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Jönsson, G.; Kröll, Stefan; Persson, Anders; Svanberg, Sune

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Natural radiative lifetimes in the $3sns\ {}^1S_0$ and $3snd\ {}^1D_2$ sequences of magnesium

G. Jönsson, S. Kröll, A. Persson, and S. Svanberg

Department of Physics, Lund Institute of Technology, S-220 07 Lund 7, Sweden

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Natural radiative lifetimes have been determined in the $3sns\ {}^1S_0$ ($n=4-15$) and the $3snd\ {}^1D_2$ ($n=3-15$) sequences of Mg I employing a pulsed-laser system. The radiative lifetimes in the ${}^1S_0$ sequence and of the higher members in the ${}^1D_2$ sequence are unperturbed and scale as $(n^*)^{2.6}$ (where n^* is the effective principal quantum number), while the lifetimes of the lower members in the ${}^1D_2$ sequence are perturbed by the doubly excited $3p^2$ configuration. The measured lifetimes are compared with available theoretical calculations, and a very good agreement is obtained.

INTRODUCTION

The main perturbers of the Rydberg series in the heavier alkaline-earth atoms $_{20}$Ca, $_{38}$Sr, and $_{56}$Ba are states belonging to doubly excited configurations with one of the excited electrons in a low-lying, normally empty d shell within the electronic core. The main features of the perturbations in these Rydberg states could, to a large extent, be parametrized and treated in a unified way using multichannel quantum-defect theory (MQDT).[1] Lately, a considerable amount of new information about the interactions in these Rydberg series has been obtained in studies of Landé factors, lifetimes, and hyperfine-induced singlet-triplet and n mixing; see, e.g., Refs. 2—5. This has resulted in a refinement of the MQDT theory.

The lighter alkaline-earth atoms $_4$Be and $_{12}$Mg have no empty d shells within the electronic core. The main perturbers of the singly excited even-parity Rydberg series belong to the $2p^2$ and $3p^2$ configurations, respectively. In this investigation, natural radiative lifetimes of the $3sns\ {}^1S_0$ ($n=4-15$) and the $3snd\ {}^1D_2$ ($n=3-15$) sequences have been determined. The measurements were performed on a beam of Mg atoms emanating from a resistively heated oven. A pulsed-laser system was used for excitation. Time-resolved detection was employed in registering the fluorescence. Two-step excitation, two-photon absorption, or one-step excitation of metastable atoms, produced in a discharge in the atomic beam, was used for populating the investigated states.

Beigang and co-workers have recently measured energy-level positions and hyperfine structures in Mg.[6] References to earlier work on Mg can be found in a monograph on Mg I through Mg XII.[7] Schaefer has measured the lifetimes for several states in the $nd\ {}^1D_2$ sequence using the delayed-coincidence technique in a pulsed hollow-cathode discharge.[8] Several other authors have also performed lifetime measurements in Mg I (see Refs. 9 and 10, and references therein).

EXPERIMENTAL TECHNIQUES

The setup used in this investigation is shown in Fig. 1. In the measurements we used one or two dye lasers, depending on the excitation scheme. The dye lasers were pumped by a Lambda Physik model EMG-102-E excimer laser operating with XeCl at 308 nm. The excimer laser produced 100 mJ per pulse at 10 Hz repetition rate. When performing two-step excitation, about 10% of the excimer-laser light was used to pump a homebuilt Littman-cavity dye laser[11] operating on Coumarin-153 dye. Yellow light, with a pulse energy of approximately 1 mJ, was frequency-doubled in a KD*P (deuterated potassium dihydrogen phosphate) crystal to yield the 285-nm uv light necessary for the first step. The second-step tunable radiation was obtained from a Lambda Physik model FL-2002 dye laser, operating on TBS, Stilbene-3, Coumarin-120, or Coumarin-47 dye. The two beams were spatially and temporally overlapped in a beam of magnesium atoms formed in a vacuum system.

