Radiative lifetimes for some $4p$ and $4d$ levels of singly ionized sulfur

L. Maleki and Charles E. Head
Physics Department, University of New Orleans, New Orleans, Louisiana 70122
(Received 28 July 1975; revised manuscript received 28 August 1975)

We have used the beam-gas technique to make the first reported measurements of the radiative lifetimes of six terms of S II using visible transitions. A gas-jet target and a doubly-differentially-pumped gas cell were used to populate the excited levels of fast ions in an S^+ beam. The weighted averages of the lifetimes and the standard deviations of the means in nanoseconds are as follows: for $4p\ ^4D^o$, 10.25 ± 0.07; $4p\ ^4P^o$, 8.95 ± 0.03; $4p\ ^4S^o$, 5.46 ± 0.05; $4p'\ ^2F^o$, 10.20 ± 0.09; $4d\ ^4F$, 4.83 ± 0.04; and for $4d\ ^4D$, 5.23 ± 0.05. Total uncertainties are estimated to be in the range 5–10%.

I. INTRODUCTION

Transition rates for visible transitions of singly ionized sulfur have previously been measured using emission spectra.[1-4] There have also been some theoretical calculations based on L-S coupling and intermediate coupling.[5-7] All previously measured values are subject to uncertainties ranging from 18% to higher than 50%. These large uncertainties can be reduced somewhat by scaling the transition rates with the help of accurately-measured radiative lifetimes.

We have used the beam-gas technique to measure the radiative lifetimes of levels from the following terms: $4p\ ^4D^o$, $4p\ ^4P^o$, $4p\ ^4S^o$, $4p'\ ^2F^o$, $4d\ ^4D$, and $4d\ ^4F$. Except for preliminary work in our laboratory, these are thought to be the first measurements reported for these levels.[8,9]

We have recently modified our target to enable us to measure shorter lifetimes with greater accuracy and have also modified our rf ion source to enable us to obtain a relatively pure beam of S^+.

II. APPARATUS AND EXPERIMENTAL METHOD

Our experimental technique and apparatus have been discussed in detail elsewhere.[10-12] Here we shall present only a brief outline and discuss only the most recent changes in our apparatus.

In the beam-gas method a beam of fast ions is directed through a gas target in order to populate the excited levels. After passing through the target into an observation region, the levels decay according to the well-known exponential decay law $N = N_0 e^{-t/\tau}$, where τ is the lifetime for a specific level. Because the ions are moving with a definite speed v, one may write instead for the level population $N = N_0 e^{-x/v\tau}$, where x is the distance downstream from the target. By measuring the spatial decay of radiation from the decay of these levels one can readily, in principle, extract the lifetimes. In practice, of course, one must also take into account such things as cascade from higher levels and background radiation.

In the present study we investigated a 20–30-keV S^+ beam incident on a helium-gas target.

In order to obtain a sufficiently pure beam of S^+, we found it necessary to modify our rf ion source because our initial investigation using SO_2 gas revealed severe spectral overlap of sulfur and oxygen lines from mixed S^+ and O_2^+ beams. A further attempt to use SF_6 gas also proved unsuccessful. Fluorine generated in the source interacted with the silica from the ion bottle, thereby releasing oxygen and producing the same difficulty as with SO_2. Attempts to use H_2S were also unsuccessful. As a final solution we attached a side arm to the ion source in which elemental sulfur was placed and heated to produce a sulfur vapor. A plasma was then produced using helium as a buffer gas. The resulting S^+ beam was found to be almost completely free of O_2^+ and was reasonably strong and stable.

A doubly-differentially-pumped gas target (DDPGT)[13] was used for some measurements; however, short-lived transitions were found to decay too rapidly between the high-density region inside the target cell and the vacuum in the observation chamber, thereby preventing accurate measurements on those transitions. To circumvent this problem we constructed a gas-jet target. This target consists of a hypodermic needle inside a cylindrical cell; the basic arrangement is shown in Fig. 1. The cell has two collimating holes on opposite sides of the cylinder to allow passage of the beam. One end of the cylinder opens into a cold trap above a diffusion pump, and the other end is fitted with an observation window. The needle is placed inside the cell so that its opening is just short of the line connecting the collimating holes. It is placed adjacent to the ion-beam exit port and is pointed toward the pump. With this geometry, the target gas streams out of the needle in the form of a high-velocity jet and is quickly pumped out by the diffusion pump. The ions in the ion beam are excited by collisions with the target gas in the most

dense region of the jet, immediately before exiting into the observation region.

