Lifetimes and energy levels for some core-excited quartet states in Na I

J. O. Gaardsted and T. Andersen
Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark
(Received 30 June 1987)

The core-excited quartet spectrum of Na I produced by beam-foil excitation has been studied in the 3300–5500-Å region. Sixteen new lines, representing transitions between the $2p^5 3s 3p$, $2p^5 3s 3d$, and $2p^5 3s 4s$ configurations, are reported, together with the lifetimes for 12 of the levels belonging to the $2p^5 3s 3d$ and $2p^5 3s 4s$ configurations. Some of the lifetimes deviate considerably from recently published values [L. Engström, L. Young, L. P. Sommerville, and H. Berry, Phys. Rev. A **32**, 1468 (1985)], including the lifetimes of the $2p^5 3s 3d\ ^4D_{3/2}$ and $^4F_{5/2}$ levels, which have both been suggested for use in an extreme ultraviolet (xuv) laser. The experimental data for fine-structure splittings and lifetimes are in good agreement with multiconfiguration Hartree-Fock calculations.

I. INTRODUCTION

The core-excited quartet levels of Na I have attracted new interest[1–4] because of their metastability against autoionization. For this reason, these levels are of interest for atomic spectroscopy, for studies of atomic and molecular collisional phenomena, and for construction of extreme-ultraviolet (xuv) lasers.

Before 1985, only two of the more than 50 possible transitions between the lower-lying ^4L terms belonging to the $2p^5 3s 3p$, $2p^5 3s 3d$, and $2p^5 3s 4s$ configurations had been observed.[5,6] Holmgren *et al.*[1] established 15 of the quartet levels in these configurations from 30 identified transitions. The spectra were obtained with a high-power, pulsed hollow-cathode discharge. The identifications were confirmed by observing enhanced fluorescence when the population of the upper level was selectively increased through the use of a laser. The experimental assignments were supported by theoretical calculation, using the atomic code RCN/RCG (Ref. 7) which is based on a multiconfiguration Hartree-Fock model with empirically adjusted Slater parameters.

Holmgren *et al.*[1] also proposed two xuv lasers based on population storage in the $2p^5 3s 3p\ ^4S_{3/2}$ level and followed by radiative transfer to the upper laser level, the $2p^5 3s 3d\ ^4D_{3/2}$ or $^4F_{5/2}$ levels which could subsequently decay to the lower laser level $2p^6 3d\ ^2D$ with emission of 379-Å photons. The properties of the upper laser levels such as the radiative lifetime or the autoionization rate were based only on calculations. Engström *et al.*[2] tested the theoretical predictions by performing lifetime measurements for eight of the excited $3s3d$ and $3s4s$ levels, using the beam-foil technique. They reported that the measured and predicted lifetimes could deviate by up to a factor of 3. Significant deviations were observed both for levels with a negligible autoionization rate ($3s4s\ ^4P_{5/2}$) and for levels with a rather large autoionization rate ($3s3d\ ^4D_{3/2}$).

More recently, Froese Fischer[3] has reported the results of a multiconfiguration Hartree-Fock (MCHF) calculation with relativistic effects included through the Breit-Pauli (BP) approximation.[8] The MCHF+BP method provides a mechanism for determining a portion of a spectrum in a single calculation, a portion that in the case of Na I contains many levels. The MCHF+BP calculation was able to reproduce all of the fine-structure splittings obtained experimentally.[1]

A comparison between the autoionization rates reported by Froese Fischer[3] and those obtained by Cowan's code[1,2] shows deviations by up to a factor of 10^4. It should be noted that the two sets of calculations are based on principally the same method and deviate only in the mathematical details and exactness.[3,9] Since the autoionization rates of interest for ^4L levels in Na I are of the order of 10^6–10^{10} s^{-1}, reasonably accurate predictions for autoionization rates are needed to predict reliable lifetimes which are needed for the proposed upper laser levels. Plausible autoionization rates are also needed for the correct assignment of levels. The level $3s3d\ ^4D_{5/2}$ (Ref. 1) should be reassigned as $3s3d\ ^4P_{5/2}$ (Ref. 3) since the autoionization rate for $^4D_{5/2}$ may be 4 orders of magnitude larger than predicted by Cowan's code. This reassignment is supported by the fine-structure data[3] and by the intensity[1] of the 3489.0-Å line.

