Singlet-triplet mixing in 4*snd* Rydberg states of Ca

R. Beigang, K. Lücke, and A. Timmermann
Institut für Atom und Festkörperphysik, Freie Universität Berlin, 1000 Berlin 33, West Germany
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Singlet-triplet mixing of $4snd\ ^1D_2$ and $^3D_2$ states of Ca was determined between principal quantum numbers $7 \leq n \leq 42$ with the use of Doppler-free two-photon spectroscopy. The hyperfine structure of the $4snd\ ^1D_2$ states was used to probe admixtures of triplet character into the singlet wave functions. It turned out that, in the region of series crossings, an enlarged singlet-triplet mixing was observed.

Systematic investigations of hyperfine structures in Rydberg states of two-electron systems can provide detailed information about perturbations by other configurations or series. The influence of hyperfine induced perturbations on the hyperfine structure was shown as early as 1932[1,2] for Hg. Similar effects have been observed in Rydberg states of other two-electron systems like Yb,[3] and systematically for Sr, Ca, and Ba.[4] The important role of hyperfine induced singlet-triplet mixing for the character of high Rydberg states was pointed out by Liao *et al.*[5] for ^{3}He. This type of mixing gives rise to a significant modification of hyperfine structure and isotope shifts of ^{3}He $ns\ ^3S$ ($n=4-6$) and $nd\ ^3D$ ($n=3-6$) levels.[6–8]

Hyperfine induced interactions become dominant if the energy separation between states with the same angular momentum F is comparable to the Fermi contact term of the lower s electron. Recently, the influence of singlet-triplet mixing on the hyperfine structure was demonstrated for the $5snd\ ^1D_2$ and $^3D_2$ Rydberg states of ^{87}Sr in an energy range where the above-mentioned hyperfine perturbations can be neglected.[9] The change of coupling between the two electrons in the region of the avoided crossing between the $^1D_2$ and $^3D_2$ series was clearly related to the variation of the hyperfine structure. The admixtures determined from the hyperfine-structure measurements were in agreement with data obtained from a multichannel quantum-defect theory (MQDT) analysis.[10] The data obtained from hyperfine-structure measurements can, of course, also be used as additional information for MQDT analysis if the phase of the admixed wave functions is needed.[11]

In Ca, the crossings of the $4snd\ ^1D_2$ and $^3D_2$ series between $n=8$ and 9 and $n=14$ and 15 do not lead to strong interactions of the two series, thus no singlet-triplet mixing was observed in earlier measurements using pulsed dye lasers and a MQDT analysis.[12] The hyperfine structure, however, is by far more sensitive to variations of the coupling compared to the level energies. The determination of the hyperfine structure of the $4snd\ ^1D_2$ Rydberg states of ^{43}Ca in the range of the series crossing is therefore an interesting test for the sensitivity of the hyperfine structure on singlet-triplet mixing. Using the hyperfine structure as the probe, even a weak singlet-triplet mixing should be detectable. We report here on a systematic investigation of the hyperfine structure of the $4snd\ ^1D_2$ Rydberg states between principal quantum numbers $7 \leq n \leq 42$, performed by Doppler-free two-photon spectroscopy from the $4s^2\ ^1S_0$ ground state.

The natural mixture of calcium contains six stable isotopes, the even-mass ^{40}Ca with 96.6% abundancy, ^{42}Ca (0.46%), ^{44}Ca (2.06%), ^{46}Ca (0.003%), ^{48}Ca (0.185%), and the odd-mass ^{43}Ca (0.135%) with the nuclear spin $I=\frac{7}{2}$. This very low abundant odd isotope requires a high sensitivity detection method, all the more because the weak ^{43}Ca signal is spread over five hyperfine components. In addition, a single-mode output power, high enough to excite two-photon transitions, is needed in the deep-blue spectral range. The ionization limit of Ca at 49 305.94 cm^{-1} (Ref. 12) makes tunable single-mode output at wavelengths as short as 406 nm necessary to allow investigations of even high members of Rydberg series.

The experimental setup used here is shown schematically in Fig. 1. A narrow-band cw ring dye laser was applied in combination with a space-charge limited thermionic diode. From the $4s^2\ ^1S_0$ ground state, the $4snd\ ^1D_2$ Rydberg states are accessible with two photons of a dye laser working with stilbene 1 in the wavelength from 405 to 430 nm. A ring laser configuration provided a maximum single-mode output power of about 140 mW when pumped with the uv lines of an Ar$^+$ laser at pump powers of 3.6 W. The dye laser was frequency stabilized to an external Fabry-Perot reference cavity resulting in a laser linewidth of about 1 MHz.