Under normal operation the background gas in the target cylinder was kept in the range $(1-5)\times10^{-3}$ Torr. The background pressure in the observation region was in the neighborhood of 6×10^{-6} Torr. We conservatively estimated the ratio of the pressure of the target gas in the region of the beam-gas interaction to the pressure of the background gas in the observation region to have been greater than 10^4 to 1.

Our experience indicated that the DDPGT works best for $v\tau$ greater than about 4 mm while the jet target works best for $v\tau$ shorter than 4 mm.

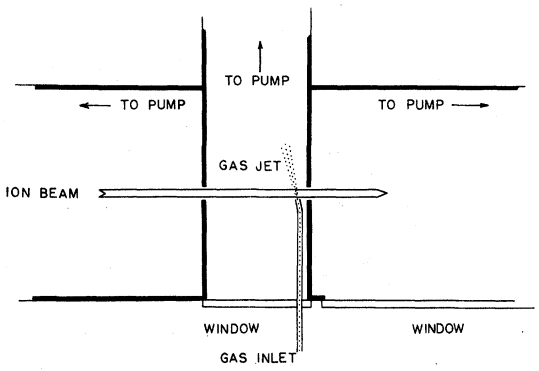

FIG. 1. Schematic drawing of the gas-jet target. Beam entrance and exit ports are greatly exaggerated.

III. ANALYSIS AND RESULTS

A partial scan of the spectrum of the S^+ beam taken about 1 mm downstream from the target is given in Fig. 2. Higher resolution scans (e. g., with 3.2-Å spectral windows and chart speeds giving 10 Å/in) were used for analysis.

Our choice of particular lines for lifetime measurements was made to ensure that no blending of lines from different multiplets occurred.

All data were analyzed by means of an iterative computer program which fitted the intensity data by the equation

$$I=Ae^{-x/v\tau_k}+Be^{-x/v\tau_j}+C\ ,$$

where I is the intensity; A, B, and C are constants; x is the distance downstream from the target; v is the speed of the ions; and τ_k and τ_j are the lifetimes of levels k and j, respectively.[11,12] The first exponential represents the natural decay of the energy level E_k, the second exponential represents the contribution of intermediate-lived cascade(s), and C (sometimes set equal to zero) represents background intensity and contributions from long-lived cascades. An example of a decay curve and the computed fit is given in Fig. 3.

We have assumed throughout that there is no dependence of the lifetimes on the J values. No such dependence was found experimentally for the various J values for the $4p\,^4P^o$ term to within our experimental error, but we were unable to readily verify this property for the other terms studied.

In the text which follows uncertainties quoted with results represent statistical errors. Estimates of the total uncertainties are given in Table I in parentheses following the lifetimes. Discussion of errors follows the presentation of the results.

