

## High-Resolution Three-Photon Spectroscopy of $6s\ 15p\ ^{1,3}P_1$ Rydberg States of Yb

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High-resolution three-photon laser spectroscopy has been performed for the first time to gain new spectroscopic information. Starting from the  $6s^2\ ^1S_0$  ground state of Yb,  $6s\ 15p\ ^{1,3}P_1$  Rydberg states were populated by two-photon-resonant, three-photon absorption via the  $6s\ 7s\ ^1S_0$  intermediate level. As a result of two-photon line narrowing Doppler-free spectra, showing well resolved isotope shifts and hyperfine structures, were obtained. From the hyperfine coupling constants  $^{171,173}A(^1P_1)$  the singlet-triplet mixing was derived.

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Multiphoton excitation is a well established technique to investigate high-lying atomic or molecular states.<sup>1</sup> The high power densities available with pulsed dye-laser radiations allow a considerable number of photons to be absorbed simultaneously. On the contrary, up to now high-resolution studies were limited to two-photon absorptions because of the modest power densities of tunable cw dye-laser radiation. In this Letter we demonstrate two-photon-resonant, collinear three-photon spectroscopy to be a high-resolution technique which promises wide applicability for the investigation of highly excited atomic (Rydberg) states. Starting from the ground state  $|g\rangle$ , velocity-selective coherent two-photon absorption excites the atom to a suitably chosen intermediate level  $|i\rangle$ . In contrast to conventional Doppler-free two-photon spectroscopy, in our experiment two photons with identical wave vectors are absorbed. Also, Doppler tuning allows excitation of all isotopes at fixed laser frequency. The transition to the final state  $|f\rangle$  is induced by a second, collinear, i.e., copropagating or counter-propagating, laser beam. As a result of two-photon line narrowing, Doppler-free spectra are obtained, scanning the frequency of the second dye laser across the upper atomic transition. Our technique is related to line narrowing by single-photon absorption,<sup>2-4</sup> which is the basis of many methods of high-resolution laser spectroscopy.<sup>1</sup>

Generally, the coherent two-photon absorption cannot be replaced by a two-step excitation to the intermediate level. At fixed laser frequencies one isotope at most can be promoted by stepwise excitation. It follows that for high-resolution studies resonant three-step excitation is not feasible. Compared to coherent three-photon absorption our scheme offers several advantages. As a result of a two-photon resonance, the overall absorption cross section  $\sigma_{gf}$  is enhanced consid-

erably. This greatly relaxes the requirements for the power densities of the dye-laser radiations employed. Furthermore, whereas three laser beams intersecting each other at an angle of  $120^\circ$  are necessary to eliminate the Doppler effect when three photons of equal frequency are absorbed coherently,<sup>1</sup> in our experiment collinear laser beams are used. In this way the interaction volume is increased significantly, resulting in an enhanced sensitivity. It should be noted, however, that only certain velocity ensembles are excited, contrary to coherent three-photon absorption, where all atoms are involved in the excitation process. However, the advantages of our technique more than compensate for the small fraction of atoms with a particular velocity component along the laser beam axis. Whereas our high-resolution technique is well suited to measuring relative line positions, it is less useful for precise determinations of absolute transition frequencies.

The first experimental evidence of Doppler-free three-photon absorption was presented by Gryneberg *et al.*<sup>5</sup> Starting from the ground state of sodium, the  $3p\ ^2P_{1/2}$  level was excited by means of a quasiresonant hyper-Raman process. In order to minimize detunings and consequently optimize the total cross section for this process, two cw dye lasers of slightly different frequencies were employed. Since the hyperfine structure of the sodium  $D_1$  line is well known, no new spectroscopic information was derived.

We have applied two-photon-resonant, high-resolution three-photon spectroscopy to investigate the  $6snp\ ^{1,3}P_1$  Rydberg series<sup>6</sup> of Yb with principal quantum numbers ranging between  $n = 13$  and  $50$ . From hyperfine structures and isotope shifts detailed information concerning the electronic wave functions of the corresponding Rydberg states can be derived. For illustration