The use of the *LS* notation for some of the levels belonging to the $2p^5 3s 3d$ configuration may not be meaningful since this configuration exhibits strong deviations from *LS* coupling. Froese Fischer[5] has calculated the percentages for the level called "$^4D_{5/2}$" to be 48% ^4D, 27% ^4F, and 18% ^4P, whereas "$^4P_{5/2}$" has the percentages 45% ^4P, 44% ^4D, and 9% ^4F. The use of the *LS* notation for some of the $2p^5 3s 3d$ levels in this paper is justified only by the use of this notation in the three publications[1–3] which initiated this study, and to which the reader is often referred.

On the basis of the significant discrepancies pointed out above between the two sets of calculations[1,3] and between some of the experimental[2] and calculated lifetimes,[1,3] the present study was initiated with the purpose of exploring some of the reasons for these discrepancies. In addition, we wanted to investigate whether it would be possible, by means of the beam-foil technique, to identify

additional levels belonging to the $2p^5 3s 3p$, $2p^5 3s 3d$, or $2p^5 3s 4s$ configurations, but which were not reported by Holmgren *et al.*[1]

II. EXPERIMENT

The experimental setup has been described previously,[10] and only the few changes from the original setup will be mentioned here. Na^+ ions with energies ranging from 80 to 150 keV were passed through 5-$\mu g/cm^2$ carbon foils. Observation of the light emitted in the 2000–6000-Å wavelength region was performed with a 1.0-m McPherson model 2051 spectrometer equipped with a 2400-line/mm or a 1200-line/mm grating. A circular encoder was mounted on the spectrometer, permitting accumulation of data from several scans in a NORD-12 satellite computer which also controlled the spectrometer.

The assignment of unknown spectral lines was based upon a number of criteria: Line intensity versus beam-energy measurements or Doppler-shift measurements were used to determine the charge states of the light-emitting particles; lifetime measurements were used to test assignment of spectral lines assumed to originate from the same upper level; relative line-intensity measurements were performed and compared with line intensities predicted on the basis of theoretical calculations, assuming the *LS* coupling is valid, and, finally, the Ritz-Rydberg combination principle was used to test closed loops, utilizing the fact that many quartet levels for Na I already were well established on the basis of Holmgren *et al.*'s study.[1]

Careful attention has been paid to the observation of spectral lines at various distances very near the surface since it was observed that the spectra contained lines with very short lifetimes (less than 70 ps). The decay curves have been recorded and analyzed as described previously.[10,11]

III. RESULTS AND DISCUSSION

A. Energy levels

All the 30 spectral lines reported by Holmgren *et al.*[1] for transitions between the $2p^5 3s 3p$ and the $2p^5 3s 3d$ and $2p^5 3s 4s$ configurations have been observed within the accuracy of 0.2 Å given.[1] The relative intensities of the spectral lines were in good agreement with the observations of Holmgren *et al.*[1] except for a few transitions. These intensity deviations are connected to spectral lines used for laser pumping.[1] Most noticeable was the change in the line intensities for the spectral lines depopulating the $2p^5 3s 4s\ ^4P_{5/2}$ level. Holmgren *et al.* reported the experimental intensity ratio for the lines at 4432.3 Å (decay to $2p^5 3s 3p\ ^4S_{3/2}$) and 5071.2 Å (decay to $2p^5 3s 3p\ ^4D_{7/2}$) to be 3.1:2.7. Our data show that the ratio is close to 1:3, in good agreement with calculated branching ratios.[1]

The beam-foil spectra exhibit a large number of spectral lines belonging to the Na I ^4L-term scheme. Among these, 16 spectral lines can be assigned to transitions either between already established levels[1] such as $2p^5 3s 3d\ ^4D_{3/2} \rightarrow 2p^5 3s 3p\ ^4D_{5/2}$ or to $^4P_{3/2}$, or to transitions between levels, of which one had not been identified before. Table I gives the assignment of the transitions, and the experimental and theoretical wavelengths.[3] Figure 1 shows a small portion of the spectrum fitted to the experimental data. Figure 2 (see later) exhibits another section.

