PHYSICAL REVIEW A VOLUME 20, NUMBER 2 AUGUST 1979

Experimental and theoretical study of Stark patterns in Rb Rydberg levels

E. Luc-Koenig, S. Liberman, and J. Pinard
Laboratoire Aimé Cotton, Centre National de la Recherche Scientifique II, Bâtiment 505, 91405 Orsay, France

(Received 15 May 1978)

Stark patterns of high-lying excited states of rubidium (Rydberg states $n \sim 48$) in electric fields from 0 to 20 V/cm have been studied both experimentally and theoretically. Recordings have been obtained with high-resolution laser techniques. Theoretical interpretation takes into account a great number of close-lying levels in the diagonalization process. In order to reproduce the positions as well as the intensities of the one-photon transitions from the ground state, it is necessary to use for s, p, and d levels the wave functions calculated from a central potential specific to the Rb spectrum.

As mentioned in the preceding paper of this issue,[1] Stark patterns of the Rydberg states and their evolution as a function of intensity of an applied dc electric field have been investigated experimentally. Previous experiments on Na atoms[2] were made at relatively low spectral resolution, so that fine- and hyperfine-structure splittings were not observed. Moreover, oscillator strengths could not be obtained from these data because of saturation in the ion detector. The understanding of the resulting patterns was made easier by the fact that the quantum defect is small enough that the atom could be treated as hydrogenic for l values higher than 2. (In the case of Rb, the quantum defect is higher; it is still 1.33 for d levels and can be considered as small only for $l \geqslant 3$.)

As explained in the preceding paper, our high-resolution laser atomic-beam experiments provide excitation of Rydberg states by single-photon absorption from the ground state. For a weak dc electric field, the resolution permits one to separate the four expected components taking into account the hyperfine structure of the ground state of the Rb isotope as well as the fine structure of the Rydberg levels. Typical recordings are shown in Figs. 1 and 2 corresponding to π and σ excitations, respectively. The Stark shift of the ground state $5\,^2S_{1/2}$ is negligible, so that Figs. 1 and 2 give a true map of the energy levels of the excited states $m_l = 0$ and $m_l = 1$, respectively. Line intensities give a measurement of the oscillator strengths for absorption from the ground state.

Wishing to interpret both the intensities and positions of the recorded Stark structures, we have undertaken a theoretical study of the Stark effect of the rubidium Rydberg states. The Stark Hamiltonian of an alkali atom can be written

$$H = h_0 + h_1 = h_0 - ezF\,,$$

where h_0 describes the motion of the optical electron in the central potential $U(r)$ created by the nucleus and the core electrons. From a nonrelativistic central potential, which does not introduce explicitly the core-electron orbitals, it is not possible to interpret the fine-structure splittings nor the intensity ratios of the doublet lines. Indeed, in previous papers we have shown that, in alkali-like systems, the anomalously narrow or inverted fine structures[3] and the line strength anomalies in the doublet resonance lines[4] can be explained in the framework of a relativistic central potential which introduces automatically and in an effective way configuration interactions coming from the relativistic Pauli operators (spin-orbit, Darwin, and mass-velocity terms).

For electric fields F lower than the critical field F_c, the Stark Hamiltonian h_1 can be treated as a perturbation. The calculation of the perturbation is straightforward provided the radial part of the eigenfunctions of h_0 is known. Levels with angular momenta $l \geqslant 3$ have a very small quantum defect and are, therefore, closely approximated by hydrogenic wave functions. Radial wave functions of s, p, and d levels, which have large quantum defects ($\sigma_s \sim 3.14$, $\sigma_p \sim 2.66$, and $\sigma_d \sim 1.33$), have been calculated by the so-called parametric central potential method,[5] in which $U(r)$ is represented by an analytical function depending on three parameters; optimum values of these parameters are obtained by minimizing the root-mean-square difference between the eigenvalues of h_0 and the experimental energies of the 20 deeper s, p, d, and f levels of the spectrum. These levels lie over 32 000 cm^{-1} and are fitted within an average root-mean-square error of 19.0 cm^{-1}. The central potential optimized this way allows one to determine radial wave functions for all levels of the spectrum, as well as for radial integrals which are needed for studying h_1 or even the transition intensities. The original computer program[5] has been modified recently in order to permit us to calculate radial wave functions of high-lying excited states exhibiting numerous oscillations[6] ($n \leqslant 100$); it uses a Numerov algorithm