Ca vapor was produced in a stainless-steel hot-pipe oven heated to a temperature which corresponds to a vapor pressure of approximately 25 mTorr. The excited Rydberg atoms were then detected with a

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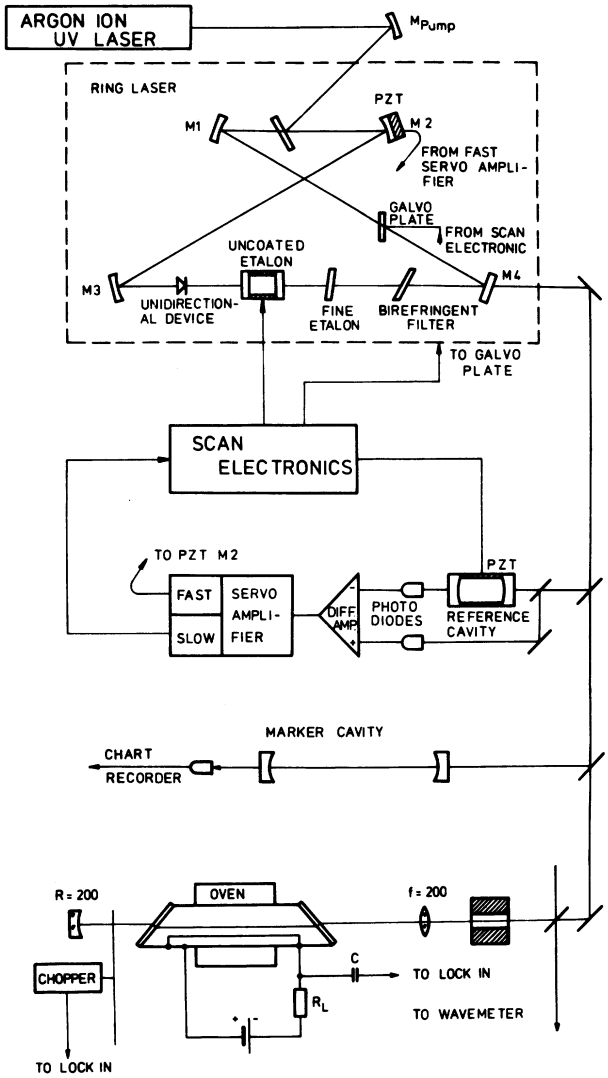

FIG. 1. Experimental setup for Doppler-free two-photon spectroscopy.

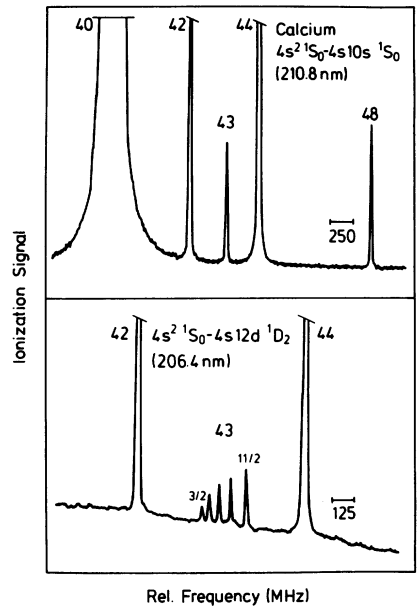

FIG. 2. Doppler-free two-photon excitations from the $4s^2\,{}^1S_0$ ground state into the $4s\,10s\ {}^1S_0$ level (upper part) and, on an enlarged scale, into the $4s\,12d\ {}^1D_2$ state for the isotopes ^{42}Ca, ^{43}Ca, and ^{44}Ca (lower part). For the $4s\,12d\ {}^1D_2$ state, the ^{43}Ca signal is split into five hyperfine components.

space-charge-limited thermionic diode,[13] formed by a stainless-steel wire inserted in the pipe and negatively biased (−0.5 V) through a load resistor (10–100 kΩ). The sensitivity of the thermionic diode increases with decreasing energy difference to the ionization limit, thus partly compensating for the decreasing transition probability.

To identify the excited Rydberg levels unambiguously, a wavemeter with an absolute accuracy of $\pm 0.01\ \mathrm{cm}^{-1}$ was used. This accuracy is required, in particular, for high principal quantum numbers. The hyperfine splittings were determined by means of a confocal Fabry-Perot interferometer with a free spectral range of 125 MHz.

