DETERMINATION OF ABSOLUTE LEVEL ENERGIES OF 5sns $^1S_0$ AND 5snd $^1D_2$ RYDBERG SERIES OF Sr

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Using an evacuated wavemeter the energies of members of the 5sns $^1S_0$ and 5snd $^1D_2$ Rydberg series of Sr have been determined between principal quantum numbers $10 < n < 80$ with an absolute accuracy of ±30 MHz. The high accuracy allows for the detection of weak perturbations as demonstrated for the $4d^2\ ^3P_0$ perturber of the 5sns $^1S_0$ series. Refined ionization limits for the stable Sr isotopes are presented.

The advent of precise wave meters in combination with frequency stabilized cw dye lasers and Doppler-free spectroscopic methods offers the possibility to improve the accuracy of experimentally determined energy levels by at least two orders of magnitude [1, 2]. Investigations of high Rydberg states using wave meters with an accuracy up to 10^{-8} have been reported recently for the alkaline elements [3,4]. Due to the high accuracy information about weak interactions or perturbations and refined ionization limits can be obtained directly.

Here we report on the determination of level energies for the 5sns $^1S_0$ and 5snd $^1D_2$ Rydberg series of Sr between principal quantum numbers $10 \leqslant n \leqslant 80$. Rydberg states were excited via two-photon transitions from the $5s^2\ ^1S_0$ ground state with a cw ring dye laser working in the wavelength range 420 nm $\leqslant \lambda \leqslant$ 470 nm with Stilbene 3.

A single mode output power up to 200 mW in a bandwidth of 1 MHz was achieved, sufficient for two-photon excitation. The excited Rydberg atoms were detected with a shielded thermionic diode [5] in a stainless steel oven which was heated to 650°C corresponding to a vapor pressure of 25 mTorr. In fig. 1 the optical set-up is shown schematically following the conventional set-up for two-photon spectroscopy. To prevent the feedback into the laser cavity an optical isolator was used which consisted of an optical Faraday rotator and a Glan-Thompson polarizer. For the time necessary to determine the laser frequency the laser was locked to the ^{88}Sr component. This isotope has the highest abundancy in the natural mixture of strontium (82.56%). The energy difference to the other three stable isotopes ^{84}Sr,

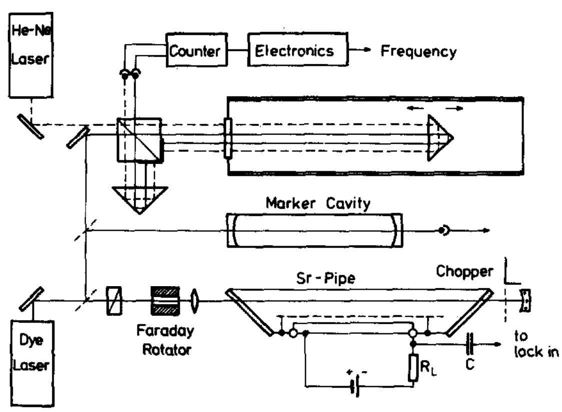

Fig. 1. Principle scheme of the experimental set-up.

^{86}Sr, ^{87}Sr was determined using a stable Fabry-Perot interferometer with a free spectral range of 125 MHz.

The wave meter used in our experiment was of the Michelson type with an optical arrangement similar to the one described in ref. [6]. The basic interferometric assembly consists of two solid retroreflectors and a precision beam splitter cube, whose outer surfaces partially serve as mirrors in the fixed and moving arms of the interferometer, respectively, making internal alignment neither possible nor necessary. The travelling retroflector is mounted on a carriage, which is moved on polished steel rods in the evacuated chamber ($p < 0.1$ Torr), making corrections regarding pressure, temperature, and humidity unnecessary. The angular movement of this retroflector (BK-7) is limited to less than 0.5 deg, resulting in a negligible chromatic error for measurements in the visible spectral range. As the wave meter is a true Michelson interferometer where the reflected beam is collinear with the incoming beam, parallelism of the reference and the signal beam is easily achieved by adjusting both beams for maximal interaction between the wave meter and the respective laser (and thereafter decoupling the wave meter from the lasers by means of optical isolators, if necessary); we estimate that the deviation from parellelism of the two beams is less than 0.1 mrad, resulting in an uncertainty of the frequency determination of less than 5×10^{-9}.