TABLE I. Na I quartet transition wavelengths.

Upper level	Lower level	λ_{expt}[a] (Å)	λ_{theor}[b] (Å)
$3s4s\ ^4P_{3/2}$	$3s3p\ ^4S_{3/2}$	4326.3±0.4	4315
	$^4D_{5/2}$	5019.8±0.2	4977
	$^4D_{3/2}$	5109.6±0.2	5065
	$^4P_{5/2}$	5451.9±0.2	5440
	$^4P_{3/2}$	5569.9±0.9	5536
	$^4P_{1/2}$	5628.5±0.5	5619
$3s4s\ ^4P_{1/2}$	$^4D_{3/2}$	4975.3±0.3	4931
	$^4D_{1/2}$	5049.4±0.2	5003
	$^4P_{3/2}$	5411.0±0.4	5396
	$^4P_{1/2}$	5466.4±0.5	5455
$3s3d\ ^4D_{3/2}$	$^4D_{5/2}$	3833.6±0.2	3850
	$^4P_{3/2}$	4146.2±0.4	4188
$3s3d\ ^4D_{1/2}$	$^4D_{1/2}$	3911.8±0.2	3932
	$^4P_{1/2}$	4157.0±0.4	4205
$3s3d\ ^4P_{1/2}$	$^4D_{1/2}$	4056.6±0.2	4076
$3s3d\ ^4F_{3/2}$	$^4D_{1/2}$	3852.3±0.5	3870

[a]Air wavelengths.
[b]Reference 3.

Table I shows that it is difficult even with rather extensive calculations to predict accurate term-energy separations for core-excited quartet states in Na I. The present accuracy, however, may be sufficient to allow identification of the spectrum. Preliminary experimental investigations of quartet states in Mg II (Ref. 12), which have been predicted with similar accuracy,[3] seem to support this statement. The two spectral lines observed at

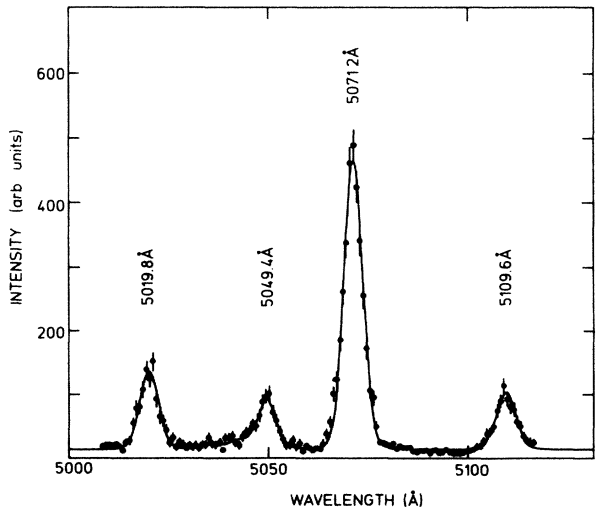

FIG. 1. Beam-foil spectrum of Na near 5000 Å recorded at 150 keV. The curve is a fit to the experimental points.