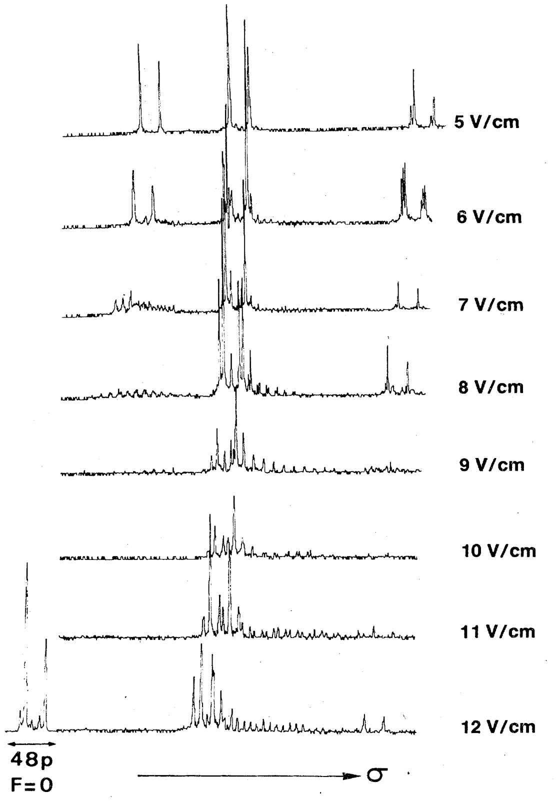

FIG. 1. Experimental recordings of Stark patterns with π excitation, using single-photon absorption from the 5s ground state. The arrow with σ shows the increasing wave number; it must be distinguished from the polarization notation. All traces are referred to the same common origin given by the zero-field spectrum of the $5s \rightarrow 48p$ transition, the scanned interval corresponding roughly to the range 48p to 49p. Note that the hyperfine structure of the ground state as well as the fine structure of Rydberg states are resolved in these recordings obtained with the single isotope of mass number 85. The first trace which corresponds to $F = 5$ V/cm shows three well-resolved groups of lines: the first one corresponds to 47d, the second one to 49s, and the third one to 49p.

based on a scaled linear mesh similar to that introduced by Herman and Skillman.[7]

For weak electric fields ($F < 2$ or 3 V/cm $n \sim 46$), first-order perturbation theory is valid and it is possible to distinguish two different sorts of levels: on the one hand, s, p, and d levels which exhibit quadratic Stark effect; and on the other hand, levels with angular momenta $l > 3$ which have nearly the same energy in zero field and which exhibit linear Stark effect. In the first case transitions such as $5s \rightarrow ns$ and $5s \rightarrow nd$ become possible due to mixing of states ns-$n'p$ and nd-$n'p$. Table I contains the results of a first-order calculations of the shift of $m = 0$ sublevels corresponding to 49p, 49s, and 47d levels, and intensities of π transitions starting from the ground state.

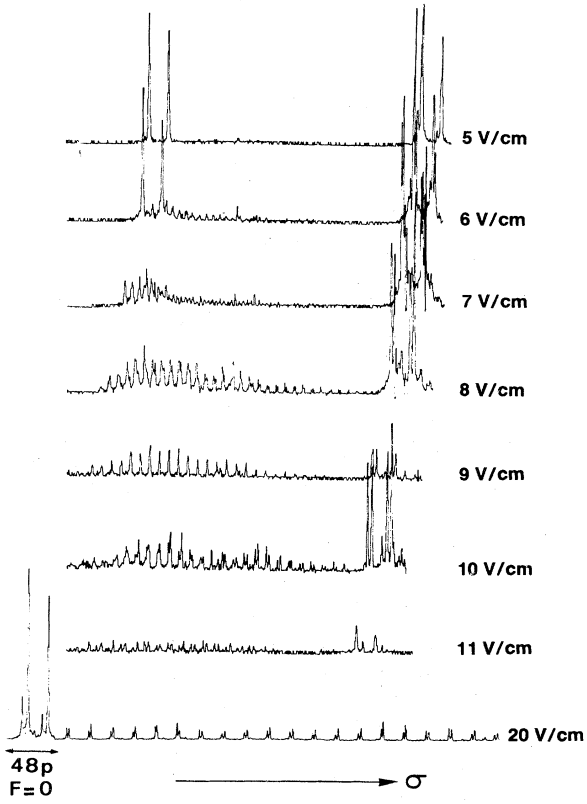

FIG. 2. Same as Fig. 1, using σ excitation. Referring to the first trace obtained with $F = 5$ V/cm, the group of lines on the left corresponds to 47d whereas the group of lines on the right corresponds to 49p.

