

RADIATIVE LIFETIMES OF ULTRAVIOLET MULTIPLETS IN Si, P, S, O, Ne II, AND Ar II*

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ABSTRACT

Radiative lifetimes have been measured by the phase-shift method for seventeen multiplets in Si I, Si II, P I, P II, S I, S II, and one each in O I, Ne II, and Ar II. The lifetimes range from 0.4 to 200 nsec. Most of the transitions exhibited cascading for which a correction was necessary. Measurement of phase shift versus frequency at a number of different frequencies makes possible the cascade correction. Excitation was by collision of 200-volt electrons with molecules containing the atom of interest. When possible the radiative lifetimes have been converted into absolute multiplet transition probabilities.

I. INTRODUCTION

The possibility of observing interstellar absorption lines in the ultraviolet with satellite telescopes has made desirable experimental and theoretical work on ultraviolet resonance transition probabilities. In a previous paper (Lawrence and Savage 1966; hereinafter called "Paper I") radiative lifetimes and transition probabilities of ultraviolet transitions in B I, B II, C I, C II, N I, and N II were reported as measured by the phase-shift method. Of those transitions investigated, C I λ 1657, C I λ 1560, C II λ 1334, N I λ 1200, N I λ 1135, and N II λ 1085 might appear as interstellar absorption lines (Spitzer and Zabriskie 1959). The present paper reports on radiative lifetimes measured in Si, P, S, their ions, and a transition each in O I, Ne II, and Ar II. Some of the transitions investigated for these atoms are also expected to appear as interstellar absorption features.

For silicon, phosphorus, sulfur, and their ions, the authors found no other existing experimental work on ultraviolet transitions. The only theoretical calculations available for ultraviolet transitions in Si, P, and S are the Coulomb approximation (Bates and Damgaard 1949) and the screening method of Varsavsky (1961). The status of the experimental work on ultraviolet transition probabilities up to 1966 was summarized by Lincke and Griem (1966). These authors mentioned only five experimental papers on ultraviolet transition probability determinations. Most of these determinations were restricted to the light atoms ($Z < 10$).

II. METHOD

The method employed here, a modification of the phase-shift method, has been described by Lawrence (1965) and in Paper I. The basic method consists of measuring the time response of emitted radiation from atoms after excitation with a modulated electron beam. The phase delay in the modulation of the photon flux is a measure of the mean life of the excited state. If the phase delay is determined over a number of frequencies it is possible to understand non-exponential decay processes, i.e., cascading. In this work measurements were made at nine logarithmically spaced frequencies from 0.54 to 54 Mc/s. The obvious advantage of a lifetime method is that the number density of absorbing or radiating atoms is not needed. However, the problem of cascading causes some difficulties in the interpretation of the phase shift versus frequency curves.

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The multiplets are excited by bombardment with 200-volt electrons of molecules containing the atom under study. Low molecule pressures ($P < 10 \mu$ Hg) prevent de-excitation through collisions. The sample gas is pumped through the excitation region to prevent high atom densities from building up and causing photon entrapment. The lack of a pressure effect on the measured lifetimes demonstrated that collisional de-excitation and photon entrapment are not important effects.

The photomultiplier used in this work was an EMR 542F. As phase *differences* between the state in question and a reference transition are taken to obtain the lifetime, τ , the time response of the multiplier should not cause systematic errors unless (1) the time response changes with the wavelength of the radiation; (2) the time response changes with changes in the exposed photocathode area or with photocurrent. Müller, Lumry, and Kokubun (1965) discuss these problems for the EMI 9558B and RCA 6217 multipliers. These authors found a wavelength dependence of the pulse transit time of ≈ 0.5 nsec for a twofold increase in λ . They also found a transit time dependence on the illuminated photocathode area. This dependence amounted to ≈ 0.5 nsec for a twofold change in the illuminated area. Such dependences were checked in this experiment by measuring phase shifts for two multiplets differing greatly in λ but having the same upper state, thus the same lifetime, and also by investigating the change in the observed lifetime with a change in the positioning of the radiation on the photocathode. In the cases investigated with the EMR 542F and our geometry it was found that these errors are < 0.2 nsec. The multiplets measured were: N I λ 1492 and λ 1742 (upper state $4s^2P$) and C I λ 1930 and λ 2478 (upper state $3s^1P^o$).