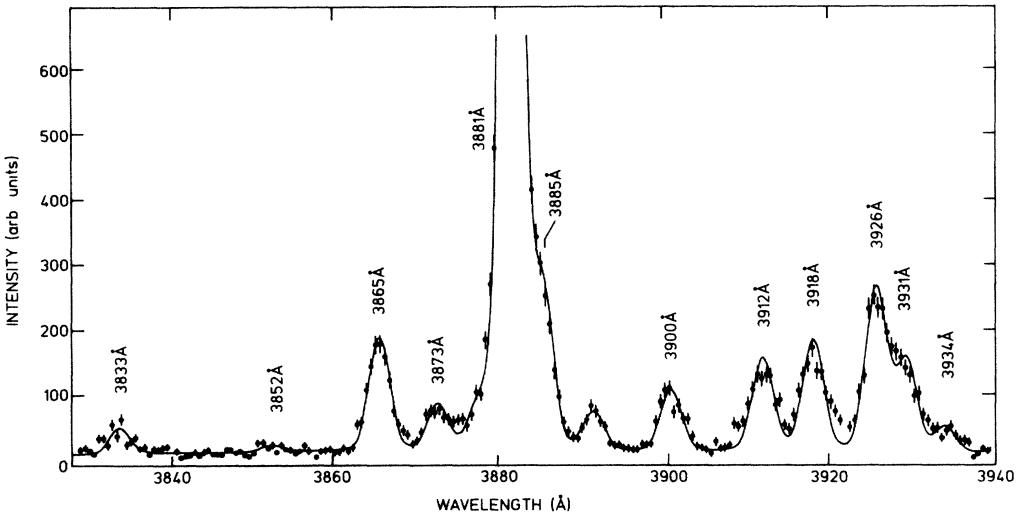

FIG. 2. Beam-foil spectrum of Na near 3900 Å recorded at 150 keV. The curve represents a fit to the experimental points.

TABLE II. Fine-structure splittings in Na I ^4L.

Splitting	Expt. (cm^{-1})	Theor.[a] (cm^{-1})
$3s3p\ ^4P_{1/2}-3s3p\ ^4P_{3/2}$	187±2	202
$3s4s\ ^4P_{1/2}-3s4s\ ^4P_{3/2}$	528±2	536
$3s4s\ ^4P_{3/2}-3s4s\ ^4P_{5/2}$	550±2	566
$3s3d\ ^4D_{1/2}-3s3d\ ^4D_{3/2}$	122±2	103
$3s3d\ ^4F_{3/2}-3s3d\ ^4F_{5/2}$	614±3	609

[a]Reference 3.

TABLE III. Energy levels (in cm^{-1}) for ^4L states of Na I relative to the $2p^53s3p\ ^4S_{3/2}$ level which is located 263 773±15 cm^{-1} above the Na I ground level (Ref. 3).

Configuration	Term	J	Expt. energy
$2p^53s3p$	^4D	$\frac{7}{2}$	2840
		$\frac{5}{2}$	3187
		$\frac{3}{2}$	3536
		$\frac{1}{2}$	3830
	^4P	$\frac{5}{2}$	4770
		$\frac{3}{2}$	5153
		$\frac{1}{2}$	5340
$2p^53s4s$	^4P	$\frac{5}{2}$	22 555
		$\frac{3}{2}$	23 105
		$\frac{1}{2}$	23 633
$2p^53s3d$	^4P	$\frac{1}{2}$	28 474
		$\frac{3}{2}$	28 543
		$\frac{5}{2}$	28 654
	^4F	$\frac{9}{2}$	28 595
		$\frac{7}{2}$	28 703
		$\frac{5}{2}$	29 167
		$\frac{3}{2}$	29 781
	^4D	$\frac{3}{2}$	29 264
		$\frac{1}{2}$	29 386

5411.0 and 5451.9 Å may account for two of the unidentified spectral lines observed recently in light emitted from sputtered particles generated when sodium-containing solids were bombarded with energetic Ar^+ ions.[13] The spectral lines from sputtering appeared at 5411±5 and 5448±5 Å. Light emitted from the $2p^53s4s\ ^4P_{5/2}$ level has previously been observed from sputtering.[13]

Table II gives a comparison between the fine-structure (FS) splittings for quartet levels identified in the present study and the theoretical predictions.[3] The data deviate only 1–3 % if we neglect the $3s3d\ ^4D$ term. The FS splittings obtained by Holmgren *et al.*[1] exhibited a similar good agreement with predictions.[3] The experimental ordering of the levels for the $3s3d\ ^4D$ term ($\frac{3}{2},\frac{7}{2},\frac{1}{2},\frac{5}{2}$) indicate a highly intermediate coupling.

Table III summarizes the experimental energies for the lower-lying quartet levels determined by Holmgren *et al.*[1] and by the present study. The uncertainty is ±2 cm^{-1} for most of the levels. For $3s3d\ ^4D_{1/2}$ and $^4F_{3/2}$, the uncertainty is ±5 cm^{-1}.

