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Radiative Lifetimes of uv Multiplets in Boron, Carbon, and Nitrogen*

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Radiative lifetimes of fourteen of the strongest vacuum uv multiplets in B I, B II, C I, C II, N I, and N II were measured by the phase-shift method with accuracies of 10–20%. All but one are transitions to the ground-state configuration. When necessary the measurements were corrected for the presence of delayed excitation by cascading. Of the transitions reported, eight exhibited cascading. The lifetimes range from 0.9 to 23 nsec. Multiplet transition probabilities determined from the lifetimes are compared with some previous determinations. Excitation was by collision of 200-V electrons with molecules containing the atom under study. The electron current was modulated sinusoidally at frequencies between 0.54 and 54 Mc/sec. The phase shift in the modulation of the emitted light was measured and used to determine the radiative lifetimes.

I. INTRODUCTION

The work described here is a continuation of a program to determine atomic and molecular transition probabilities of astrophysical and theoretical importance in the vacuum ultraviolet. The phase-shift method of Lawrence[1] has previously been used to obtain radiative lifetimes and thus absolute transition probabilities in molecular transitions of neutral and singly ionized NO and CO.[2] Reported here is work on uv multiplets in neutral and singly ionized B, C, and N. The lifetimes determined range from 0.9 to 23 nsec. Use of the radiative lifetimes to determine atomic transition probabilities is especially useful in the case of B, C, N, and their ions because of the technical difficulty of determining the concentration of such species.

In the following we review the phase-shift method,[1,3] describe our version of it, and treat the special problems that arise when cascading is present. The method of performing cascading corrections is described. Tables I and II contain the experimental results and comparison with some other values.

II. METHOD

Experimental. The multiplets under study are excited by a 200-V electron beam in a suitable low-pressure gas ($p \approx 10\ \mu$ Hg) containing the atom under study. A "line" consisting of an unresolved atomic multiplet is isolated with a $\frac{1}{2}$-m vacuum monochromator. When necessary the spectrum was studied with a 3-m vacuum monochromator to check spectral purity of the lines with higher resolution. In order to obtain the time response of the emitted light, the excitation current is modulated sinusoidally at radio frequencies. The phase delay in the modulation of the emitted photon flux is a measure of the mean lifetime of the excited state. In our variation of the phase-shift method the phase delay is determined over a range of frequencies in order to understand nonexponential decays produced when electron excitation is used.

The molecular sample gas is pumped through the excitation region to keep the atom density low and thus eliminate entrapment of photons. It is assumed that the molecules dissociate upon excitation in approximately the time of a molecular vibration, 10^{-12} sec. The use of molecules, however, leads to an unpredictable pattern of cascading.

The experimental arrangement has been described in the previous paper.[1] Some changes, however, have been made to improve the time resolution in the nanosecond range. In order to work with a photoelectron rate on the order of 1000/sec, a narrow-band detection system is used. The modulation signal is heterodyned from the radio frequency to 100 cps at which frequency the phase measurement is made. The heart of the heterodyning process is a phase-shift–type side-band generator which has been somewhat stabilized since the previous work. The system is switched for operation at 10 logarithmically spaced frequencies from 0.54 to 54 Mc/sec.

A Bendix magnetic multiplier with a CsI-coated cathode, an EMI 9526B photomultiplier, and an EMR 542F tube gave satisfactory time response. The Bendix multiplier had to be operated at voltages below 1700 V to prevent spurious delays due to after-pulsing.

Zero-phase standard. At each frequency the reading of the phase meter contains a poorly known, additive

Table I. Cascade-free multiplets.

Atom	Gas	λ (Å)	Multiplet $2s^2 2p^n$-$2s2p^{n+1}$	This experiment (nsec)	*A* This experiment (10^8 sec^{-1})	*A* Other determinations (10^8 sec^{-1})
B I	BF_3	2089	$2p\ ^2P^0$-$2p^2\ ^2D$	23.0 ± 2.0	0.44	
B II	BF_3	1624	$2p\ ^3P^0$-$2p^2\ ^3P$	1.0 ± 0.2	10.0	8.4[a]
C I	CH_4	1560	$2p^2\ ^3P$-$2p^3\ ^3D^0$	8.0 ± 0.8	1.25	1.5[b]
C II	CO	1335	$2p\ ^2P^0$-$2p^2\ ^2D$	3.9 ± 0.4	2.56	
N I	N_2	1134	$2p^3\ ^4S^0$-$2p^4\ ^4P$	7.2 ± 0.7	1.39	
N II	N_2	1085	$2p^2\ ^3P$-$2p^3\ ^3D^0$	2.7 ± 0.3	3.7	

[a] SCF, A. W. Weiss, see Refs. 5 and 11.
[b] G. Boldt, see Refs. 5 and 8.