III. CASCADE CORRECTION

The method of cascade analysis has been described in Paper I. Corrections for the effect of cascading from several states with lifetimes T_i can be made if $T_i \gg \tau$. An attempt is made in each case to estimate the value of the smallest T_i . The cascading transitions occur between excited states so that the Coulomb approximation is justified and gives an accuracy of ≈ 30 per cent. This value of T_i is taken as the nominal T (ninth col., Table 1) for a model in which cascading occurs from a single state with lifetime T and cascading rate β compared to direct excitation. For the lifetimes reported here, good fits were obtained for $\omega > 1/T$. Further, as shown in Paper I, the values of τ and β/T obtained in the fit are quite insensitive to the exact value of T as long as $T \gg \tau$. It was shown that $\beta/T \sim \sum_i \beta_i/T_i$ (see tenth col., Table 1). The most important frequencies are near $\omega\tau \approx 1$ and hence $\omega T \ll 1$. At these high frequencies, the modulation in the cascading radiation has become small, and therefore influences the phase shift only slightly.

For transitions where τ is not $\ll T$ the cascading correction is more difficult to make. Each transition must be considered separately on the basis of (1) observed cascading transitions; (2) knowledge of the lifetimes of these cascading transitions; (3) knowledge of the approximate lifetime of the transition being measured, either by theory or by the observed θ vs. ω curves. In approximately one-third of the cases it was found that cascading corrections could not be made in an unambiguous way. Transitions of this type have not been reported. The cases reported represent results for cascade-free transitions and for cascading transitions for which the information on τ and T show that a correction is possible. An exception to this listing is the lifetime of Si II λ 1808 for which a reliable correction could not be made. (Note large possible error for this multiplet in Table 1.)

IV. RESULTS

Table 1 lists the measured lifetimes in Si I and II, P I and II, S I and II and three measurements in O I, Ne II, and Ar II. The gases from which the atoms were excited are listed in the second column. The third column lists the wavelength of the shortest line in the multiplet. The fourth column lists the multiplet designations from Moore (1950).

The $S\text{ I } \lambda 1687.51 \text{ \AA}$ line is not included in Moore's multiplet tables. We use the classification of Toresson (1960). The upper level is $3s\ 3p^5\ ^1P_1$ at 81440.3 cm^{-1} which implies the two transitions $\lambda 1687.51\ p^5\ ^1P_1-p^4\ ^1S_0$ and $\lambda 1385.02\ p^5\ ^1P_1-p^4\ ^1D^2$. This classification is consistent with the observed freedom from cascading of $\lambda 1687.51$ and the $p^5\ ^3P-p^5\ ^1P$ energy difference fits smoothly in the S isoelectronic sequence. The fifth column lists the experimental lifetimes in nsec. The quoted error is largely an estimate of possible systematic errors. In the sixth column the quantity A_{mn} is the total multiplet transition probability between the upper term m and the lower term n . It is given by $\tau^{-1} \times (\text{branching ratio})$, where the branching ratio is the fraction of transitions going to the lower term of the multiplet in question. For cases where the branching ratio is not

TABLE 1
EXPERIMENTAL RADIATIVE LIFETIMES

Atom	Gas	$\lambda(\text{\AA})$	Multiplet $n \quad m$	τ (nsec)	A_{mn} (10^8 sec^{-1})	$\Sigma_n A_{mn}$ (10^8 sec^{-1})	Σgf	Nomi- nal T (nsec)	β/T (nsec $^{-1}$)
Si I ..	SiF ₄	2506	$3p^2\ ^3P-4s\ ^3P^o$	6.1 ± 0.8	1.64	.	1.40	40	0.01
Si I	SiF ₄	2208	$3p^2\ ^3P-3d\ ^3D^o$	18 ± 3.0	0.556	.	0.584	120	0.01
Si II .	SiF ₄	1526	$3p\ ^2P^o-4s\ ^2S$	0.9 ± 0.2	11.1	.	0.779	15	0.03
Si II .	SiF ₄	2072	$3p^2\ ^2D-4f\ ^2F^o$	3.2 ± 0.4	...	3.12	...	40	.03
Si II .	SiF ₄	1190	$3p\ ^2P^o-3p^2\ ^2P$	<0.4	>25.0	...	>3.2	Cascade free	
Si II .	SiF ₄	1261	$3p\ ^2P^o-3d\ ^2D$	0.7 ± 0.2	14.3	.	3.43	Cascade free	
Si II .	SiCl ₄	1808	$3p\ ^2P^o-3p^2\ ^2D$	$200 - 400$	.	.	*	*	*
P I	PF ₅	1859	$3p^3\ ^2D^o-4s'\ ^2D$	2.9 ± 0.4	$2.84^\dagger$	3.45	1.47	50	0.15
P I .	PF ₅	1775	$3p^3\ ^4S^o-4s\ ^4P$	4.0 ± 0.5	2.50	.	1.43	50	.035
P I	PF ₅	2135	$3p^3\ ^2D^o-4s\ ^2P$	2.4 ± 0.3	$3.07^\dagger$	4.17	1.26	50	.023
P II .	PF ₅	1533	$3p^2\ ^3P-3p^3\ ^3D^o$	78 ± 8.0	0.128	.	0.0679	Cascade free	
P II .	PF ₅	1302	$3p^2\ ^3P-3p^3\ ^3P^o$	6.4 ± 0.8	1.56	.	0.359	30	0.02
S I .	H ₂ S	1425	$3p^4\ ^3P-3d\ ^3D^o$	2.1 ± 0.3	4.76	.	2.18	50	0.05
S I .	H ₂ S	1667	$3p^4\ ^1D-4s'\ ^1D^o$	1.5 ± 0.3	6.67	.	1.38	50	.05
S I .	H ₂ S	1688	$3p^4\ ^1S^o-3p^5\ ^1P$	$17. \pm 2.0$	...	0.588	.	Cascade free	
S I .	H ₂ S	1807	$3p^4\ ^3P-4s\ ^3S^o$	1.5 ± 0.3	6.67	.	4.95	50	.05
S II	H ₂ S	1251	$3p^3\ ^4S^o-3p^4\ ^4P$	25 ± 3.0	0.400	.	0.113	Cascade free	
O I ...	CO	1302	$2p^4\ ^3P-3s\ ^3S^o$	2.4 ± 0.3	4.17	.	0.319	30	0.06
Ne II..	Ne	1908	$3s\ ^2P-3p'\ ^2P^o$	3.5 ± 0.4	...	2.86	.	Cascade free	
Ar II .	Ar	1575	$3p^6\ ^2S-4p'\ ^2P^o$	4.7 ± 0.5	...	2.13	.	Cascade free	