As a reference laser we use a longitudinal Zeeman HeNe laser [7] whose frequency was measured as 473 612 196 MHz ± 1.5 MHz. The moving retroreflector travels over a distance of 87 cm, covering 5.5×10^6 fringes of the reference laser in approximately 5 s, which results in an average fringe frequency of about 1.1 MHz. Due to efficient mechanical decoupling of the travelling carriage from its driving system, the modulation spectrum of the cariage velocity is essentially limited to frequencies well below 100 Hz. Therefore fringe interpolation by means of frequency multiplication is easily achieved. Using two phase-locked loops, we multiply both, reference and signal fringe frequency, by a factor of 10. The multiplied reference fringe frequency is fed to a counter preset to 47361220, which starts and stops the counting of the 10-fold signal fringe frequency. The content of the signal counter is displayed, directly indicating the frequency of the dye laser in 10 MHz units.

The basic uncertainty of this wave meter results from the limited reference count, giving a measurement error of ±10 MHz. The next important error sources are the 8-digit approximation of the reference laser frequency, resulting in a systematic error of 4 MHz, and the non-collinearity of signal and reference beam, giving ±2.5 MHz uncertainty. We estimate that the total inaccuracy of our wave meter is smaller than ±15 MHz.

In addition to errors induced by the wave meter itself, there are several sources for uncertainties which have to be taken into account when claiming an accuracy of 2×10^{-8}. Frequency shifts due to the dc Stark effect are avoided by inserting a grid between the excitation and detection regime of the diode and operating the diode at a very low voltage ($\lesssim 0.5$ V). The influence of the voltage across the diode was checked for different principal quantum numbers n and up to $n = 40$ no shift was observed. For higher quantum numbers n there was a small dependence on the bias voltage and the measured energy values had to be corrected to zero voltage.

Pressure shifts caused by collisions with foreign gas or Sr ground state atoms were checked independently by changing the buffer gas pressure or the temperature of the oven. The influence of foreign gas shifts was reduced by keeping the buffer gas pressure low or extrapolating to zero pressure. We have operated the pipe at an Ar-buffer gas pressure of 100 mTorr. Increasing the pressure to 1 Torr and 10 Torr resulted in a frequency shift of 20 MHz and 200 MHz, respectively for $n = 60$. Corrections were necessary starting at principal quantum numbers $n \sim 35$. For higher principal quantum numbers the influence of perturbing effects on the accurate level position becomes more severe and detailed studies of pressure shifts should be carried out to extract level energies with an accuracy of 2×10^{-8}.

From the $5s^2\ ^1S_0$ ground state the $5sns\ ^1S_0$ and $5snd\ ^1D_2$ Rydberg series are accessible via two-photon transitions. In the region around principal quantum numbers $n = 16$ strong singlet–triplet mixing between the $^1D_2$ and $^3D_2$ series results in a breakdown of pure Russel–Saunders coupling and transitions to $5snd\ ^3D_2$ levels become allowed [8].

It is convenient to describe unperturbed Rydberg series by Langer's formula, which is derived from second order perturbation theory [9]:

$$\delta = n - n^* = a + bT_n + cT_n^2 + dT_n^3 + \sum_i \frac{\alpha_i}{T_n - T_i} \quad (1)$$

where δ is the quantum defect and

$$n^* = R_{\mathrm{Sr}}/T_n\,, \quad T_n = E_{\mathrm{ion}} - E_n\,.$$

E_{ion} is the ionization limit, E_n the level energy and R_{Sr} the Rydberg constant for Sr(R_{Sr} = 109 736.627 cm^{-1} [10]). Weak perturbations are included in eq. (1) using additional constants α_i corresponding to term values T_i of perturbing energy levels. Strong perturbations, like singlet–triplet mixing of the 5snd $^1D_2$ and $^3D_2$ series of Sr, cannot be treated with Langer's formula and a more sophisticated MQDT analysis has to be applied. In the case of Sr this was done using a five channel fit by Esherick [8].