In the approximation labeled in Table I by "hyd," we use the hydrogenic value for the dipole matrix elements $\langle nlm | r | n'l'm \rangle$. The corresponding re-

TABLE I. Results of a first-order calculation giving the shift ΔE of $m = 0$ sublevels of 49p, 49s, and 47d levels (F is expressed in V/cm) and the intensities of π transitions starting from the ground state.

	ΔE (cm^{-1})	I
49p	$-6.6 \times 10^{-3} F^2$	~ 100
hyd	$+4.2 \times 10^{-3} F^2$	~ 100
expt	$-9.3 \times 10^{-3} F^2$	
49s	$-7.7 \times 10^{-4} F^2$	$1.2 \times 10^{-2} F^2$
hyd	$-7.1 \times 10^{-3} F^2$	$8.3 \times 10^{-3} F^2$
expt	$-3.4 \times 10^{-3} F^2$	
47d	$+3.5 \times 10^{-3} F^2$	$1.9 \times 10^{-2} F^2$
hyd	$3.8 \times 10^{-4} F^2$	$8.5 \times 10^{-6} F^2$
expt	$3.4 \times 10^{-3} F^2$	

sults do not reproduce the experimental data: the intensity of the transition 5s-47d is almost negligible, and the shift of the 47d levels are of an order of magnitude too small; moreover, the observed and calculated shifts for the 49p levels are in the opposite direction. On the other hand, calculations using the specific wave functions of the rubidium spectrum for the low-angular-momentum levels are in good agreement with the experiment. In particular they show that the intensities of the 5s-47d and 5s-49s transitions are of the same order of magnitude.

Levels with angular momenta $l > 3$ have almost the same energy in zero field. They exhibit therefore a linear Stark effect very similar to that of hydrogen. The electric field removes the degeneracy of the $n - |3|$ "Stark sublevels" f, g, h, having the same m and n quantum numbers ($|m| \leq 2$). The overall extension of the structure is approximately given by $\delta E = 3Fn^2 \sim 0.245F$ for $n = 46$ (with F measured in V/cm and δE in cm^{-1}). In a weak electric field no 5s-nl transition is observable for $l \geq 3$.

At intermediate electric field, such as $3 < F < 20$ V/cm, it is no longer possible to treat the problem by keeping only the lowest nonvanishing term of perturbation theory. It is necessary to diagonalize the H matrix built with an ensemble of eigenvectors of h_0 having the same magnetic quantum number m and considered as "quasidegenerate." The more intense the electric field, the larger is the ensemble. For electric fields higher than 8 V/cm, Stark sublevels corresponding to different n values overlap, so that in the study of the $n = 46$ "manifold" the $n' = n - 1$ and $n'' = n + 1$ manifolds and levels of n_1s and n_1p with $n - 1 \leq n_1 \leq n + 6$ and n_2d levels with $n - 2 \leq n_2 \leq n + 5$ must be taken into account. We also introduced n_3f levels ($n - 2 \leq n_3 \leq n + 3$), which interact noticeably with $n_3'd$ levels ($n_3' = n_3 + 1$ and $n_3 + 2$). The corresponding matrix for $m = 0$ has the dimension 156. For given values of F and m, the eigenvalues of the matrix give the position of Stark sublevels Ψ, whereas the eigenvectors permit one to calculate the intensity of the $5s \rightarrow \Psi$ transition

$$I_\Psi \propto |\langle 5s|r|\Psi\rangle|^2 = \left| \sum_{n_1 = n-1}^{n+6} \langle 5s|r|n_1p\rangle \right|^2 .$$

The results that we obtained for the $n = 46$ and $|m| = 0$ and 1 sublevels, π and σ polarization, respectively, are presented in Figs. 3 and 4. The agreement between calculated and observed Stark structure, for positions as well as for intensities, is satisfactory considering that neither fine structure nor hyperfine structure is introduced into the calculations.