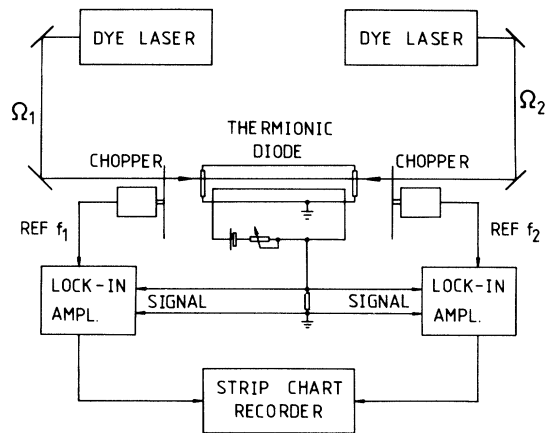
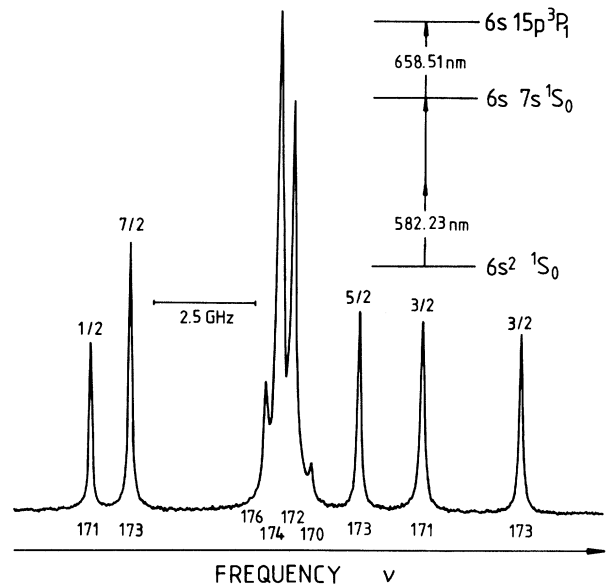


FIG. 1. Experimental setup.

here we report the hyperfine structures and isotope shifts of the  $6s15p^1,^3P_1$  Rydberg levels and determine their singlet-triplet mixing. A comparison between our experimental results pertaining to the entire Rydberg series and the predictions of a multichannel quantum-defect analysis<sup>7</sup> will be published elsewhere.<sup>8</sup>

The experimental setup used in our experiment is shown in Fig. 1. Two stabilized cw dye ring lasers with bandwidths of about 1 MHz were employed. The first ring laser, providing about 2.2 W at  $\lambda_1 = 582.23$  nm, was tuned to the two-photon transition  $6s^2^1S_0 \rightarrow 6s7s^1S_0$ . The intensity of the first laser beam was modulated at a frequency  $f_1 \sim 1.6$  kHz in order to detect the Doppler-broadened two-photon transition. The second dye ring laser could be tuned between 615 and 690 nm and excited the atoms from the intermediate  $6s7s^1S_0$  level to the final  $6s15p^1,^3P_1$  Rydberg states. The Doppler-free signals were recorded, scanning the frequency of the second dye ring laser across the upper atomic transition, while the wavelength of the first dye laser was kept fixed at an arbitrary position within the Doppler contour of the two-photon resonance. Phase-sensitive detection at the modulation frequency  $f_2 \sim 73$  Hz was employed to observe the Doppler-free signals. Both laser beams were superimposed and copropagated or counterpropagated (cf. Fig. 1) through a stainless steel pipe, filled with Yb and heated to about  $625^\circ\text{C}$ . To prevent coating of the windows, the pipe was filled with about 100 mTorr of Ar buffer gas. For thermionic detection<sup>9</sup> the stainless steel pipe was taken as anode, while a thin tungsten wire running along its center served as cathode. The voltage drop across a  $50\text{-k}\Omega$  load resistor was fed into the lock-in amplifiers. Both laser

FIG. 2. High-resolution three-photon excitation spectrum of the  $6s15p^3P_1$  Rydberg state.

beams were focused into the center of the oven by lenses of 300 mm focal length.

A typical high-resolution spectrum of the  $6s15p^3P_1$  Rydberg state is shown in Fig. 2. This spectrum has been recorded with use of counterpropagating laser beams. The signals appearing at the center correspond to the even isotopes  $^{170,172,174,176}\text{Yb}$  with the isotope shifts being clearly resolved. In addition, the hyperfine structure of the odd isotopes  $^{171}\text{Yb}$  ( $I = \frac{1}{2}$ ) and  $^{173}\text{Yb}$  ( $I = \frac{3}{2}$ ) is displayed. The line positions measured relative to  $^{176}\text{Yb}$  are given in Table I. In addition, the frequencies recorded with copropagating laser beams are included.