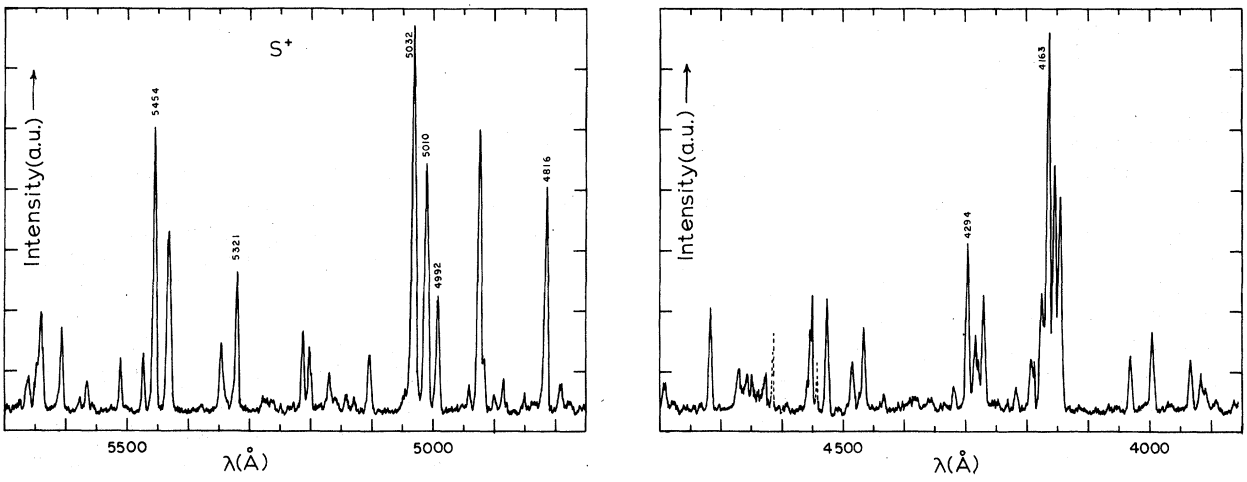

FIG. 2. Tracing of a partial scan of the spectrum resulting from collisions of 24-keV S^+ ions with a helium gas jet. Beam was viewed approximately 1 mm downstream from the target cell. Lines used in making lifetime measurements are labeled with their wavelengths. Features with dashed lines are caused by spurious signals.

A. $4p\,^4D^o$

The lifetime for levels in the $4p\,^4D^o$ term was obtained from measurements on the $4p\,^4D^o_{7/2} \rightarrow 4s\,^4P_{5/2}$ ($\lambda = 5454$ Å) transition. A spectral window of 10.8 Å was used, and five decay curves were obtained with the gas-jet target. Data were fitted by the sum of two exponentials. A few decay curves were also obtained using the DDPGT.

The partial Grotrian diagram[14] in Fig. 4 indicates that the $4p\,^4D^o$ term receives important cascades from the $5s\,^4P$, $4d\,^4D$, and $4d\,^4F$ terms. These cascades could possibly lengthen the measured lifetime for the $4p\,^4D^o$ levels if some effort were not made to eliminate their effects. Using branching ratios for the cascade transitions calculated from tabulated transition rates[5] and using crude estimates for the relative populations of the cascade levels, we concluded that the cascade contribution to the population of the $4p\,^4D^o$ levels was probably less than 10%.

The lifetimes of the cascading levels are approximately a factor of two smaller than the lifetime of the $4p\,^4D^o$ levels; therefore, significant cascade contributions would make the part of the decay curves near the target appear convex when viewed from above.[12] Visual inspection of all decay curves failed to produce evidence for such a growing-in cascade, indicating that we were viewing the radiation sufficiently far downstream that the cascade contributions from short-lived states were not very large.

In addition to the visual inspection, the first few points of each decay curve taken with the gas-jet target were systematically deleted one at a time, with the lifetime being computed with each deletion. The computed lifetimes were expected to at first decrease with each successive deletion and then to level off as the cascades became less significant. This effect was seen; however, the decrease in the computed lifetimes was not much greater than the statistical uncertainties, indicating, in agreement with our estimates, that cascades were contributing only a minor portion of the excitation of the $4p\,^4D^o$ levels. Results obtained were used along with the results from the DDPGT to yield a lifetime of 10.25 ± 0.07 nsec.

We have listed in Table I along with our results upper limits to the lifetimes computed from three somewhat incomplete sets of transition rates. Definite uncertainties for these transition rates are known only for the work of Miller *et al.*[3] and Wiese *et al.*[5] They are generally in the range of (25–50)%.

B. $4p\,^4P^o$

The lifetime for this term was obtained from measurements on three transitions. They were $4p\,^4P^o_{5/2} \rightarrow 4s\,^4P_{5/2}$ ($\lambda = 5032$ Å), $4p\,^4P^o_{1/2} \rightarrow 4s\,^4P_{3/2}$ ($\lambda = 5010$ Å), and $4p\,^4P^o_{3/2} \rightarrow 4s\,^4P_{3/2}$ ($\lambda = 4992$ Å). The 5032-Å line was the strongest line in the spectrum at the point at which we viewed the beam. A spectral window of 8 Å was sufficiently small in all cases to prevent line blending.