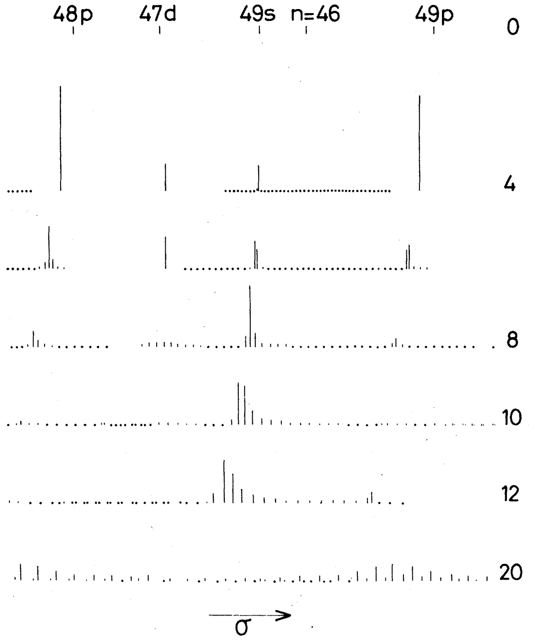

FIG. 3. Calculated Stark patterns corresponding to π excitation. These results are to be compared to experimental ones given in Fig. 1. Notice that in these spectra, both ground-state hyperfine-structure splitting and upper-state fine-structure splitting have been intentionally omitted. Points represent level position but with zero transition probability. Concerning level position in zero field, as represented at the top of the figure, $n = 46$ corresponds to levels which have zero quantum defect. In the case of Rb it includes all levels with $l > 3$.

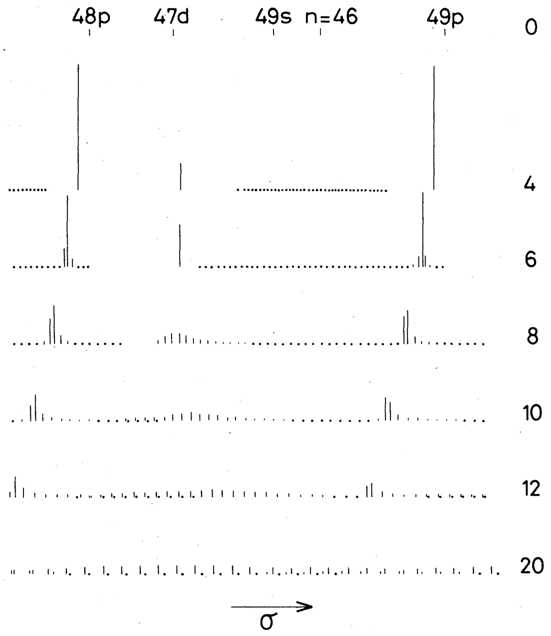

FIG. 4. Calculated Stark patterns for σ excitation, to be compared with the experimental results given in Fig. 2.

In π polarization (Fig. 3), for weak fields (lower than 4 V/cm) only absorption transitions towards $48p$, $47d$, $49s$, and $49p$ are observable as predicted by first-order perturbation theory. For stronger fields one can see the appearance of structures containing almost equidistant lines. The Stark manifold of $n=46$, which overlaps the closer s, p, and d levels, is shifted by the electric field, so that significant n_1p components occur in the wave functions of the close-lying levels of the Stark manifold.

As the electric field is increased, with π polarization, one sees first the appearance and then the disappearance of a structure close in energy to the unperturbed $47d$ level, whereas a periodic structure appears at an energy close to the zero-field position of the $49s$ level. For intermediate values of the electric field (10 V/cm) annihilation phenomena in the calculation of I_Ψ cause levels located in the neighborhood of the unperturbed $49p$ level to disappear and then reappear in agreement with experimental observations. In fact, for such values of the electric field, identification of nlm levels is no longer possible and it would be much preferable to make use of the so-called parabolic quantum numbers nn_1n_2m. For instance, for $F=12$ V/cm the observed transition toward a $49p$ level actually corresponds to a level whose wave function is

$$\begin{aligned}\Psi=&(0.2127)^{1/2}|48d\rangle+(0.2093)^{1/2}|49s\rangle+(0.0903)^{1/2}|47f\rangle-(0.0760)^{1/2}|48p\rangle+(0.0482)^{1/2}|49p\rangle-(0.0421)^{1/2}|50p\rangle\\&+(0.0370)^{1/2}|50s\rangle+(0.0341)^{1/2}|47d\rangle-(0.0337)^{1/2}|47g\rangle+(0.0167)^{1/2}|46,l=43\rangle+(0.0119)^{1/2}|47h\rangle\\&-(0.0114)^{1/2}|46,l=42\rangle+(0.0113)^{1/2}|49d\rangle+\cdots\end{aligned}$$