B. Lifetimes

Table IV gives the radiative lifetimes for the 12 excited $3s3d$ and $3s4s$ levels which can be studied by optical emission. The present data are compared with the experimental lifetimes reported by Engström *et al.*[2] and by the two theoretical predictions.[1–3]

The lifetimes were studied, using initial energies ranging from 80 to 150 keV. The use of several initial energies helped solve the cascade problem which often is most severe for beam-foil lifetimes. Several decay channels were used, if possible, to determine the lifetime of a given level. The data obtained from different decay channels depopulating a given level were always in agreement within the experimental errors. The lifetimes given in Table IV represent the weighted average of the lifetimes for each level, with a one-standard-deviation uncertainty. The decay curves were in most cases analyzed using two exponential functions and a constant background. The

ratio between the two lifetimes was usually larger than five, allowing an accurate determination of the primary lifetime through a multiexponential fitting procedure. The energy loss suffered by the ion beams passing through the carbon foil was estimated on the assumption that only a minor part of the nuclear-energy loss ΔE_n^* should be added to the electronic energy loss ΔE_e for the velocity evaluation in beam-foil experiments for heavier elements.[14] The velocity corrections due to the energy loss influenced the measured lifetimes by $\sim 4\%$.

There is within the quoted errors a good agreement between the present lifetimes and the data reported by Engström *et al.*[2] for the $3s3d\ ^4P_{3/2}$, $^4P_{1/2}$, $^4F_{9/2}$, and $^4F_{7/2}$ levels. For the levels $3s3d\ ^4D_{3/2}$, $^4F_{5/2}$, $^4P_{5/2}$, and $3s4s\ ^4P_{5/2}$, however, the data differ.

Engström *et al.*[2] reported the lifetime for the $3s3d\ ^4D_{3/2}$ level to be 0.70 ± 0.07 ns. They performed the decay measurements, observing the $3s3d\ ^4D_{3/2}-3s3p\ ^4D_{1/2}$ transition at 3931 Å. Figure 2 shows the beam-foil spectrum recorded in this region. The 3931-Å line is not well resolved from other lines. We have used the decay channel at 3833.6 Å (to $3s3p\ ^4D_{5/2}$), which is well separated from other lines, and observed no sign of a short-lived component with a lifetime like that of Engström *et al.* Our value of 2.2 ± 0.3 ns is in good agreement with the cascade lifetime obtained by Engström *et al.*, indicating that their original lifetime of 0.70 ns may be due to a line-blending effect. We also used the 3885-Å line to test the $^4D_{3/2}$ lifetime by recording the spectrum from 3878 to 3888 Å at a series of distances from the foil and then reproducing the spectra on a computer, taking into account that the lifetime for the line at 3882 Å ($3s3d\ ^4F_{9/2}-3s3p\ ^4D_{7/2}$) is known. The result for the $^4D_{3/2}$ level obtained by this method was 2.0 ± 0.4 ns, in good agreement with the result given in Table IV.

The $3s3d\ ^4F_{5/2}$ level was studied by Engström *et al.*[2] who used the 3427-Å line (decay to $^4S_{3/2}$). They explain the very high uncertainty (50%) associated with this short-lived level as being due to the low intensity of this transition and to the fact that their monochromator viewed a distance of 0.5 mm, which is larger than the decay length for this level. The latter effect often leads to too-long lifetimes if the cascade analysis is not simple. We have used the ~ 3 times more intense line at 3900 Å (decay to $^4D_{3/2}$) and a slit width which is a factor of 4 shorter than the decay length. It is then possible to determine a rather short lifetime, in the present case 0.11 ± 0.02 ns. The present apparatus can be utilized at the initial energies applied in this study to determine lifetimes larger than ~ 70 ps, which is the upper limit we have given for the $3s3d\ ^4F_{3/2}$ lifetime.

The lifetime of the $3s4s\ ^4P_{5/2}$ level has been studied in great detail since it also deviates considerably from the data given by Engström *et al.*[2] who used the 4432-Å line (decay to $^4S_{3/2}$) for intensity measurements. As described above, this line is not nearly as intense as quoted by Holmgren *et al.*[1] We have performed studies where we used the three most-intense lines depopulating the $^4P_{5/2}$ level. The line at 5071 Å (decay to $^4D_{7/2}$), the second-most-intense line in the quartet spectrum, was used to obtain the data shown in Fig. 3. The data recorded with the lines at 4432 Å (decay to $^4S_{3/2}$) or 5162 Å (decay to $^4D_{5/2}$), which are of nearly equal intensity, are very similar to those shown in the figure. All the decay curves analyzed (more than 20) could be fitted to a lifetime of ~ 10 ns and a weak cascade with a lifetime of ~ 50 ns. There was no sign of a cascade component with a lifetime near 20 ns, as quoted by Engström *et al.*[2] who obtained a lifetime of 4.4 ns for the primary lifetime. As shown in Fig. 1, the line at 5071 Å is well separated from other lines, so

TABLE IV. Lifetimes in nanoseconds and autoionization rates (10^8 s^{-1}) for quartet levels in Na I. A denotes autoionization rate.

