Lifetime measurements of core-excited quartet levels in Na I

L. Engström, L. Young, L. P. Somerville, and H. G. Berry
Physics Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 15 March 1985)

In a recent spectroscopic study [D. E. Holmgren *et al.*, Phys. Rev. A **31**, 677 (1985)], many metastable core-excited quartet levels in Na I have been identified, and based on calculated decay rates (both radiative and autoionizing) some of these levels have been suggested for use in an extreme ultraviolet (xuv) laser. In order to test the theoretical calculations we have used the beam-foil technique to determine experimental lifetimes for eight quartet levels in the core-excited configurations $2p^5 3s\,3d$ and $2p^5 3s\,4s$. The agreement between theory and experiment is within a factor of 2, but with systematic discrepancies.

I. INTRODUCTION

Very recently Holmgren *et al.*[1] established 15 quartet levels in the $2p^5 3s\,3p$, $3d$, and $4s$ configurations of Na I from 28 newly identified transitions. The spectra were obtained with a high-power, pulsed hollow-cathode discharge, and the identifications were confirmed by the enhanced fluorescence observed when a laser was used to selectively increase the population in the upper levels.

If L and S were good quantum numbers, the observed levels would be pure quartet states, and although they are above the first ionization limit, the only available decay mode would be radiative transitions within the quartet manifold. However, because of the spin-orbit interaction there will, in general, be a significant mixing between quartet and doublet levels which results in two additional decay channels: autoionization and extreme ultraviolet (xuv) transitions to some of the doublets in the normal ($2p^6 nl$) term system of Na I.

Only the quartet level of highest L and J within a given configuration cannot mix with doublet levels (since there is no similar J level). Thus, the single transition $3p\,^4D_{7/2}$–$3d\,^4F_{9/2}$ at 3882 Å had been observed and its lifetime measured in previous beam-foil spectra.[2]

Harris *et al.*[3] pointed out that for some of the mixed quartets the autoionization rate could be expected to be rather low. This would be the case for those quartet levels which primarily mix with doublet levels which are forbidden to autoionize due to selection rules for L and parity, for example, the odd-parity $2p^5 3s\,3d\,^2D$ states. It is this particular mixing which also opens the xuv decay branch (e.g., $2p^6 3d\,^2D$–$2p^5 3s\,3d\,^4D$) mentioned above.

Because of these decay characteristics, several schemes involving the quartet levels in Na I have been proposed for the construction of a xuv laser operating around 370 Å.[1] The feasibility of these plans depends, of course, on the transition probabilities for the various decay channels which, in turn, depend critically on the detailed composition of the quartet levels. In Ref. 1, Holmgren *et al.* give theoretical transition probabilities for both the radiative and autoionizing decay modes. These were calculated in a superposition-of-configurations Hartree-Fock approximation with empirically adjusted Slater parameters using the RCN/RCG computer program of Cowan.[4]

In the present paper we report experimental measurements, using the beam-foil technique, of the mean lives of all eight identified quartet levels in the $2p^5 3s\,3d$ and $2p^5 3s\,4s$ configurations of Na I. The experimental lifetimes are then used as a test of the theoretical predictions in Ref. 1.

It is well known that the beam-foil interaction produces a substantial population in doubly excited and core-excited states.[5,6] This effect was clearly seen in the strong excitation of the 3882-Å line in the previous beam-foil spectra[2] and is noted again here for the somewhat weaker excitation of the other quartet spectral lines. However, we find that spectra obtained from gas-target excitation show no evidence of excitation of these quartet levels. This result is discussed in more detail in the next section.

II. EXPERIMENTS

The Na^+ ions were produced in a Danfysik 910 ion source and electrostatically accelerated to a maximum energy of 120 keV. After magnetic analysis the beam passed through either a carbon foil or a gas cell, in a standard beam-foil arrangement. The gas cell had the dimensions $200\times50\times50$ mm, with a quartz window as one side, and was electrically isolated from the target chamber to serve also as a Faraday cup for beam normalization during the spectral scans.

The light emitted after the foil, or from within the gas cell, was analyzed with a 0.75-m monochromator (Spex, Czerny-Turner mount), optically coupled to the target chamber. The monochromator was equipped with a 1200 lines/mm grating, and the light intensity was registered by a Peltier-cooled Centronic 4249 BA photomultiplier operated in a photon-counting mode.