Eleven decay curves obtained for the above transitions were each fitted to the sum of two exponentials. The results obtained for individual transitions (i. e., different J values) were in excellent agreement. A weighted average of all decay curves yielded 8.95 ± 0.03 nsec for the lifetime of the $4p\,^4P^o$ levels.

The theoretical lifetime computed from Aymar's transition rates is 7.1 nsec.[7]

C. $4p\,^4S^o$

The $4p\,^4S^o_{3/2} \rightarrow 4s\,^4P_{5/2}$ ($\lambda = 4816$ Å) transition was used to measure the lifetime of the $4p\,^4S^o$ levels. The 4816-Å line was well separated from other lines; consequently, a spectral window of 14.5 Å

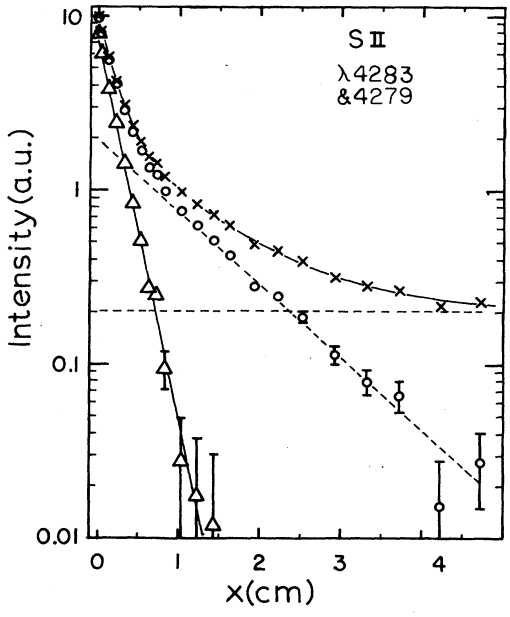

FIG. 3. Decay curve (×) for the 4279- and 4283-Å lines of S II. Data were fitted by the sum of two exponentials and a constant. The constant and long-lived exponential, representing background and cascade, are indicated by dashed lines on the semilog plot. The primary exponential component, associated with the natural decay of the $4d\,^4D$ levels, is indicated by a solid straight line through the delta's (Δ). Error bars for each point are indicated only if they exceed the size of the symbol. Initial point is normalized to ten by the computer program. Lifetime for the $4d\,^4D$ levels computed from this particular decay curve is 5.18 ± 0.12 nsec.

TABLE I. Mean radiative lifetimes for some excited levels of S II.

Levels	τ (nsec) This work[a]	Computed from transition rates MWRB[b]	WSM[c]	$L-S$[d]	Aymar[e]
$4p\,^4D^o$	10.25 ± 0.07 (6%)	<6.8[f]	< 8.6[f]		<6.6[f]
$4p\,^4P^o$	8.95 ± 0.03 (6%)	<8.1[f]	< 9.4[f]		7.1
$4p\,^4S^o$	5.46 ± 0.05 (7%)	6.1[g]	10.1[g]		7.9[g]
$4p'\,^2F^o$	10.20 ± 0.09 (5%)	<9.2[f]	<11.9[f]		<9.0[f]
$4d\,^4F$	4.83 ± 0.04 (10%)	3.8	4.4	4.6	
$4d\,^4D$	5.23 ± 0.05 (10%)	<5.0[h]	4.4	<4.8[h]	

[a] The percentage given in parentheses following each lifetime is our estimate of the total uncertainty in that lifetime. The error preceding it is the standard deviation of the mean and represents only our precision in making the measurement.
[b] Reference 3.
[c] Reference 5.
[d] L–S coupling calculation. Taken from Ref. 3.
[e] Reference 7.
[f] Incomplete set of transition rates.
[g] Does not include the $4p\,^4S^o \rightarrow 3d\,^4D$ transition rate ($\lambda = 5951$ Å). This transition violates the $\Delta L = 0, \pm 1$ selection rule for L–S coupling, but is included in the Grotrian diagram in Ref. 14.
[h] Does not include the $\Delta J = -1$ ($\lambda = 3971.2$ Å) transition, which, according to Ref. 5, is relatively weak. The effect of omitting its transition rate from the computation of the lifetime should not exceed ±5%.

was used. Four different decay curves were taken for this transition and gave a weighted average of 5.46 ± 0.05 nsec for the lifetime.