Term	J	Transition (Å)	$\tau_{present}$	$\tau_{other\ expt}$ (Ref. 2)	τ_{theor} (Ref. 3)	τ_{theor} (Ref. 1)	A (10^8 s^{-1}) Ref. 3	Ref. 1
$3s4s\ ^4P$	$\frac{5}{2}$	5071, 4432, 5162	10.2 ±0.6	4.4 ±0.4	8.3	10.9	0.00	0.00
	$\frac{3}{2}$	5020, 5110, 5452	0.38±0.06		0.32		28.7	
	$\frac{1}{2}$	5049, 5411	2.0 ±0.3		1.7		3.9	
$3s3d\ ^4P$	$\frac{5}{2}$	3489, 4186	4.17±0.10	3.34±0.20	4.7	6.1	0.12	
	$\frac{3}{2}$	3502, 4205	4.27±0.20	4.10±0.40	4.6	2.8	0.25	1.76
	$\frac{1}{2}$	3511	3.01±0.15	2.95±0.20	2.4	5.8	2.12	0.02
$3s3d\ ^4D$	$\frac{3}{2}$	3833, 3885	2.2 ±0.3	0.70±0.07	2.0	0.48	1.80	15.5
	$\frac{1}{2}$	3912	1.45±0.20		1.7		3.13	
$3s3d\ ^4F$	$\frac{9}{2}$	3882	4.67±0.20	4.38±0.20	5.1	6.1	0.00	0.00
	$\frac{7}{2}$	3918, 3866, 4177	1.07±0.20	0.94±0.15	1.4	2.9	4.99	1.76
	$\frac{5}{2}$	3900	0.11±0.02	0.40±0.20	0.20	0.18	46.7	50.8
	$\frac{3}{2}$	3852	≤ 0.07		0.15		66.0	

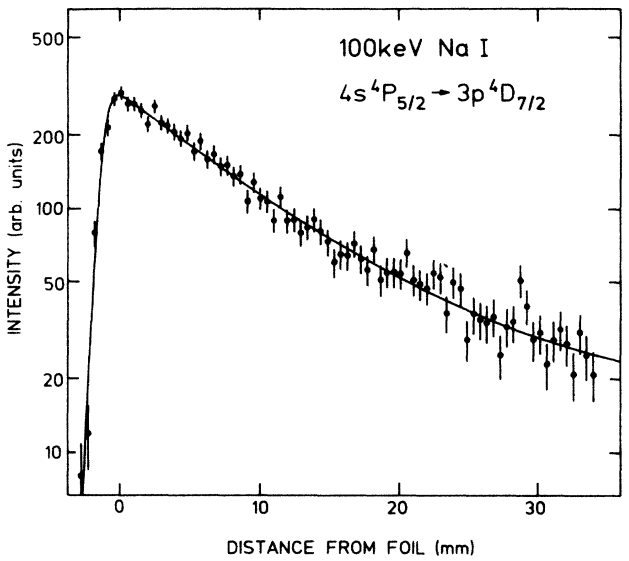

FIG. 3. Decay curve for the spectral line at 5071 Å, representing the $3s4s\,^4P_{5/2}-3s3p\,^4D_{7/2}$ transition. The primary lifetime was determined to be 10.2±0.6 ns with a cascade lifetime of 51 ns.

line admixture can be excluded.

The lifetime for the $3s3d\,^4P_{5/2}$ level also differs between the two sets of experimental data, but in this case, the deviation is smaller than for the three levels discussed above. The present investigation also yielded four lifetimes not measured before.