The Na spectrum was studied in the 2500–5500-Å region using several different beam energies between 30 and 120 keV. In addition to the known Na I and Na II lines[7] which were generally very intense, we observed all the lines identified in Ref. 1 as transitions between the core-excited levels in Na I. Figure 1 shows a small section of a

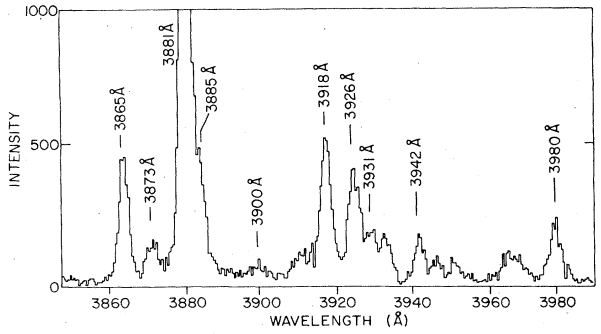

FIG. 1. Beam-foil spectrum of Na recorded at 100-keV beam energy. The indicated lines arise from transitions between the core-excited quartet levels. Foil thickness is 2 $\mu g/cm^2$.

spectrum recorded at 100-keV beam energy. The ten indicated lines arise from transitions between the quartet levels.

Several aspects of the experiments can be discussed in relation to Fig. 2. The lower part of Fig. 2 shows the Na I** transitions $2p^5 3s\,3p\,{}^4S_{3/2}-2p^5 3s\,3d\,{}^4P_{3/2,1/2}$ at 3502 and 3511 Å and ${}^4S_{3/2}$-${}^4D_{5/2}$ at 3489 Å,[1] obtained with a 60-keV Na beam after passage through a 5 $\mu g/cm^2$ carbon foil. In the upper part of the figure the foil is exchanged with a gas cell containing He at a pressure of 0.2 Torr, and we note the complete absence of the core-excited lines in this case. This large reduction in yield of doubly excited states on changing to a gas target has been used to verify the spectral identifications. Beam-gas spectra were thus recorded for all lines reported in Ref. 1 (below 5000 Å) using different beam energies, gases (Ar, air and He), and gas pressures. In all cases we could confirm the core-excited origin of the lines identified in Ref. 1. Only the 3882-Å line, which is very intense in the beam-foil spectrum (Fig. 1), showed any intensity at all in the gas-excited spectra. With Ar or air in the gas cell this comparison with the foil-excited spectrum was sometimes complicated by the presence of molecular bands.

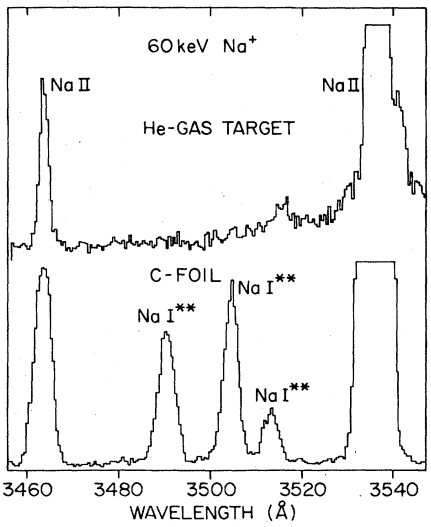

FIG. 2. Comparison between a beam-foil (lower part) and a beam-gas (upper part) spectrum of Na. The lines marked Na I** are transitions between core-excited quartet terms in Na I.

Similar effects in the optical spectra of doubly excited He I and Li I have been mentioned in Ref. 8. These results are interesting both because they provide an important way to distinguish the core-excited lines from other transitions and for the understanding of the beam-gas and beam-foil excitation mechanisms. It should be noted, however, that using atoms excited in a gas under single-collision conditions, a large number of doubly excited and core-excited states have been identified by observation of the electrons emitted during the autoionizing decay in flight of these levels. See, e.g., Rødbro *et al.*,[9] and references therein. In particular, several core-excited states in Na I were identified by Pegg *et al.*[10] with this technique, using a 70-keV Na^+ beam and a He gas target, i.e., under conditions similar to those of the present study. A possible explanation of these seemingly contradictory results is that while the production of multiply excited states does decrease in gas excitation, the higher probability for autoionization and the greater detection efficiency of the electron spectrometer still allows these states to be observed.