D. $4p'\,^2F^o$

The lifetime for this term was measured using the $4p'\,^2F^o_{7/2} \rightarrow 4s'\,^2D_{5/2}$ ($\lambda = 5321$ Å). Ten decay curves were obtained using SF_6^+ to generate a S^+ beam. The 5321-Å line was one of the few visible lines that had no possible overlap with O II lines and could therefore be safely studied even with O_2^+ contamination of the beam. The majority of the curves were obtained using the DDPGT, but a few were taken with the gas-jet target. The agreement between the results obtained was excellent. The weighted average of all decay curves gave a lifetime of 10.20 ± 0.01 nsec.

This term was erroneously designated $4d\,^2F^o$ in the NBS tables,[5] in Ref. 3, and subsequently in one of our preliminary reports.[9]

E. $4d\,^4F$

The lifetime for this term was measured using the $4d\,^4F \rightarrow 4p\,^4D^o$ multiplet. The monochromator was set to pass the 4163-Å line with a spectral window of 13 Å. Five decay curves were each fitted to the sum of two exponentials and a constant, yielding a lifetime of 4.83 ± 0.04 nsec.

This lifetime is directly convertible to a transition rate for the 4294-Å transition, yielding a rate of 2.1×10^8 sec^{-1}. We estimate it to be accurate to within 10%. It indicates that the number previously recommended by Wiese *et al.*[5] (i. e., 2.3×10^8 sec^{-1}) is less uncertain than they had previously estimated (i. e., 50%).

F. $4d\,^4D$

The lifetime for the $4d\,^4D$ term was measured using the $4d\,^4D \rightarrow 4p\,^4P^o$ multiplet, which was well isolated from other multiplets. Four decay curves were obtained with the monochromator set to pass

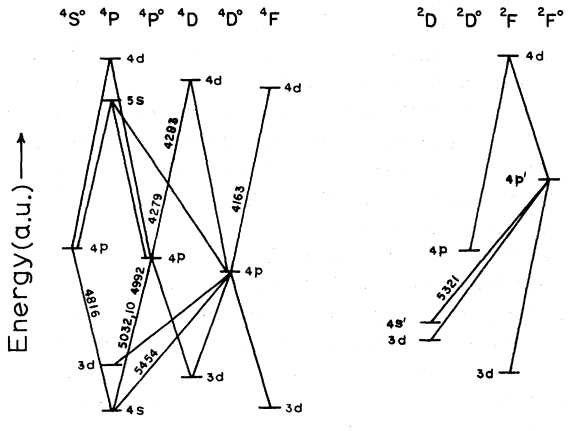

FIG. 4. Partial energy-level diagram for S II containing those levels relevant to this study. Wavelengths of transitions used to make lifetime measurements are given in angstroms (adapted in part from Ref. 14).

light in a 13-Å window about 4281 Å. This meant that both the 4283- and 4279-Å lines contributed to the signal. The weighted average from these curves was 5.23 ± 0.05 nsec, which is in satisfactory agreement with 4.4 nsec (50%) computed from the NBS tables.[5]

IV. ERRORS

As a rule cascade errors are responsible for the greatest limitation to the accuracy of present-day measurements of atomic lifetimes using ion-beam techniques not involving selective excitation of the levels being studied. Because the cascade levels usually have several possible radiative decay channels and have less favorable excitation mechanisms than the levels of interest, one can nonetheless usually achieve accuracies of (5–20)%.

There are circumstances, however, under which cascade can become even more significant. We now believe this to have been the case in a recent study of Ne I done in our laboratory by Lawrence and Head.[15] In that study lifetimes for some $2p$ (Paschen notation) levels of Ne I were measured using beam-gas spectroscopy. The Ne levels were excited by passing fast (22–26 keV) Ne^+ ions through a differentially pumped helium-gas target at pressures of 10–35 mTorr. Despite good statistics, lifetimes obtained were not as reliable as those from similar measurements on the other systems.[10–13]