Typical excitation spectra are shown in Fig. 2. A two-photon transition to the $4s\,10s\ {}^1S_0$ Rydberg state is shown in the upper part. With the exception of the ^{46}Ca all stable isotopes are resolved with a high signal-to-noise ratio. The intensity of the ionization signals is directly proportional to the isotope abundancy in the natural mixture. The signal of the ^{43}Ca ($I=\frac{7}{2}$) is split into five hyperfine components for a $4s\,12d\ {}^1D_2$ state, as can be seen in the lower part of Fig. 2. All components with the total angular momenta $F=\frac{3}{2}$ to $\frac{11}{2}$ are resolved and the hyperfine coupling constant A can be determined easily. This was done in this work up to the principal quantum number $n=42$.

In Fig. 3 the experimentally determined values for A factors of the $4snd\ {}^1D_2$ Rydberg series are shown. Applying a least-squares fit procedure to all frequency differences between all possible F values of a given level, A factors were derived with an accuracy in the order of 1 MHz. Due to the fact that the Landé interval rule is well obeyed, the quadrupole coupling constant B was assumed to be zero. Hyperfine induced perturbations can also be neglected as the separation between fine-structure levels is considerably larger than the Fermi contact term of the $4s$ electron up to principal quantum numbers $n \sim 60$.

It is well known that pure LS-coupled singlet terms produce no hyperfine structure at all.[14] Thus the observed splittings have to be interpreted in terms of the admixture of a considerable amount of triplet character into the singlet levels.

For a quantitative description the intermediate coupling scheme has to be applied.[14] The Hamiltonian

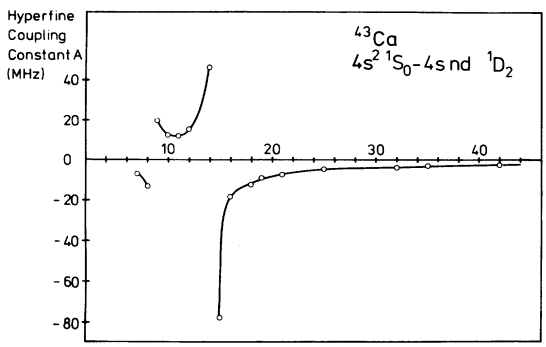

FIG. 3. n dependence of the experimentally observed hyperfine coupling constant A for $4snd\ ^1D_2$ states of ^{43}Ca.

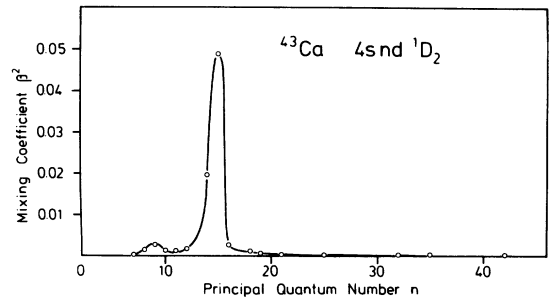

FIG. 4. Singlet-triplet mixing coefficient β^2 as a function of the principal quantum number n for the $4snd\ ^1D_2$ Rydberg series derived from hyperfine-structure measurements.

operator for the hyperfine structure is given by

$$W = A\vec{I}\cdot\vec{J}\ , \tag{1}$$

where A is the hyperfine coupling constant, $\vec{I}$ the nuclear spin, and $\vec{J}$ the angular momentum. Because the hyperfine coupling constant A depends critically on the type of coupling in two-electron systems, the $4snd$ $(J=2)$ wave functions have to be taken as a linear combination of unperturbed, LS-coupled $^1D_2^0$ and $^3D_2^0$ wave functions:

$$\begin{aligned} |(^1D_2)\rangle &= \alpha|(^1D_2^0)\rangle - \beta|(^3D_2^0)\rangle\ , \\ |(^3D_2)\rangle &= \alpha|(^3D_2^0)\rangle + \beta|(^1D_2^0)\rangle\ , \end{aligned} \tag{2}$$

where α and β are mixing coefficients.

Assuming no configuration interaction, the hyperfine coupling constant A for the $^1D_2$ levels can be calculated using magnetic dipole matrix elements in intermediate coupling[14]:

$$A\,(^1D_2) = \left(\frac{c_1^2}{4} - \frac{c_2^2}{6}\right)a_{4s}\ . \tag{3}$$

a_{4s} is the Fermi contact term of the lower valence electron. The magnetic interaction of the outer excited electron is small compared to a_{4s} and can be estimated using Goodsmit's formula.[15] For principal quantum numbers $n > 7$, this contribution remains always smaller than 1 MHz. From Eqs. (2) and (3) the mixing coefficients α and β are determined. The sign of β depends on the relative position of singlet and triplet states.[16] The crossing of these two series between $n=8$ and 9 and $n=14$ and 15 results in a change of sign of β which, in turn, determines the sign of A. Similar behavior was observed in Sr and Ba.[9,11] In addition to the singlet-triplet mixing, which is described by the coefficients α and β, admixtures from other configurations have to be taken into account. In particular, $3s5d\ ^1D_2$ and $3d^2\,^1D_2$ levels are admixed over many $4snd\ ^1D_2$ states and the mixing coefficients were determined in an MQDT analysis by J. A. Armstrong *et al.*[12]