From Fig. 2 it is also seen that the Na II lines in the beam-foil spectrum are significantly broader than those in the beam-gas case, although the experimental conditions were otherwise the same. This is due to Doppler broadening, caused by the increased line-of-sight velocities of the ions from multiple scattering in the foil. This effect increases with foil thickness,[11,12] and thus most of the spectral scans and all decay measurements were made with very thin foils (2 $\mu g/cm^2$).

The mean life measurements were made at beam energies of 80 and 100 keV. At these low energies the foils lasted generally less than 10 min with a beam current of 0.5 μA. Because of the short decay lengths of the quartet levels, a charge of foils during a measurement often led to a visible discontinuity in the decay curve. Since this is unacceptable, we increased the speed of the measurements to ensure that the whole decay was recorded with a single foil. To compensate for the reduced statistics in each in-

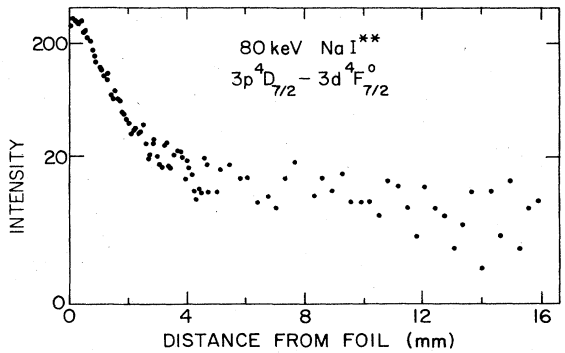

FIG. 3. The intensity decay of the $2p^5 3s\,3p\,{}^4D_{7/2}$ $-2p^5 3s\,3d\,{}^4F_{7/2}$ transition at 3866 Å, plotted on a semilogarithmic scale.

dividual curve, all decays were measured between three and five times. A typical decay curve recorded with a single foil is shown in Fig. 3.

For each level the intensity decay was measured only in the most intense channel since both the analysis of Holmgren *et al.*[1] and our comparison between the beam-foil and beam-gas spectra mentioned above ensure that these transitions are unblended.

Lifetime analyses and results

After background subtraction the recorded decay curves were analyzed with the multiexponential fitting program DISCRETE.[13] Good numerical stability of the results was obtained when the start channel for the fits was varied beyond the point corresponding to the maximum intensity in each curve. Furthermore, the different recordings of the same decay yielded lifetimes that agreed within the quoted uncertainties.

The weighted average of the lifetimes obtained for each level is given in Table I, and the quoted uncertainties represent a one standard-deviation estimate from one of the individual analyses. This error estimate is chosen since we believe that the uncertainty in the results is dominated by statistical errors associated with the rather low intensities in the decay curves. In the following, we discuss some sources of systematic errors.

The major problem in extracting accurate lifetimes from measured decay curves is usually to account for the repopulation of the level by cascades from higher-lying levels.[14] The decays of the quartet levels (Fig. 3 is a typical example) are in all cases best fitted by a two-exponential function including a long-lived cascade component. Table I shows that the "lifetime" of this component is sufficiently different from the fast decay to allow an accurate determination of the primary lifetime through a multiexponential fitting procedure. However, since no information is available on the lifetimes of higher-lying core-excited states, the exact cascade situation is unknown.

The very high uncertainty (50%) associated with the short-lived $^4F_{5/2}$ level is due to the low intensity of the 3472-Å transition (the individual decay curves for this transition had only 60—70 counts at the maximum) and to the fact that the monochromator viewed a distance along the beam (0.5 mm) larger than the decay length for this level ($v\tau=0.33$ mm).

Uncertainty in the particle velocity originates from two sources: (1) the energy calibration of the accelerator, and (2) energy loss in the foil. The energy of the accelerator was calibrated to better than 0.01% by measuring the Doppler shifts of accurately known Ne I lines,[15] using a tunable dye laser in a collinear geometry and a Burleigh wavemeter. The neutral Ne atoms were formed by charge exchanging the accelerated Ne^+ ions in Na vapor. In the lifetime analyses the energy loss in the carbon foils must be taken into account. We used the electronic stopping power of carbon calculated according to Garnir-Monjoie *et al.*,[16] and the foil thicknesses quoted by the manufacturer. This correction to the measured lifetimes is around 2%, and the total uncertainty due to the velocity determinations should be less than 1%.

