 1296 (1976).

[6] A. C. Rivière and D. R. Sweetman, Proceedings of the 6th International Conference on Ionization Phenomena in Gases, Paris, 1963, p. 105.

[7] T. W. Ducas, M. G. Littman, R. R. Freeman, and D. Kleppner, Phys. Rev. Lett. 35, 366 (1975).

[8] C. Fabre, M. Gross, and S. Haroche, Opt. Commun. 13, 393 (1975).

[9] W. H. Wing, K. R. Lea, and W. E. Lamb, Jr., At. Phys. 3, 119 (1973).

[10] H. T. Duong, S. Liberman, and J. Pinard, Opt. Commun. 18, 533 (1976).

[11] P. Avan, C. Cohen-Tannoudji, J. Dupont-Roc, and C. Fabre, J. Phys. (Paris) 37, 993 (1976).

[12] J. Pinard and S. Liberman, Opt. Commun. 20, 344 (1977).

[13] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic, New York, 1957).

[14] A. F. J. Van Raan, G. Baum, and W. Raith, J. Phys. B 9, L173 (1976).

[15] T. F. Gallagher, L. M. Humphrey, R. M. Hill, and S. A. Edelstein, Phys. Rev. Lett. 37, 1465 (1976).

[16] E. Fermi, Z. Phys. 59, 680 (1930).

[17] E. Luc-Koenig (private communication).

[18] J. R. P. Angel and P. G. H. Sandars, Proc. R. Soc. A 305, 125 (1968).

[19] E. Luc-Koenig, S. Liberman, and J. Pinard, following paper, Phys. Rev. A 19, 519 (1979).

[20] S. Feneuille, S. Liberman, J. Pinard, and P. Jacquinot, C. R. Acad. Sci. Ser. B 284, 291 (1977).

[21] H. G. Kuhn, *Atomic Spectra* (Longmans, London, 1969), p. 162.

[22] W. E. Cooke and T. F. Gallagher, Phys. Rev. A 17, 1226 (1978).

[23] K. A. Smith, F. G. Kellert, R. D. Rundel, F. B. Dunning, and R. F. Stebbings, Phys. Rev. Lett. 40, 1362 (1978).