The wave function for $^1D_2$ states has to be expanded by an additional term accounting for the perturbing levels

$$\begin{aligned} |(^1D_2)\rangle = \alpha|(^1D_2^0)\rangle - \beta|(^3D_2^0)\rangle \\ + \gamma|(3s5d, 3d^2)\,^1D_2\rangle\ . \end{aligned} \tag{4}$$

The normalization has to be replaced by

$$\alpha^2 + \beta^2 + \gamma^2 = 1\ . \tag{5}$$

The direct contribution of the perturbing levels to the A factor can be neglected in first order. This is certainly true for the $3d^2$ configurations because of the small core polarization of the two $3d$ electrons. In the case of the $3d5s$ configuration, the main contribution is due to the $5s$ electron. The Fermi contact term, however, scales as $1/n^{*3}$, so that, for small admixtures, a negligible hyperfine-structure constant can be expected. Under the assumption that only singlet states are admixed, as determined by Armstrong *et al.*,[12] there is no direct contribution to the A factor at all.

By using Eqs. (2), (3), and (7) the admixture β^2 of triplet character into singlet series was calculated. Admixture coefficients γ^2 were taken from Armstrong *et al.*[12] The result is shown in Fig. 4. At the lower crossing of $^1D_2$ and $^3D_2$ series, the interaction of $^1D_2$ and $^3D_2$ levels is localized and very weak. Between $n=14$ and 15 a stronger interaction results in a larger singlet-triplet mixing. While the largest admixture ($\sim$5%) occurs at $n=15$, most other states have admixtures far below 1%. Such small admixtures, however, can safely be determined detecting variations of the hyperfine splittings.

In summary, singlet-triplet mixing in $4snd\ ^1D_2$ and $^3D_2$ Rydberg series of ^{43}Ca was determined by means of hyperfine-structure measurements. Even very low admixtures ($<1\%$) can be detected using the hyperfine structure as the probe. Between principal quantum numbers $n=8$ and 9 and $n=14$ and 15, where singlet and triplet series cross, an increase of singlet-triplet mixing was observed with a maximum of 5% at $n=15$. For high principal quantum numbers, the $4snd\ ^1D_2$ series is almost purely LS coupled.

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[1]H. Schüler and E. G. Jones, Z. Phys. 77, 801 (1932).
[2]H. Casimir, Z. Phys. 77, 811 (1932).
[3]L. Barbier, and R. J. Champeau, J. Phys. (Paris) 41, 947 (1980).
[4]R. Beigang and A. Timmermann, Phys. Rev. A 25, 1496 (1982).
[5]P. F. Liao, R. R. Freeman, R. Panock, and L. M. Humphrey, Opt. Commun. 34, 195 (1980).
[6]E. De Clerque, F. Biraben, E. Giacobino, G. Grynberg, and J. Bauche, J. Phys. B 14, L183 (1981).
[7]F. Biraben, E. De Clerque, E. Giacobino, and G. Grynberg, J. Phys. B 13, L685 (1980).
[8]R. R. Freeman, P. F. Liao, R. Panock, and L. M. Humphrey, Phys. Rev. A 22, 1510 (1980).
[9]R. Beigang, E. Matthias, and A Timmermann, Phys. Rev. Lett. 47, 326 (1981).
[10]P. Esherick, Phys. Rev. A 15, 1920 (1977).
[11]H. Rinneberg and J. Neukammer, Phys. Rev. Lett. 49, 124 (1982).
[12]J. A. Armstrong, P. Esherick, and J. J. Wynne, Phys. Rev. A 15, 180 (1977).
[13]K. C. Harvey, Rev. Sci. Instrum. 52, 204 (1981).
[14]A. Lurio, M. Mandel, and R. Novick, Phys. Rev. 126, 1758 (1962).
[15]S. Goudsmit, Phys. Rev. 37, 663 (1931).
[16]R. Beigang, K. Lücke, D. Schmidt, A. Timmermann, and P. West, Phys. Scr. 26, 183 (1982).