The $^1S_0$ series can be described with eq. (1). Using a least square fit procedure the constants a, b, c, d, α_1 and the ionization limit were determined. To exclude errors due to pressure shifts or other uncertainties at high n values only level energies from n = 10 to 34 were used for the fit. Fig. 2 shows the experimental data and the theoretical curve for the quantum defect δ using the following parameters: a = 3.26897, b = -1.23508×10^{-6} cm, $c = 4.87532 \times 10^{-10}$ cm^2, $d = -7.005 \times 10^{-14}$ cm^3, $\alpha_1 = 3.6059 \times 10^{-2}$ cm^{-1}, and E_{ion} (^{88}Sr) = 45 932.1982 cm^{-1}. According to previous measurements there should be no perturber above n = 10 [8]. Due to the accuracy of this experiment, however, a weak influence of the 4d^2 $^3P_0$ state at 44 525.82 cm^{-1} is clearly observed. This state has to be included in the fit to obtain an agreement with the experimental data which is within our error bars of ±0.001 cm^{-1}. The ionization limits for the isotopes ^{84}Sr are determined to E_{ion} (^{84}Sr) = 45 932.1833 cm^{-1}, and E_{ion} (^{86}Sr) = 45 932.1912 cm^{-1}. The odd isotope ^{87}Sr with a nuclear spin I = 9/2 interacts with its F = 9/2 counterpart of the $^3S_1$ series [11] so that an additional frequency shift $\Delta E = -\frac{1}{2}a_{5s}(I+1)$ has to be included to determine the exact ionization limit (a_{5s} is the Fermi contact term of the lower s electron) [11]. The ionization limit is then given by E_{ion} (^{87}Sr) = 45 932.2861 cm^{-1}.

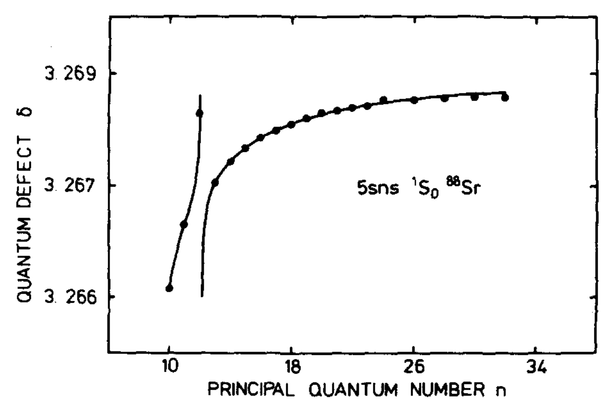

Fig. 2. Plot of the quantum defect σ versus the principal quantum number n for $^1S_0$ states. The solid line is calculated from Langer's formula with the parameters given in the text.

In table 1 the experimental energy values for the $^1S_0$ series are compared with data predicted by eq. (1). The error for these data is less than ±0.001 cm^{-1} for principal quantum numbers $n \leqslant 34$. For higher n the deviations from the predicted data increase due to frequency shifts caused by self or foreign gas broadening. The data show an n-dependence of the frequency shift with a maximum around $n \sim 57$. In addition there is an oscillation superimposed on the frequency shift as a function of n. Similar effects were observed in the case of the alkaline elements [12,13]. The n-dependence of the pressure shift may be caused by collisions between Rydberg and ground state atoms [14]. For an interpretation of this effect a systematic study in the region of high principal quantum numbers is required.

The 5snd $^1D_2$ series is strongly perturbed by the $^3D_2$ series and the 4d6s $^1D_2$ and $^3D_2$ states. The latter two are spread over many principal quantum numbers n as determined by Esherick [8]. Although a fit to Langer's formula is not suitable under these conditions, a simple fit can still be used to predict level positions with the following assumptions:

1) The 4d^2 $^3P_2$ and the 5s14d, 15d, 16d, 17d $^3D_2$ states were included as perturbers. The four $^3D_2$ states are mixed into the singlet series with a considerable amount and are therefore necessary for the fit.