In the two-photon absorption experiments, the light from the FL-2002 dye laser alone was focused in the atomic beam in order to populate low-lying ${}^1S_0$ and ${}^1D_2$ levels. Excitation from the metastable $3s\,3p\ {}^3P$ states, populated by a discharge in the atomic beam, was also performed with this dye laser. A pair of Helmholtz coils generated a static magnetic field of about 2 mT in the excitation volume to ensure that the frequency of the produced Zeeman quantum beats was beyond the high-frequency cutoff limit of the detection system. The fluorescent light passed through appropriate colored-glass and interference filters and was detected by an EMI model 9816 QB photomultiplier tube. The optical transients were captured by a Biomation model 8100 transient
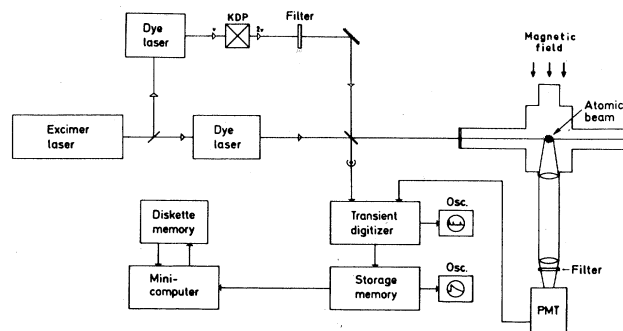

FIG. 1. Experimental setup.

digitizer and the signals were added in a storage memory in order to increase the signal-to-noise ratio. The added signals were transferred to a floppy disk and a nonlinear least-squares fit to an exponential was performed in a Digital Equipment Corporation PDP-11 V03 computer.

MEASUREMENTS AND RESULTS

Figure 2 shows a schematic energy-level diagram for Mg I. Excitation wavelengths were calculated from Ref. 7. Wavelengths for the $3sns$ $^1S_0$ states above $n = 10$ were calculated assuming a constant quantum defect in the $^1S_0$ sequence. Generally, two-step excitation via the short-lived $3s\,3p$ $^1P_1$ state [~ 2 ns (Ref. 9)] was employed. For the four lowest states, two-photon absorption from the ground state was used. Populating the metastable $3s\,3p$ $^3P_1$ level in an electric discharge and exciting on the $\lambda = 4621$ Å intercombination line yielded consistent results for the lifetime of the $3s\,4s$ $^1S_0$ state. In the measurements on the higher $^1S_0$ states, detection could be made in the cascade fluorescence from the $3s\,4p$ $^1P_1 - 3s^2$ $^1S_0$ transition as well as on the laser wavelength. The influence on the recorded signal from the lifetime of the $4p$ $^1P_1$ state [~ 10 ns (Ref. 9)] can be disre-
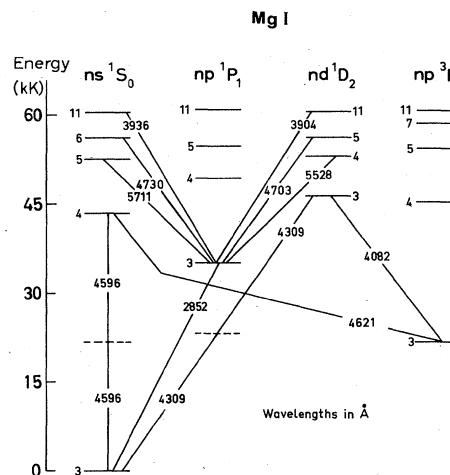

FIG. 2. Schematic energy-level (given in kilokaysers, 1 K $\equiv 1$ cm^{-1}) diagram for Mg I.

garded. For the $^1D_2$ states, detection via the $4p$ $^1P_1$ state turned out to be very disadvantageous. This is in agreement with calculations by Froese Fischer,[12] where the

TABLE I. Experimental values for the natural radiative lifetimes. Excitation wavelength and method of excitation are included. In case of two-step excitation, the first-step laser was tuned to the $3s^2$ $^1S_0 - 3s\,3p$ $^1P_1$ transition at $\lambda = 2852.13$ Å. (TS denotes two-step excitation, TP denotes two-photon absorption, and M denotes excitation from a metastable state.)