As an overall test of our results we also measured the intensity decay of the unresolved $3s\ ^2S-3p\ ^2P$ transitions in Na I. The lifetimes of the $3p\ ^2P$ levels [$\tau(^2P_{3/2})=16.339$, $\tau(^2P_{1/2})=16.396$ ns] have been obtained with high accuracy in beam-laser experiments.[17] A multiexponential fit of the observed decay curve gave a lifetime of 18.6 ± 1.5 ns. However, it is well known that such fits tend to overestimate the $3p$ lifetime because of incomplete correction for cascades.[18] The situation is particularly difficult in Na I because the lifetime of the $3d$ level, 19.8 ns,[19] is so close to that of $3p$. In an attempt to better correct for this cascading we performed an arbitrarily normalized decay curves (ANDC) analysis,[20] using the computer program CANDY,[21] of the measured decay together with a simulated yrast cascade including the $3d$, $4f$, $5g$,and $6h$ terms with theoretical lifetimes from Ref. 19. This analysis reduced the $3p$ lifetime to between 17.5 and 18 ns, depending on the assumed relative level populations of the yrast terms. Since this lifetime is much longer, and hence much more susceptible to systematic errors, than for any of the quartet levels, the fairly good agreement (within 10%) obtained with the accurate $3p$ lifetime[17] is interpreted as a support for the error limits given in Table I.

TABLE I. Lifetimes of quartet levels in Na I.

Transition	Wavelength (Å)	Lifetime of upper level (ns) This experiment[a]	Theory	τ(exp)/τ(theory)	A (autoionization)[b] (s^{-1})
$3p\ ^4S_{3/2}-4s\ ^4P_{5/2}$	4432	4.4 ±0.4 (21±9)	10.9[c]	0.40	3×10^{-3}
$3p\ ^4S_{3/2}-3d\ ^4P_{1/2}$	3511	2.95±0.20 (25±6)	5.8[c]	0.51	2×10^{6}
$3p\ ^4S_{3/2}-3d\ ^4P_{3/2}$	3503	4.10±0.40 (13±4)	2.8[c]	1.46	2×10^{8}
$3p\ ^4S_{3/2}-3d\ ^4D_{5/2}$	3489	3.34±0.20 (15±5)	6.1[c]	0.55	1×10^{6}
$3p\ ^4S_{3/2}-3d\ ^4F_{5/2}$	3427	0.40±0.20 (7±5)	0.18[c]	2.22	5×10^{9}
$3p\ ^4D_{1/2}-3d\ ^4D_{3/2}$	3931	0.70±0.07 (2.4±0.4)	0.48[c]	1.46	2×10^{9}
$3p\ ^4D_{7/2}-3d\ ^4F_{7/2}$	3866	0.94±0.15 (15±3)	2.9[c]	0.32	2×10^{8}
$3p\ ^4D_{7/2}-3d\ ^4F_{9/2}$	3882	4.38±0.20 (58±10)[d]	6.1,[c] 6.0[e]	0.72	0

[a]Cascade lifetime is given in parentheses.

[b]Calculated autoionization probability (Ref. 1).

[c]Holmgren *et al.* (Ref. 1), superposition-of-configurations Hartree-Fock with empirically adjusted Slater parameters.

[d]Also measured in Ref. 2, $\tau=7.6\pm1.0$.

[e]A. W. Weiss, quoted in Ref. 2.

The only previous experimental lifetime in the quartet system of Na I is that of the $^4F_{9/2}$ level.[2] Our new value (Table I) is significantly lower, most probably because the improved signal-to-noise ratio allowed us to include a cascade correction to the decay data.

III. COMPARISON WITH CALCULATED DECAY RATES

Table I gives a comparison between the experimental and theoretical lifetimes of the quartet levels. The latter results are derived from branching ratios, including both radiative and autoionizing decay channels, and transitions probabilities given by Holmgren *et al.*[1] Although we were not able to make accurate branching-ratio measurements, the relative intensities of the observed transitions are in qualitative agreement with the theoretical branching ratios. Holmgren *et al.*[1] estimate the calculated transition rates to be accurate to within a factor of 2 to 4. Table I shows that this estimate is correct. In fact, the average deviation is 1.99. However, the discrepancy between the experimental and theoretical results appears to be systematic. The last two columns of Table I give the ratio τ(exp) to τ(theory) and the calculated autoionization rate,[1] respectively. There is a correlation between large (small) autoionization probability and large (small) τ(exp) to τ(theory) ratio. The only exception to this rule is for the $^4F_{7/2}$ level.