In retrospect it now seems clear that the problem in that case resulted from heavy cascade into the $2p$ levels from the $3s$ and $2s$ levels, which were being populated by the well-known He-Ne laser population-inversion mechanism, i. e., by collisional excitation transfer from the $2\,^1S$ and $2\,^3S$ metastable levels of the He target atoms.[16] As a result, we were measuring apparent lifetimes which were too long. For example, our reported lifetime for the $2p_4$ level was 24.8 ± 0.5 nsec with 15% estimated accuracy. By comparison the value reported from the classic selective-excitation study by Bennett and Kindlmann was 19.1 ± 0.3.[17] This latter result has been rather conclusively confirmed by the recent beam-gas-laser experiment of Harde and Guthöhrlein, which yielded 19.6 ± 0.2 nsec.[18] This means that our $2p_4$ lifetime is actually in error by about 30%, or twice what we had previously estimated on the basis of past experience.

It is interesting to note that the lifetime of the $3s_2$ level which cascades into the $2p_4$ level was measured by Klose to be 25 ± 2 nsec for Ne at low pressures.[19]

Thus, while accuracies of (5–20)% can usually be achieved in lifetime measurements using the beam-gas technique without selective excitation, one must take care that an accidental resonance between levels of the target atoms and those of the fast beam atoms not lead to excessive cascade. On the other hand, by a judicious choice of target gases, it might be possible to use excitation transfer as a means of selectively populating resonant levels of beam atoms for the purpose of making accurate direct lifetime measurements.

In taking into account possible cascade errors for S II we have also considered many other factors, including the spread resulting from fitting the decay curves with varying numbers of parameters. We have also generated sets of synthetic data with specific lifetimes for the primary and cascade components and with mixtures typical of those found in the actual data. In all cases our computer program was able to return the correct lifetime for the primary component, although the computed coefficients (i. e., A, B, C) were sometimes somewhat different from the input values.

The computer program determines A, B, τ_k, τ_j, etc., by minimizing the least-squares sum using either (i) a Taylor's series expansion about starting estimates to arrive at a set of linear equations or (ii) the method of steepest descent if the first method fails. Following convergence to a preset convergence criterion, the program computes an error matrix and the χ-square integral and generates a plot file for the computer plotter.

Because the χ-square integral applies to the complete decay curve, which usually extends for 10–20 decay lengths of the primary component, and because of the representation of the obviously numerous long-lived cascades by one exponential and a constant the χ-square integral is not particularly useful for determining the accuracy of the fit to the primary component. We have found that it is more reliable to take several decay curves and arrive at a decision concerning the goodness of the fit from the reproducibility of the results.

In addition to possible cascade errors there is an uncertainty of 2% caused by uncertainty in the speed of the S^+ ions. The error associated with measurements of x is negligible. Random errors are reported with the lifetimes in Table I and range from 0.3 to 1.0%. If these errors are added in quadrature with the estimates of uncertainty caused by possibly unresolved cascade, one finds that the latter completely dominates the others. Our final estimates for the total uncertainties for the individual lifetimes are entered in Table I in parentheses following the reported lifetimes.

V. SUMMARY AND CONCLUSION

We have made what are believed to be the first direct measurements of the radiative lifetimes for

some 4p, 4p', and 4d levels of S II giving rise to strong lines in the visible region of the spectrum. These lifetimes are estimated to be accurate to within about (5–10)% and should be useful in establishing anchor points for transition rates arrived at either by measurement or by calculation. Any further gain in absolute accuracy will probably have to come from the use of selective excitation, such as that found in work recently reported involving laser excitation of fast neutral and ion beams.[18,20]

ACKNOWLEDGMENTS

We wish to especially recognize the early work[8] of Dr. James H. Clark (University of California, Santa Cruz) on S II in our laboratory. He is also the author of many of our computer programs for data reduction. Thanks are due also to T. N. Lawrence for computer programming and to D. B. King for help in data acquisition. The work of C. (Bud) Schuler, P. Martin, and J. Buckley of the UNO Machine Shop in constructing our special apparatus has been invaluable, as has the help of H. Rees in providing electronics service. One of us (CEH) wishes to acknowledge discussions with Dr. J. O. Stoner, Jr., at the Third International Conference on Beam-Foil Spectroscopy which led us to try the gas-jet target, for which we extend our thanks.

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