TABLE I. Line positions corresponding to the  $6s15p^3P_1$  Rydberg state, obtained with copropagating and counterpropagating laser beams.

A	F	$\delta\Omega_2^{A-176}/2\pi$ (MHz)	
		$\vec{k}_1 \cdot \vec{k}_2 < 0$	$\vec{k}_1 \cdot \vec{k}_2 > 0$
176		0	0
174		333(10)	-158(10)
173	7/2	-3340(20)	-4109(20)
	5/2	2281(15)	1508(15)
	3/2	5893(20)	5118(20)
172		681(10)	-329(10)
171	3/2	3738(20)	2303(15)
	1/2	-4351(20)	-5777(20)
170		1120(15)	-542(10)

Since these data correspond to moving atoms, the recorded line positions depend on the geometry chosen. In order to derive isotope shifts and hyperfine structures for atoms at rest the experimentally observed shifts  $\delta\Omega_2^{A-176}/2\pi = (\Omega_2^A - \Omega_2^{176})/2\pi$  are expressed as

$$\delta\Omega_2^{A-176}/2\pi = [\delta\omega_2^{A-176} \mp (\omega_2/\omega_1)\delta\omega_1^{A-176}]/2\pi, \quad (1)$$

where the upper (lower) sign holds for copropagating (counterpropagating) laser beams. The symbol  $\omega$  refers to atoms at rest, while the capital letter  $\Omega$  corresponds to moving atoms. It follows from Eq. (1) that the isotope shifts  $\delta\omega_1^{A-176} = \omega_1^A - \omega_1^{176}$  and  $\delta\omega_2^{A-176} = \omega_2^A - \omega_2^{176}$  of the first and second transitions, respectively, contribute to the measured frequency differences  $\delta\Omega_2^{A-176}/2\pi$ . Since the hyperfine splittings of the odd isotopes  $^{171,173}\text{Yb}$  are determined by the final state only, the separations between the corresponding hyperfine components do not depend on the geometry chosen. However, their centers of gravity (c.g.) are shifted by different amounts [see Eq. (1)]. This considerably facilitates the identification of the observed hyperfine components. With the aid of Eq. (1), the isotope shifts of the first and second transitions have been deduced from the data given in Table I. The isotope shifts  $\delta\omega_1^{A-176}$  obtained in this way are in excellent agreement with the splittings appearing in the Doppler-free spectrum of the two-photon transitions  $6s^2\ ^1S_0 \rightarrow 6s7s\ ^1S_0$ .<sup>8</sup> The isotope shifts and hyperfine structures of the  $6s15p\ ^3P_1$  Rydberg state are given in Table II. The line positions  $\delta\omega^{A-176} = \delta\omega_1^{A-176} + \delta\omega_2^{A-176}$  correspond to the splittings which would be ob-

served performing a Doppler-free one-photon transition ( $\lambda = 201.87\text{ nm}$ ) starting from the atomic ground state. Besides the  $6s15p\ ^3P_1$  Rydberg level, the results obtained for the  $^1P_1$  fine-structure component are also included in Table II. A typical high-resolution spectrum of the  $6s15p\ ^1P_1$  Rydberg state is shown in Fig. 3, recorded with counterpropagating laser beams.

In the remaining part of this Letter we derive the degree of singlet-triplet mixing from the hyperfine structure of the  $6s15p\ ^1P_1$  Rydberg state. Since the hyperfine interaction of the  $15p$  Rydberg electron is negligible compared to that of the  $6s$  valence electron, the Hamiltonian  $H_{\text{hf}}$  describing the magnetic hyperfine coupling can be written as

$$H_{\text{hf}} = a_{6s} \vec{s}_{6s} \cdot \vec{I}, \quad (2)$$

where  $a_{6s}$  represents the hyperfine splitting factor of the free ion. The singlet-triplet mixing of the  $6s15p$  configuration due to spin-orbit interaction of the  $15p$  Rydberg electron is taken into account, expanding the state vector of the  $6s15p\ ^1P_1$  level,

$$|^1P_1\rangle = \Lambda|^1P_1\rangle_{LS} + \Omega|^3P_1\rangle_{LS}, \quad (3)$$

in terms of pure-configuration, exactly LS-coupled basis vectors. It is known from a multichannel quantum-defect analysis<sup>7</sup> of the  $6snp\ ^{1,3}P_1$  Rydberg series of Yb that the configuration at  $n = 15$  is pure. This is supported by the isotope shifts between even Yb isotopes measured for  $6snp\ ^{1,3}P$  ( $13 \leq n \leq 50$ ) Rydberg states.<sup>8</sup> With the aid of Eqs. (2) and (3) the hyperfine splitting factor  $A$  of the  $6s15p\ ^1P_1$  level is calculated to be,

TABLE 2. Isotope shifts and hyperfine structures of the  $6s^2\ ^1S_0 \rightarrow 6s15p\ ^{1,3}P_1$  transitions.