| | Experimental lifetimes | | | |
| | This work | Schaefer[a] | Wavelength[b] | |
State	(ns)	(ns)	(Å)	Methods of excitation
$3s\,4s$ $^1S_0$	47(3)		4596.00, 4621.30	TP,M
$3s\,5s$ $^1S_0$	100(5)	163(8)	3804.30	TP
$3s\,6s$ $^1S_0$	211(12)	201(4)	4730.03	TS
$3s\,7s$ $^1S_0$	350(16)		4354.53	TS
$3s\,8s$ $^1S_0$	548(35)		4165.10	TS
$3s\,9s$ $^1S_0$	846(40)		4054.69	TS
$3s\,10s$ $^1S_0$	1155(58)		3984.21	TS
$3s\,11s$ $^1S_0$	1650(140)		3936.30[c]	TS
$3s\,12s$ $^1S_0$	2150(180)		3902.15[c]	TS
$3s\,13s$ $^1S_0$	2507(225)		3876.92[c]	TS
$3s\,14s$ $^1S_0$	2960(210)		3857.73[c]	TS
$3s\,15s$ $^1S_0$	3500(260)		3842.79[c]	TS
$3s\,3d$ $^1D_2$	81(6)	57.0(3.6)	4308.76	TP
$3s\,4d$ $^1D_2$	57(3)	54.9(1.4)	3762.89	TP
$3s\,5d$ $^1D_2$	50(4)	44.3(2.4)	4702.99	TS
$3s\,6d$ $^1D_2$	54(3)	50.3(2.2)	4351.91	TS
$3s\,7d$ $^1D_2$	70(6)	73.1(2.7)	4167.27	TS
$3s\,8d$ $^1D_2$	93(7)	85.4(10.5)	4057.51	TS
$3s\,9d$ $^1D_2$	127(8)	99.4(9.4)	3986.75	TS
$3s\,10d$ $^1D_2$	167(17)	66(15)	3938.40	TS
$3s\,11d$ $^1D_2$	239(25)	37.1(3.4)	3903.86	TS
$3s\,12d$ $^1D_2$	298(20)	32.1(2.9)	3978.31	TS
$3s\,13d$ $^1D_2$	359(26)		3858.86	TS
$3s\,14d$ $^1D_2$	430(30)		3843.63[d]	TS
$3s\,15d$ $^1D_2$	535(50)		3832.76[d]	TS

[a]From Ref. 8.
[b]When nothing else is noted, wavelengths are taken from Ref. 23.
[c]Calculated values assuming a constant quantum defect of 1.524 in the $^1S_0$ sequence.
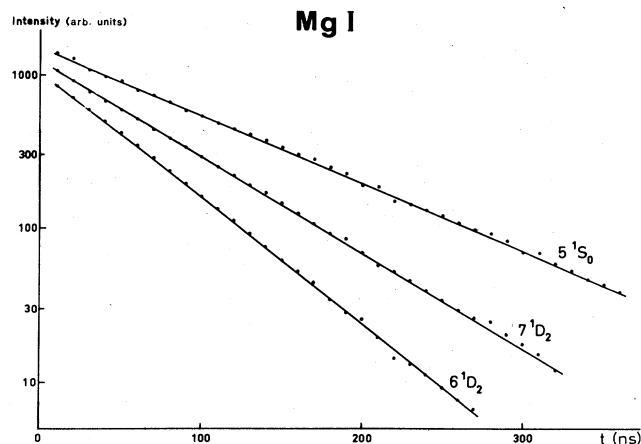[d]Calculated from Ref. 7.

FIG. 3. Three experimental decay curves shown on a semilogarithmic scale. The $5s$ $^1S_0$ state was excited by two-photon absorption.

transition probabilities from nd $^1D_2$ to $4p$ $^1P_1$ for $n=3-8$ are 1 or 2 orders of magnitude lower than those from nd $^1D_2$ to $3p$ $^1P_1$. However, for the ns $^1S_0$ states, transition probabilities to $3p$ $^1P_1$ and $4p$ $^1P_1$ are of comparable size.[13] For the $4s$ $^1S_0$ and $3d$ $^1D_2$ states, detection was made at the $3s\,3p$ $^1P_1-3s^2$ $^1S_0$ resonance transition. By lowering the density in the atomic beam it was assured that multiple scattering did not affect the lifetimes. In the same way, it was also assured that the lifetimes of the long-lived $^1S_0$ states were not affected by collisions. Other possible errors and disturbances such as flight-out-of-view effects and rf noise from the excimer laser were taken care of as in previous measurements.[14,15] A more thorough discussion of possible systematic errors in lifetime measurements can be found in Ref. 16.