* See text
† For branching ratios used, see text.

1, $\tau = (\Sigma_n A_{mn})^{-1}$, the sum being over the lower terms. The seventh column lists $\Sigma_n A_{mn}$ for these cases. Where the branching ratio is available or known to equal 1 from selection rules or experiment, the multiplet transition probability is listed in the sixth column. The branching ratios for $P\text{ I } \lambda 1859$ and $P\text{ I } \lambda 2135$ were calculated in intermediate coupling by Lawrence (1966) and are 0.825 and 0.728, respectively. These are within 2 per cent of the LS -coupling values. Some of the missing values of A_{mn} in Table 1 are for upper levels from which transitions originate which violate the selection rule $\Delta l = \pm 1$. Hence no simple calculations of the branching ratios are possible. The eighth column lists the *multiplet* Σgf -values. These are obtained from the relation

$$\Sigma gf = 1.499 \times 10^{-8} (S_{up} + 1) (2L_{up} + 1) A_{mn} \lambda^2_{mn} .$$

where λ_{mn} is the mean wavelength for the multiplet in microns. For the transitions measured, λ -values for the various lines in the multiplets have a spread of <1 per cent; and S_{up} and L_{up} are the total spin and angular momentum quantum numbers for the upper term. It should be noted that the formula is strictly true only if the states involved

are in LS coupling. The final two columns supply the cascade correction information. The transitions observed to be free of cascading, i.e., those fitting a $\theta = \tan^{-1} \omega\tau$ phase versus frequency curve are indicated as "cascade free."

The silicon multiplets were measured by electron excitation of silicon in two different gases, SiF_4 and SiCl_4 . Although the multiplets excited in these different gases showed different amounts of cascading, the lifetimes obtained after the cascade correction were in agreement.

Our understanding of the cascade processes for $\text{Si II } \lambda 1808$ is marginal. The apparent lifetime is included to illustrate an interesting anomaly. The lifetime of 200–400 nsec is 10–50 times larger than expected from LS -coupling theory. This may perhaps be understandable in terms of configuration mixing with the nd^2D series. The effect of such mixing on the term structure of Si II is described by Shenstone (1960). A similar situation occurs with $\text{P II } \lambda 1533$ where the lifetime is 78 nsec. An analysis of P II by Martin (1959) indicates much less perturbation, however.

Comparison with theory and other experiment is possible for the $\text{O I } \lambda 1302$ measurement. The multiplet Σgf -value of 0.319 obtained here can be compared with the Σgf -value of 0.2267 obtained by Kelly (1964) with an analytical self-consistent field method. Other experimental determinations of Σgf are 0.3 by Prag, Fairchild, and Clark (1965) and 0.3 by Morse and Kaufman (1965). The results are in reasonable agreement.

Comparisons of the phase-shift method with other methods both theoretical and experimental are found in Paper I for the cases of B, C, and N.

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