A	F	$\delta\omega^{A-176}/2\pi$ (MHz)	
		$^3P_1$	$^1P_1$
176		0	0
174		643(10)	652(10)
173	7/2	-2843(15)	2667(15)
	5/2	2777(15)	228(10)
	3/2	6388(20)	-1444(15)
	c.g.	1082(15)	940(10)
172		1314(15)	1329(15)
171	3/2	4649(20)	467(10)
	1/2	-3436(20)	4457(20)
	c.g.	1954(15)	1797(15)
170		2179(15)	2212(15)

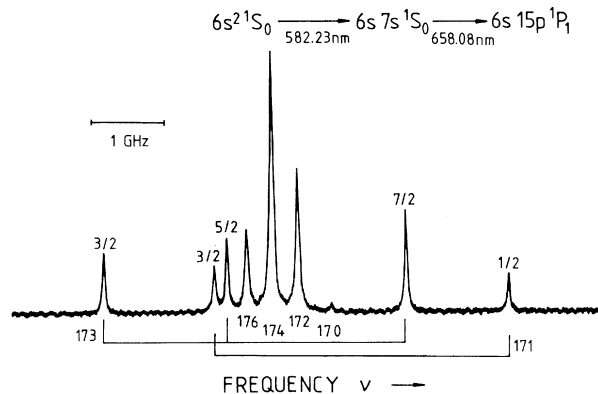


FIG. 3. High-resolution three-photon excitation spectrum of the  $6s15p\ ^1P_1$  Rydberg state.

with use of first-order perturbation theory,

$$A(^1P_1) = a_{6s} [\Omega^2(^1P_1) - 2\sqrt{2}\Lambda(^1P_1)\Omega(^1P_1)]/4. \quad (4)$$

Second-order contributions due to off-diagonal elements of  $H_{hf}$  between the  $^1P_1$  and  $^3P_{0,1,2}$  fine-structure components cause deviations from the Landé interval rule as well as displacements of the centers of gravity of the hyperfine structures of the odd isotopes. It follows from Table II that the isotope shifts between the even isotopes are nearly the same for the transitions to both fine-structure components  $^1P_1$  and  $^3P_1$ . On the contrary, for each odd isotope the centers of gravity are shifted by different amounts for the different transitions, indicating the presence of hyperfine-induced fine-structure mixing. As a result of the proximity of the  $^3P_0$  and  $^3P_2$  fine-structure components, the mixing is strong for the  $^3P_1$  state, resulting in a complete breakdown of the Landé interval rule. On the contrary, since the separation  $\Delta E_{ST} \sim 300$  GHz between the  $6s15p^1P_1$  and  $^3P$  states is considerably larger than the hyperfine coupling constants  $^{171}a_{6s} = 12.6428$  GHz<sup>10</sup> and  $^{173}a_{6s} = -3.4830$  GHz, second-order contributions play a minor role for the  $^1P_1$  state. In particular, the interval rule is obeyed to a good approximation. Hence Eq. (4) can be used to derive the triplet amplitude  $\Omega(^1P_1) = +0.36(5)$ . This value is indicative for a strong spin-orbit interaction of the  $6s15p$  configuration. It should be noted that the absolute phase of the wave function in Eq. (3) has been chosen arbitrarily to make the largest amplitude ( $\Lambda$ ) positive.

In conclusion, we have presented the first ap-

plication of high-resolution three-photon spectroscopy. Exploiting two-photon resonances only moderate power densities of the laser radiations employed are required. This renders the technique of two-photon-resonant, three-photon absorption widely applicable in high-resolution laser spectroscopy. In particular, Rydberg series of elements with high ionization limits become accessible. This has been demonstrated by measuring isotope shifts and hyperfine structures of Yb Rydberg states.

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