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Influence of Singlet-Triplet Mixing on the Hyperfine Structure of $5snd$ Rydberg States in ^{87}Sr

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A systematic study of the hyperfine structure of $5snd$ $^1D_2$ and $^3D_2$ states of ^{87}Sr was car-
ried out by Doppler-free two-photon excitation. In the region of strong singlet-triplet
mixing around $n = 16$, the hyperfine structure exhibits a marked n dependence which is
related to the amount of singlet-triplet mixing.

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For excited states of two-electron systems the
hyperfine structure (hfs) provides a sensitive
probe both for the type of coupling and for possi-
ble admixtures of other states. A typical exam-
ple is the hyperfine structure of $1snd$ ^1D levels in
^{3}He which has been shown to arise from admix-
ture of ^3D states.[1] In their recent study of the
hfs of various levels of ^{3}He, Liao *et al.*[2] empha-
sized the crucial role of the Fermi contact inter-
action of the inner s electron to the electronic
structure of high-n Rydberg states. The singlet-
triplet mixing effects observed in ^{3}He are expect-
ed to also occur in other two-electron systems.
It is therefore of interest to investigate the hfs of
Rydberg states of alkaline-earth atoms, particu-
larly in regions of the principal quantum number
n where mixing of states is indicated by other ex-
periments. The first results on a few levels in
Ba point indeed towards strong perturbations of

the levels investigated.[3] A more favorable case
is Sr, for which Esherick[4] has shown that strong
singlet-triplet mixing occurs in $5snd$ states
around $n = 16$, while for $n \lesssim 10$ and $n \gtrsim 30$ the ^1D
and ^3D can be regarded as being "pure" states.
Wynne, Armstrong, and Esherick[5] verified that
the g factors of $5snd$ $J = 2$ states accurately re-
flect the change of admixture. For the same rea-
son we expect the hfs of ^{87}Sr to vary with the prin-
cipal quantum number between $n = 10$ and 30. It
is the purpose of this Letter to present a first
systematic study of the hfs of $5snd$ Rydberg states
of ^{87}Sr for a wide range of n and to demonstrate
the drastic influence of singlet-triplet mixing on
the hfs. We expect that this will be of importance
also for other two-electron systems.

The energy difference between the ground state
and the $5snd$ states[6] in strontium can be bridged
by two-photon excitation. In our experimental

setup, we closely followed the scheme of Harvey and Stoicheff[7] in which the Doppler-free two-photon excitation was combined with thermionic detection.[8] The application of a narrow-band cw dye laser yields the spectral resolution required to measure the hfs, which is typically between ten and a few hundred MHz. To obtain the power necessary for the two-photon process, a cw ring laser configuration was used. At the peak of Stilben 3 a typical single-mode output power of 150 mW in a bandwidth of 1 MHz was produced.[9] The tuning range of this dye extends from 420 to 470 nm, and hence Rydberg states in the energy range from 42 500 cm^{-1} to the first ionization limit[4] at 45 932.19 cm^{-1} were accessible in this experiment. A wave meter provided a wavelength scale with an absolute accuracy of ± 0.01 cm^{-1}. The frequency separation between the various hyperfine components was calibrated by means of a confocal Fabry-Perot interferometer with a free spectral range of 125 MHz.

Strontium vapor was produced in a stainless-steel pipe heated to about 600 °C corresponding to a vapor pressure of 40 mTorr. No buffer gas was used. Excited Rydberg states were detected by a simple ionization probe. It consisted of a wire, inserted in the center of the pipe, that was charged with typically 0.5 V across a load resistor of 10 kΩ. Such a thermionic diode is particularly well suited for the detection of highly excited states. Its sensitivity increases with increasing n and therefore partly compensates for the decreasing transition probability. A sensitive detection technique was all the more important since the odd isotope ^{87}Sr has a natural abundance of only 7.02% and, for $J = 2$, its intensity is divided up into five hyperfine components. In our case, it was possible to observe the hfs of $5snd$ $^3D_2$ states with good singal-to-noise ratio up to $n \simeq 70$. For high-n states, however, great care was necessary to avoid Stark mixing.[10] The influence of the electric field was checked for each n by varying the voltage from 0.1 to 10 V. Up to $n = 50$, no measurable change of the hfs was observed within the experimental accuracy. For higher n the lines were broadened and their absolute position was shifted but the relative hyperfine splitting remained unchanged.