Disappearance of the "49" component corresponds thus to an algebraic cancellation of the $48p$, $49p$, and $50p$ contributions in the expression of I_Ψ.

In σ polarization (Fig. 4), similar results have been obtained, except that s levels do not play any role in this case. At $F=20$ V/cm, in agreement with experiment, we obtain a periodic structure over the entire spectral range investigated.

In Fig. 5 we compare the experimental Stark structure obtained at $F=8$ V/cm, $m=0$, with the results of two different calculations. In the first one (a) hydrogenic radial wave functions for the low-angular-momentum levels (s,p,d) are used; in the second one (b) the radial wave functions are numerically integrated with the central potential $U(r)$ typical of rubidium. The positions of the levels of the $n=46$ manifold are approximately identical in both treatments; but it is not true for the positions of the $49s$ and $49p$ levels. Moreover, intensities I_Ψ are quite different. Using hydrogenic values for all radial integrals only the transitions to the $49s$ and $49p$ levels are observed, the second one being always the more intense of the pattern and presenting no structure. On the contrary, in calculation (b), the transition to the level located at the zero-field position of the $49p$ level is weaker than those lying in the vicinity of the nonperturbed $49s$ level; moreover at the zero-field position of the $47d$ level a periodic structure appears. Similar comparisons can be made at different field values. For the hydrogenic approximation one always obtains a spectrum exhibiting a very small number of lines (4 or 5 only in the spectral range studied) which does not match actual observations.

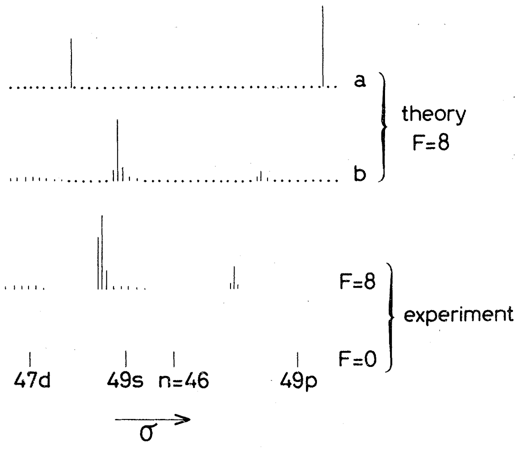

FIG. 5. Comparison of two different calculations with corresponding experimental results (where hyperfine and fine structure have been omitted); (a) hydrogenic approximation; (b) central potential approximation.

In conclusion, it is possible to theoretically interpret in a satisfactory manner absorption spectra towards Rydberg states of Rb with regard to both position and intensity in the presence of an electric field, to the extent that the Stark Hamiltonian can be diagonalized using a large basis and radial parts specific to Rb. For electric fields higher than 20 V/cm, only energy and

m remain good quantum numbers. Thus it would be desirable to find directly eigenstates of $h_0 + h_1$ by treating simultaneously the non-Coulombic central potential and the action of the electric field. Such a treatment would give both position and width of the states and could be used to interpret the discrete and very narrow lines observed in the photoionization spectrum of rubidium in the presence of a strong dc electric field.[1]

---

[1] S. Liberman and J. Pinard, Phys. Rev., preceding paper, Phys. Rev. A 19, 507 (1979).

[2] M. G. Littman, M. L. Zimmerman, T. W. Ducas, R. R. Freeman, and D. Kleppner, Phys. Rev. Lett. 36, 788 (1976).

[3] E. Luc-Koenig, Phys. Rev. A 13, 2114 (1976).

[4] A. Bachelier and E. Luc-Koenig, J. Phys. (Paris) (to be published).

[5] M. Klapisch, Comput. Phys. Commun. 2, 239 (1971).

[6] A. Bachelier (private communication).

[7] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).