2) In order to account for the 4d6s configuration a hypothetical center of gravity for the $^3D_2$ and $^1D_2$ levels was used.

This 7-parameter fit describes the $^1D_2$ series with an accuracy comparable to the 5 channel MQDT analysis. The agreement with the experimental data is better than 0.01 cm^{-1}. From the 7 parameters used

Table 1
Observed and calculated $5sns\ {}^1S_0$ series

n	E_{obs} |cm^{-1}|	E_{calc} |cm^{-1}|	ΔE |cm^{-1}|	δ_{obs}	δ_{calc}
10.	43512.1658	43512.1659	-.00006	3.26612	3.26612
11.	44097.1224	44097.1221	.00032	3.26699	3.26699
12.	44492.8348	44492.8349	-.00013	3.26847	3.26846
13.	44773.6707	44773.6714	-.00073	3.26754	3.26754
14.	44979.4540	44979.4546	-.00062	3.26783	3.26782
15.	45134.9242	45134.9230	.00122	3.26800	3.26801
16.	45255.2295	45255.2296	-.00009	3.26815	3.26815
17.	45350.2296	45350.2286	.00104	3.26825	3.26826
18.	45426.5505	45426.5499	.00054	3.26834	3.26834
19.	45488.7868	45488.7869	-.00012	3.26842	3.26842
20.	45540.2024	45540.2031	-.00077	3.26849	3.26848
21.	45583.1688	45583.1689	-.00007	3.26853	3.26853
22.	45619.4391	45619.4393	-.00021	3.26857	3.26857
23.	45650.3365	45650.3365	-.00004	3.26860	3.26860
24.	45676.8704	45676.8717	-.00128	3.26869	3.26863
26.	45719.8235	45719.8236	-.00010	3.26869	3.26869
28.	45752.7832	45752.7832	-.00003	3.26873	3.26872
30.	45778.6257	45778.6257	-.00003	3.26876	3.26876
32.	45799.2620	45799.2619	.00011	3.26877	3.26878
34.	45816.0028	45816.0018	.00101	3.26867	3.26880
36.	45829.7700	45829.7679	.00208	3.26849	3.26882
37.	45835.7511	45835.7512	-.00008	3.26884	3.26883
38.	45841.2259	45841.2251	.00080	3.26868	3.26883
39.	45846.2435	45846.2459	-.00240	3.26934	3.26884
40.	45850.8600	45850.8622	-.00224	3.26935	3.26884
41.	45855.1132	45855.1164	-.00323	3.26964	3.26885
42.	45859.0421	45859.0454	-.00327	3.26972	3.26885
43.	45862.6792	45862.6814	-.00221	3.26949	3.26886
44.	45866.0496	45866.0529	-.00334	3.26989	3.26886
45.	45869.1820	45869.1850	-.00301	3.26986	3.26887
46.	45872.0971	45872.0998	-.00268	3.26982	3.26887
47.	45874.8129	45874.8169	-.00398	3.27039	3.26887
48.	45877.3506	45877.3538	-.00318	3.27018	3.26888
49.	45879.7212	45879.7261	-.00493	3.27103	3.26888
50.	45881.9438	45881.9478	-.00400	3.27074	3.26888
51.	45884.0266	45884.0313	-.00470	3.27121	3.26888
52.	45885.9825	45885.9878	-.00535	3.27171	3.26889
53.	45887.8231	45887.8276	-.00447	3.27139	3.26889
54.	45889.5561	45889.5596	-.00351	3.27098	3.26889
55.	45891.1875	45891.1921	-.00460	3.27180	3.26889
56.	45892.7282	45892.7326	-.00444	3.27186	3.26890
57.	45894.1817	45894.1880	-.00625	3.27332	3.26890
58.	45895.5596	45895.5643	-.00466	3.27238	3.26890
59.	45896.8624	45896.8671	-.00469	3.27260	3.26890
60.	45898.0981	45898.1017	-.00361	3.27191	3.26890
61.	45899.2707	45899.2727	-.00198	3.27064	3.26890
62.	45900.3822	45900.3844	-.00216	3.27090	3.26890
63.	45901.4398	45901.4407	-.00087	3.26975	3.26891
64.	45902.4433	45902.4453	-.00196	3.27091	3.26891
65.	45903.3987	45903.4014	-.00270	3.27180	3.26891
66.	45904.3093	45904.3122	-.00285	3.27211	3.26891
67.	45905.1769	45905.1804	-.00357	3.27312	3.26891
68.	45906.0078	45906.0088	-.00097	3.27011	3.26891
69.	45906.7987	45906.7996	-.00090	3.27007	3.26891
70.	45907.5560	45907.5551	.00093	3.26766	3.26891
75.	45910.8718	45910.8708	.00098	3.26727	3.26892
80.	45913.5602	45913.5598	.00045	3.26800	3.26892