Every state was measured at several different occasions. Generally, between two and four recordings for each state were taken at every occasion. Between 500 and 2000 transients were normally appropriate for obtaining a good signal-to-noise ratio. In Fig. 3 three typical experimental curves are shown. For the $5s$ $^1S_0$ state two-photon absorption was used. Our lifetime values together with excitation wavelengths and method of excitation are given in Table I. The stated error limits include both statistical scattering and an estimation of possible systematic influences. The lifetimes of the $^1S_0$ states above $n=10$ can possibly be affected by black-body-radiation—induced transitions,[17] but due to good fitting with the rest of the $^1S_0$ sequence this effect is not expected to be more than a few percent.

At high atomic-beam densities several transitions could be observed around the $3p$ $^1P_1-10d$ $^1D_2$ and $3p$ $^1P_1-11s$ $^1S_0$ transitions. These signals were comparable in strength to the $3p$ $^1P_1-11s$ $^1S_0$ transition, but had decay times similar to that of the $10d$ $^1D_2$ level. They also required the presence of both laser beams. A possible cause of these signals is laser-enhanced formation of Mg_2 dimers in an excited state and subsequent excitation to still higher states. Two Mg atoms in their ground state can collide and form a Mg_2 molecule in its $^1\Sigma_g^+$ ground state.[18] For this state the potential curve is very shallow

and the energy of the molecule is only some 400 cm^{-1} less than the energy of two free $3s^2$ $^1S_0$ Mg atoms.

However, in a collision between a Mg atom, excited to $3s\,3p$ $^1P_1$ by the first-step laser, and a ground-state Mg atom, the formation of the A $^1\Sigma_u$ state of the molecule is an energetically very favorable process.[18] The formation of the A $^1\Sigma_u$ state after excitation with the first-step laser is also supported when observing the fluorescence from the $3s\,3p$ $^1P_1$ state when the second-step laser is blocked. Although the lifetime of the $^1P_1$ state is ~ 2 ns, fluorescence could still be observed after ~ 100 ns. This then would originate from the A $^1\Sigma_u$ molecules returning to the $^1\Sigma_g$ ground state. The effect described above was not observed when two-photon absorption was used to populate the nd $^1D_2$ and ns $^1S_0$ states[6] and thus our lifetime measurements of the $4s$ $^1S_0$ and $3d$ $^1D_2$ states employing resonance-line detection are unaffected.

DISCUSSION

In Fig. 4 a diagram of the experimental lifetimes τ versus n^* is shown on a logarithmic scale for the $^1S_0$ and $^1D_2$ sequences. A line corresponding to a $(n^*)^3$ dependence of the lifetimes, expected for a hydrogenlike case, is included. For the $^1S_0$ sequence, a least-squares fit yields $\tau=4.22(n^*)^{2.62}$, and in the $^1D_2$ sequence we obtain $\tau=0.45(n^*)^{2.65}$ for $n=8-15$. The lifetimes in the $^1S_0$ sequence seem to be essentially unperturbed, while the lifetimes of the lower $^1D_2$ are strongly affected by admixture of $3p^2$ $^1D_2$ character into the wave functions. The six lowest $3snd$ $^1D_2$ states together contain 50% of the total $3p^2$ $^1D_2$ wave function and the rest is mixed into the higher $3snd$ $^1D_2$ members and the adjacent continuum. Thus, the $3p^2$ $^1D_2$ state does not exist as a well-defined level and none of the observed levels has been assigned the $3p^2$ $^1D_2$ symbol.[19]