From this comparison it is evident that further theoretical work is needed to accurately describe the complicated decay properties of core-excited quartet levels. However, the general conclusions drawn in Ref. 1 concerning the use of the $^4D_{3/2}$ an $^4F_{5/2}$ levels in a xuv laser seem to be valid, although the estimated laser parameters may be rather uncertain.

ACKNOWLEDGMENTS

We are grateful to Dr. Kwok-Tsang Cheng for helpful discussions and to Professor Steve Harris for communicating his results prior to publication. We thank Chuck Kurtz for his help in the experimental work. This research was supported by the U.S. Department of Energy (Office of Basic Energy Sciences) under Contract No. W-31-109-Eng-38. One of us (L.E.) also gratefully acknowledges support from the Swedish Natural Sciences Research Council (NFR).

[1] D. E. Holmgren, D. J. Walker, D. A. King, and S. E. Harris, Phys. Rev. A **31**, 677 (1985).
[2] H. G. Berry, R. Hallin, R. Sjödin, and M. Gaillard, Phys. Lett. **50A**, 191 (1974).
[3] S. E. Harris, D. J. Walker, R. G. Caro, A. J. Mendelsohn, and R. D. Cowan, Opt. Lett. **9**, 168 (1984).
[4] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
[5] H. G. Berry, Phys. Scr. **12**, 5 (1975).
[6] I. Martinson, Nucl. Instrum. Methods **202**, 1 (1982).
[7] P. Risberg, Fysik Arkiv **10**, 583 (1956); S. E. Frich, Z. Phys. **70**, 498 (1931); J. S. Bowen, Phys. Rev. **31**, 967 (1928); Chien-Ming Wu, Ph.D. thesis, The University of British Columbia, 1971.
[8] H. G. Berry, J. Desesquelles, and M. Dufay, Nucl. Instrum. Methods **110**, 43 (1973).
[9] M. Rødbro, R. Bruch, and P. Bisgaard, J. Phys. B **12**, 2413 (1979).
[10] D. J. Pegg, H. H. Haselton, R. S. Thoe, P. M. Griffin, M. D. Brown, and I. A. Sellin, Phys. Rev. A **12**, 1330 (1975).
[11] G. Högberg, H. Nordén, and H. G. Berry, Nucl. Instrum. Methods **90**, 283 (1970).
[12] P. Sigmund and K. B. Winterbon, Nucl. Instrum. Methods **119**, 541 (1974).
[13] S. W. Provencher, J. Chem. Phys. **64**, 2772 (1976).
[14] L. J. Curtis, in *Beam-Foil Spectroscopy,* edited by S. Bashkin (Springer, Berlin, 1976), p. 63.
[15] J. L. Hall and S. A. Lee, Appl. Phys. Lett. **29**, 367 (1976).
[16] F. S. Garnir-Monjoie, H. P. Garnir, Y. Baudinet-Robinet, and P. D. Dumont, J. Phys. (Paris) **41**, 599 (1980).
[17] D. Schulze-Hagenest, Ph.D. thesis, Kaiserslautern, 1979. Quoted by Gaupp *et al.*, Phys. Rev. A **26**, 3351 (1982).
[18] J. O. Ekberg, L. Engström, S. Bashkin, B. Denne, S. Huldt, S. Johansson, C. Jupén, U. Litzén, A. Triguerios, and I. Martinson, Phys. Scr. **27**, 425 (1983); T. Anderson, O. H. Madsen, and G. Sørensen, Phys. Scr. **6**, 125 (1972).
[19] A. Lindgård and S. E. Nielsen, At. Data Nucl. Data Tables **19**, 533 (1977).
[20] L. J. Curtis, H. G. Berry, and J. Bromander, Phys. Lett. **34A**, 169 (1971).
[21] L. Engström, Nucl. Instrum. Methods **202**, 369 (1982).