Table 2
Observed and calculated 5snd $^1D_2$ series using a = 2.39528, b = 4.0930 × 10^{-4} cm, c = 4.91020 × 10^{-8} cm^2 and d = 2.04771 × 10^{-11} cm^3. The perturbers are listed in table 3.

n	E_{obs} |cm^{-1}|	E_{calc} |cm^{-1}|	ΔE |cm^{-1}|	δ_{obs}	δ_{calc}
10.	44239.4549	44239.4549	-.00005	1.94844	1.94844
11.	44578.6890	44578.6889	.00006	1.99580	1.99580
12.	44829.6648	44829.6648	.00002	2.02346	2.02346
13.	45012.0249	45012.0249	-.00003	2.07954	2.07954
14.	45153.2785	45153.2785	-.00004	2.13058	2.13058
15.	45263.6196	45263.6196	.00001	2.18851	2.18851
16.	45362.1272	45362.1271	.00012	2.12569	2.12569
17.	45433.2717	45433.2715	.00017	2.16944	2.16944
18.	45492.6101	45492.6201	-.01004	2.20015	2.19997
19.	45542.2955	45542.2711	.02438	2.22364	2.22417
20.	45584.1831	45584.1782	.00485	2.24271	2.24283
21.	45619.7872	45619.7890	-.00183	2.25814	2.25809
22.	45650.2617	45650.2709	-.00919	2.27122	2.27090
23.	45676.5325	45676.5461	-.01355	2.28239	2.28184
24.	45699.3308	45699.3442	-.01336	2.29192	2.29129
25.	45719.2336	45719.2462	-.01259	2.30020	2.29952
26.	45736.7165	45736.7182	-.00173	2.30685	2.30675
28.	45765.8106	45765.8110	-.00043	2.31880	2.31876
29.	45777.9907	45777.9913	-.00063	2.32385	2.32380
30.	45788.8895	45788.8870	.00252	2.32806	2.32831
31.	45798.6753	45798.6716	.00368	2.33196	2.33236
32.	45807.4942	45807.4907	.00349	2.33559	2.33601
33.	45815.4703	45815.4667	.00359	2.33884	2.33932
34.	45822.7079	45822.7034	.00450	2.34167	2.34232
35.	45829.2918	45829.2891	.00268	2.34463	2.34505
36.	45835.3098	45835.2994	.01039	2.34575	2.34755
37.	45840.8107	45840.7993	.01144	2.34767	2.34984
38.	45845.8526	45845.8447	.00787	2.35031	2.35193
39.	45850.4882	45850.4844	.00379	2.35301	2.35386
40.	45854.7641	45854.7606	.00352	2.35479	2.35564
42.	45862.3725	45862.3656	.00694	2.35684	2.35881
43.	45865.7610	45865.7552	.00579	2.35845	2.36022
44.	45868.9075	45868.9042	.00328	2.36046	2.36154
45.	45871.8381	45871.8348	.00329	2.36160	2.36276
46.	45874.5690	45874.5667	.00230	2.36303	2.36390
47.	45877.1177	45877.1174	.00028	2.36485	2.36496
48.	45879.5076	45879.5026	.00496	2.36381	2.36596
49.	45881.7351	45881.7364	-.00125	2.36747	2.36689
50.	45883.8322	45883.8311	.00110	2.36723	2.36777
51.	45885.7953	45885.7982	-.00288	2.37010	2.36859
52.	45887.6482	45887.6477	.00046	2.36911	2.36936
53.	45889.3906	45889.3889	.00165	2.36912	2.37009
54.	45891.0300	45891.0301	-.00011	2.37084	2.37078
55.	45892.5800	45892.5787	.00128	2.37058	2.37143
56.	45894.0409	45894.0416	-.00073	2.37255	2.37204
57.	45895.4215	45895.4250	-.00352	2.37523	2.37262
58.	45896.7331	45896.7346	-.00146	2.37431	2.37317
59.	45897.9755	45897.9754	.00009	2.37361	2.37369
60.	45899.1528	45899.1523	.00051	2.37373	2.37418
61.	45900.2719	45900.2695	.00239	2.37245	2.37465
62.	45901.3328	45901.3310	.00175	2.37340	2.37509
63.	45902.3404	45902.3405	-.00013	2.37565	2.37551
64.	45903.3024	45903.3013	.00109	2.37475	2.37592
65.	45904.2175	45904.2165	.00103	2.37514	2.37630
66.	45905.0896	45905.0888	.00076	2.37578	2.37667
67.	45905.9232	45905.9211	.00214	2.37438	2.37702
68.	45906.7247	45906.7155	.00915	2.36557	2.37735
69.	45907.4771	45907.4746	.00254	2.37424	2.37767
70.	45908.1945	45908.2002	-.00566	2.38595	2.37797
74.	45910.8054	45910.8052	.00023	2.37868	2.37906
75.	45911.3891	45911.3901	-.00105	2.38113	2.37931
79.	45913.5019	45913.5056	-.00368	2.38773	2.38019
80.	45913.9752	45913.9840	-.00883	2.39920	2.38039
84.	45915.7197	45915.7253	-.00556	2.39489	2.38112