In Table II our experimental lifetimes are compared with lifetimes calculated from theoretical oscillator strengths given by Froese Fischer.[12,13] Oscillator strengths calculated from the experimental lifetime values using the
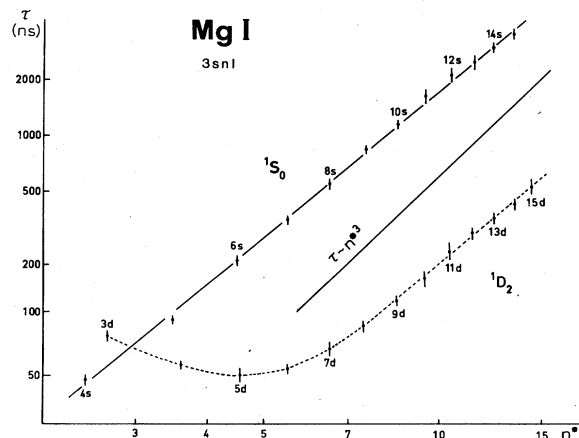

FIG. 4. Our experimental lifetime values versus the effective principal quantum number drawn on a double-logarithmic scale. A slope corresponding to a $(n^*)^3$ dependence is included.

TABLE II. Comparison between the experimental lifetimes and lifetimes calculated from theoretical oscillator strengths. (gf denotes oscillator strength in emission multiplied with the degeneracy of the upper level.)

State	Lifetimes (ns) Experiment	Theory[a]	Experimental gf values[b] in transitions to $3s\,3p\ {}^1P_1$
$3s\,4s\ {}^1S_0$	47(3)	45	0.45(3)
$3s\,5s\ {}^1S_0$	100(5)	102	0.019(1)
$3s\,6s\ {}^1S_0$	211(12)	202	0.0040(2)
$3s\,7s\ {}^1S_0$	350(16)	362	0.001 56(7)
$3s\,3d\ {}^1D_2$	81(6)	93	0.72(5)
$3s\,4d\ {}^1D_2$	57(3)	40	0.49(3)
$3s\,5d\ {}^1D_2$	50(4)	38	0.30(3)
$3s\,6d\ {}^1D_2$	54(3)	50	0.25(2)
$3s\,7d\ {}^1D_2$	70(6)	65	0.17(2)
$3s\,8d\ {}^1D_2$	93(7)	93	0.13(1)

[a]The oscillator strengths for the theoretical values are taken from Refs. 12 and 13.
[b]Branching ratios taken from Refs. 12 and 13 have been used.

branching ratio obtained from Refs. 12 and 13 are also included. In the $^1S_0$ sequence, agreement between experimental and theoretical lifetimes is excellent. The behavior of the $^1D_2$ sequence is also fully explained. The $3p^2\,{}^1D_2$ admixture is strongest in the state designated $3s\,3d\ {}^1D_2$ where the principal quantum numbers are all the same. The oscillator strength for a pure $3p^2\,{}^1D_2-3s\,3p\ {}^1P_1$ transition is large, but the mixing of $3p^2\,{}^1D_2$ character into

the $3snd\ {}^1D_2$ wave function through interference leads to a reduction of the

$$\langle \alpha 3snd\ {}^1D_2 + \beta 3p^2\,{}^1D_2 \mid P \mid 3s\,3p\ {}^1P_1 \rangle$$

matrix element for the oscillator strength (P is the dipole operator; $\alpha^2 + \beta^2 = 1$), thus increasing the actual lifetime. This effect is similar to what was recently observed for the $4d\,5p\ {}^1F_3$ perturber in the $5snf\ {}^1F_3$ series in Sr.[20] The lifetime of a state is, in general, very sensitive to the relative signs of the interacting wave functions. However, when calculating the lifetime of a perturbed state high up in a Rydberg sequence it is often reasonable to assume that interference effects average to zero when summing over all the individual transition probabilities. This approach is generally used in MQDT.[21,5] With the above assumptions it is then appropriate to only use the square of the mixing coefficients to calculate the amount of perturber character in a state,[22] even if information about the relative signs of the wave functions then is lost.

As can be seen, the experimental lifetime values support the theoretical calculations by Froese Fischer. Similar theoretical results, but with slightly weaker admixture, are obtained by Beigang et al. in MQDT calculations based on the positions of energy levels.[6] It would be interesting to further probe the interaction in the $3snd\ {}^1D_2$ sequence by studying the hyperfine structure of ^{25}Mg.

ACKNOWLEDGMENTS

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