A comparison between the present lifetimes and those derived by Froese Fischer[3] shows very good agreement. In fact, the data agree for all levels, excluding the $3s3d\,^4F_{5/2}$ and $^4F_{3/2}$, within ~10–20%. This shows that lifetimes predicted for nonautoionizing levels ($3s4s\,^4P_{5/2}$ and $3s3d\,^4F_{9/2}$) but also for levels with moderate autoionization rates ($3s4s\,^4P_{1/2}$, $3s3d\,^4P_{5/2}$, $^4P_{3/2}$, etc.) are predicted with reasonable accuracy from Froese Fischer's calculations. The two levels, $3s3d\,^4F_{5/2}$ and $^4F_{3/2}$, for which the experimental and predicted[3] lifetimes differ by more than 20%, both exhibit very large autoionization rates.

A comparison between the present lifetimes and both the theoretical data sets contains two important observations. For the non-autoionization levels, the data agree within ~25%, whereas significant deviations can be noted for levels with an autoionization channel. The lifetimes for the three levels $3s3d\,^4P_{3/2}$, $^4P_{1/2}$, and $^4D_{3/2}$ most clearly illustrate the latter. The autoionization rates obtained for these levels by means of Cowan's code deviate considerably from Froese Fischer's results, which have been shown to be reliable by the data obtained in this study. On the basis of the present data and the lifetimes predicted, it is possible to estimate the accuracy of the autoionization rates calculated by Froese Fischer to be better than ±50%. A further test of the quality of Froese Fischer's calculations would be a spectroscopic study of the ^4L levels in Mg II. A large number of these levels should not be observable by optical-emission studies due to large autoionization rates. In addition, the $2p^5 3p^2$ configuration would be present among the energetic low-lying configurations. Such a study is in progress.[12]

The present investigation has also revealed a large number of unidentified spectral lines, probably belonging to the transitions between higher-lying configurations in the Na I ^4L-term scheme and the three configurations discussed in this paper. Further studies of these spectra are in progress in this laboratory.

ACKNOWLEDGMENTS

We thank C. Froese Fischer for sending us her calculations prior to publication, I. Martinson for stimulating discussions concerning the quartet-term schemes, and R. D. Cowan for very valuable comments and correspondence concerning calculations performed with his atomic code. Financial support from the Nordic Accelerator Committee (NOAC) is gratefully acknowledged.

[1]D. E. Holmgren, D. J. Walker, D. A. King, and S. E. Harris, Phys. Rev. A **31**, 677 (1985).

[2]L. Engström, L Young, L. P. Sommerville, and H. G. Berry, Phys. Rev. A **32**, 1468 (1985).

[3]C. Froese Fischer, Phys. Rev. A **34**, 1667 (1986).

[4]A. J. Mendelsohn, C. P. J. Barty, M. H. Sher, J. F. Young, and S. E. Harris, Phys. Rev. A **35**, 2095 (1987).

[5]H. G. Berry, R. Hallin, R. Sjödin, and M. Gaillard, Phys. Lett. **50A**, 191 (1974).

[6]R. Fröhling and H. J. Andrä, Phys. Lett. **97A**, 375 (1983).

[7]R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California, Berkeley, 1981), Secs. 8-1, 16-1, and 18-7.

[8]C. Froese Fischer, J. Phys. B **16**, 157 (1983).

[9]C. Froese Fischer (private communication).

[10]S. M. Bentzen, T. Andersen, and O. Poulsen, J. Phys. B **14**, 3435 (1981); **15**, L71 (1982); T. Andersen, S. M. Bentzen, and O. Poulsen, Phys. Scr. **22**, 119 (1980).

[11]B. Denne and O. Poulsen, Phys. Rev. A **23**, 1229 (1981).

[12]J. O. Gaardsted, T. Andersen, D. Sonnek, S. Mannervik, and R. T. Short, Phys. Scr. (to be published).

[13]K. Kierkegaard, S. Ludvigsen, B. Petterson, and E. Veje, Phys. Rev. A **33**, 1398 (1986).

[14]T. Andersen, O. H. Madsen, and G. Sorensen, Phys. Scr. **6**, 125 (1972); P. Hvelplund, E. Laegsgaard, J. O. Olsen, and E. H. Pedersen, Nucl. Instrum. Methods **90**, 315 (1970).