Typical excitation spectra of the $5snd$ $^1D_2$ and $^3D_2$ series are displayed in Figs. 1 and 2, respectively. The three even isotopes of strontium with an abundancy of 0.56% (^{84}Sr), 9.86% (^{86}Sr), and 82.56% (^{88}Sr) are clearly resolved, the two latter ones being off scale. The interest of this report
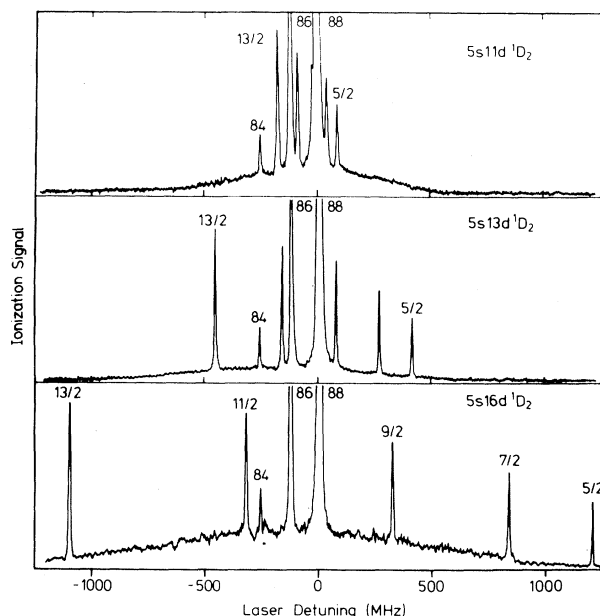

FIG. 1. Two-photon excitation spectra for $5s^2$ $^1S_0-$ $5snd$ $^1D_2$ transitions in natural strontium. Signals due to even isotopes are labeled by mass number, while hyperfine components of ^{87}Sr are marked by their F values.

focuses on the five hyperfine components of ^{87}Sr $(I = \frac{9}{2})$ with F values ranging from $\frac{5}{2}$ to $\frac{13}{2}$. The spectra in Figs. 1 and 2 were selected to demonstrate the strong dependence of the hfs on n. In Fig. 1 the vast increase of the splitting when going from $n = 11$ to 16 is shown for the singlet series. The decrease of the hfs in the triplet series for $n > 16$ is displayed in Fig. 2. The opposite sign of the hfs for triplet and singlet states is obvious from the two figures. For the triplet series there is a sign change of the hfs between $n = 12$ and 13, resulting in the same sign for both series below $n = 12$. Transitions to $5snd$ $^3D_2$ states were observed for $n \geqslant 11$, while $5snd$ $^1D_2$ states could only be excited up to $n = 18$.

All hyperfine spectra obey the interval rule, and hence the quadrupole coupling constant B was assumed to be zero. Under this assumption the magnetic coupling constant A_{exp} was extracted from the spectra by applying a least-squares-fit procedure to all ten possible combinations of hyperfine intervals. The resulting data for A_{exp} are plotted as a function of n in Fig. 3(b) for both the triplet and singlet series. The hfs shows a pronounced resonancelike behavior around $n = 16$ while it remains independent of n for $n > 30$ where pure (jj) coupling exists. In this region, the hfs
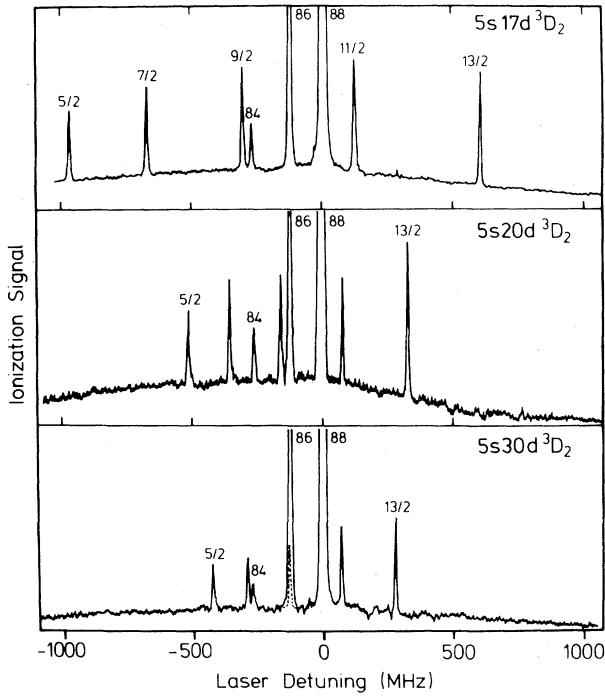
FIG. 2. Two-photon excitation spectra of the $5snd$ $^3D_2$ series. The labeling of the lines is according to Fig. 1.
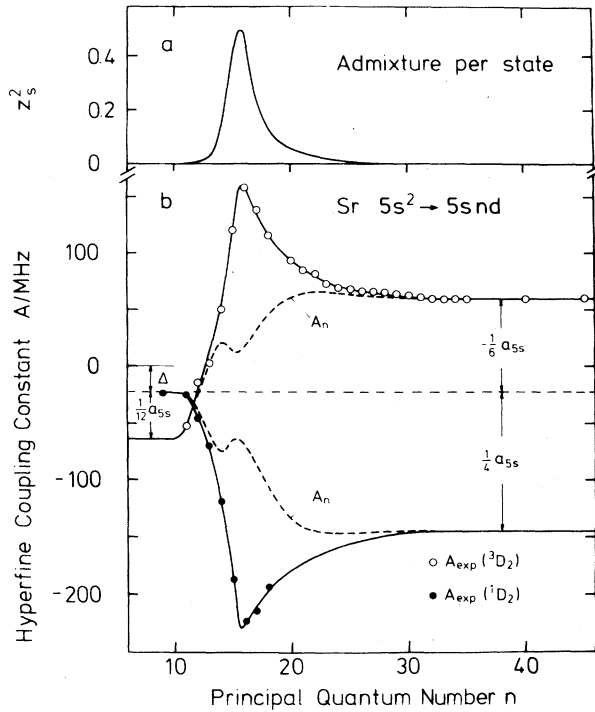