Table 3
Parameters and perturbers of the 5s*n*d $^1D_2$ series

i	configuration	α_i [cm^{-1}]	T_i [cm^{-1}]
1	$4d^2\ ^3P_2$	1.41171	44729.6 a)
2	$6s4d\ ^1D_2$	-1.24362×10^{-1}	45056.1 a)
3	$5s14d\ ^3D_2$	-1.91179×10^{-2}	45171.4855 b)
4	$5s15d\ ^3D_2$	6.30983×10^{-3}	45276.6501 b)
5	$5s16d\ ^3D_2$	2.76760	45350.5057 b)
6	$6s4d\ ^3D_2$	9.92291×10^{-1}	45367.4 a)
7	$5s17d\ ^3D_2$	-1.72120×10^{-1}	45420.8374 b)

a) Ref. [8]. b) This work.

in this fit, of course, only the parameter a has a physical meaning: a is the quantum defect δ_∞ when approaching the ionization limit.

In table 2 the experimental data are listed together with theoretical data using Langer's formula. With the exception of the 5s10d $^1D_2$ state there is good agreement with previous data obtained by Esherick [8] and Rubbmark [10]. Up to $n \approx 35$ the maximum error is again smaller than 0.001 cm^{-1}. For high principal quantum numbers there is no obvious n-dependent frequency shift as was the case for the 5s*n*s $^1S_0$ series.

In summary, the use of Doppler-free two-photon spectroscopy in combination with a wave meter allows for the energy determination of Rydberg states of Sr with an accuracy of 2×10^{-8}. Using an extended Rydber-Ritz formula the ionization limit for the isotope ^{88}Sr was determined to 45 532.1982 cm^{-1} ± 0.0010 cm^{-1}. Weak perturbations can be detected as demonstrated for the 5s*n*s $^1S_0$ series, which is perturbed by the $4d^2\ ^3P_0$ state.

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