FIG. 3. (a) Amount of admixture of singlet into triplet states taken from the results of Esherick (Ref. 4). (b) n dependence of the experimentally observed hyperfine coupling constants for $5snd$ $^1D_2$ and $5snd$ $^3D_2$ states. The uncertainty of the data is ± 3 MHz. The solid line was calculated with use of the relation given in the text. The dashed line represents the change of coupling necessary to fit the experimental data. The values of the hyperfine coupling constant for pure states in the LS- and (jj)-coupling limit are indicated.

coupling constant $A\,(^3D_2)$ is given by $-a_{5s}/6$, where a_{5s} is the splitting factor describing the Fermi contact interaction of the $5s$ electron. According to conventional analysis[11] for unperturbed states this should be the largest possible value of $A\,(^3D_2)$. The fact that at the peak of the resonance the coupling constant is more than twice the value for (jj) coupling proves the existence of strong admixtures. This is clearly related to the avoided crossing of the $5snd$ $^1D_2$ and $5snd$ $^3D_2$ series. To make this point more obvious, we have plotted in Fig. 3(a) the admixture per state of the singlet into the triplet series, as taken from the multichannel quantum-defect theory (MQDT) analysis of Esherick.[4]

A more quantitative interpretation can be reached by making the following assumptions:
(i) The hyperfine interaction is caused by the $5s$ electron and contributions of the excited electron are negligible. (ii) There is a change of coupling between the two electrons. Below $n = 10$ both series consist of pure states in LS coupling. Above $n = 30$ all states can be described by (jj) coupling. (iii) In the region of the avoided crossing between singlet and triplet series there is an intermediate coupling situation. Here the hfs is predominantly

determined by the mixing between the two series. (iv) There is a screening contribution since the promotion of one electron into higher n states causes a contraction of the $5s$ ion core, leading to an increased $5s$ electron density at the nucleus.

On these grounds the experimentally observed hyperfine coupling constant can be decomposed into three contributions,

$$A_{\mathrm{exp}} = A_n(1 + cz_{s,t}^{\,2}) + \Delta.$$

Here, A_n is the contribution of the pure state, determined by the hyperfine interaction of the $5s$ electron and the coupling between the $5s$ and nd electrons. The singlet-triplet mixing gives rise to the term $cA_n z_{s,t}^{\,2}$, where c is a constant factor, and $z_{s,t}^{\,2}$ is the admixture per state shown in Fig. 3(a). Finally, Δ describes the screening contribution. For simplicity we assume that Δ has reached its saturation value for $n = 10$ and

will remain unchanged for higher n.

Using this phenomenological approach, the data in Fig. 3(b) can be quantitatively reproduced, as indicated by the solid line which was calculated for $\Delta = -22$ MHz, $c = 8.0$, and $a_{5s} = -492$ MHz. The value for a_{5s} was taken from the hfs of the triplet series for large n, assuming (jj) coupling[11] [see Fig. 3(b)]. Unfortunately, this value could not be checked independently since no $^3D_2$ spectra were obtained for the pure LS-coupling case below $n = 10$, and the hfs of the Sr^+ ground state does not seem to be known either. The screening contribution Δ manifests itself by the finite value of $A_{exp}(^1D_2)$ for $n = 9$, since in pure LS coupling the hfs of singlet states should vanish.[11] This value for Δ is supported by the fact that $A_{exp}(^3D_2)$ also is much lower for $n = 12$ than the LS-coupling value $a_{5s}/12$. The sign of Δ originates from the negative nuclear magnetic moment of ^{87}Sr. The dashed lines in Fig. 3(b) indicate the variation of the coupling constant A_n as is required to fit the data. Although the general trend is according to what is expected for a gradual change of coupling between the $5s$ and nd electrons, it seems to be a consequence of the singlet-triplet mixing that some interference effects occur in the intermediate coupling region. However, in view of the simple model applied here, this observation should not be overinterpreted and we leave this point to a more sophisticated treatment.

In conclusion, we have demonstrated in a systematic study the pronounced effect of singlet-triplet mixing on the hfs of Rydberg states in ^{87}Sr. These results prove that hfs measurements are very well suited to detect channel mixing in two-electron systems. A quantitative analysis of the data in terms of a simple model shows that the hyperfine coupling constant contains a contribution which is proportional to the amount of singlet-triplet mixing, as determined by MQDT.[4] This suggests a refinement of MQDT by inclusion of the hyperfine interaction whenever the experimental precision calls for it.

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