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[1] G. M. Lawrence, J. Quant. Spect. Rad. Trans. **5**, 359 (1965).

[2] J. E. Hesser and K. Dressler, Ap. J. **142**, 389 (1965).

[3] The major references on the phase method are found in L. Brewer, C. G. James, R. G. Brewer, F. E. Stafford, R. H. Berg, and G. M. Rosenblatt, Rev. Sci. Instr. **33**, 1450 (1962); A. Müller, R. Lumry, and H. Kokubun, *ibid.* **36**, 1214 (1965).

TABLE II. Multiplets with cascading.

Atom	Gas	λ (Å)	Multiplet	τ This experiment (nsec)	A This experiment (10^8 sec^{-1})	A Other experiment (10^8 sec^{-1})	Nominal T (nsec)	β/T (nsec^{-1})
B I	BF$_3$	1826	$2p\ {}^2P^0$-$3d\ {}^2D$	4.5±0.5	2.1[a]		30	0.01
B II	BF$_3$	1362	$2s^2\ {}^1S$ -$2p\ {}^1P^0$	0.9±0.2	11.1		5	0.03
C I	CH$_4$	1657	$2p^2\ {}^3P$ -$3s\ {}^3P^0$	3.1±0.3	3.2	4.1[b]	40	0.01
C I	CH$_4$	1930	$2p^2\ {}^1D$ -$3s\ {}^1P^0$	2.9[c]±0.3	3.0[a]		40	0.01
N I	N$_2$	1243	$2p^3\ {}^2D^0$-$3s\ {}^2D$	2.2[d]±0.3	4.1[a]	4.6[e]	35	0.025
N I	N$_2$	1492	$2p^3\ {}^2D^0$-$3s\ {}^2P$	1.9±0.3	3.9[a]	5.5[e]	35	0.025
N I	N$_2$	1742	$2p^3\ {}^2P^0$-$3s\ {}^2P$	1.9±0.3	1.4[a]	2.0[e]	35	0.025
N I	N$_2$	1200	$2p^3\ {}^4S^0$-$3s\ {}^4P$	2.5±0.3	4.0	>0.8,[f] 5.4,[e] 1.4[g]	30	0.025

[a] Branching fractions from NBS values, see Ref. 5.
[b] G. Boldt, see Refs. 5 and 8.
[c] 2.9 nsec also represents lifetime of C I 2478, $2p^2\ {}^1S$-$3s\ {}^1P^0$.
[d] 2.2 nsec also represents lifetime of N I 1412, $2p^3\ {}^2P^0$-$3s\ {}^2D$.
[e] F. Labuhn, see Refs. 5 and 7.
[f] F. A. Morse and F. Kaufman, J. Chem. Phys. **42**, 1785 (1965).
[g] A. B. Prag, C. E. Fairchild, and K. C. Clark, Phys. Rev. **137**, A1358 (1965).

constant caused by electron transit time, cable length, reactances in the side-band generator, photomultiplier delay time, etc. The basic experimental data at each frequency were the phase *differences* between the signals of the emission being measured and a reference transition whose phase is known. The phase reference used in this work was the N II 1085 multiplet with its lifetime determined by comparison with Lyman alpha excited in CH$_4$. The Lyman alpha phases have to be corrected for cascading. This is the same reference used in Ref. 1 but with more accuracy in its lifetime because of the improved equipment and improved cascade correction techniques. The steps in the determination of the phase-reference lifetimes are as follows:

(1) N II 1085 was determined to be cascade-free on theoretical grounds and experimentally by comparison with other cascade-free transitions.

(2) The phase differences between Lyman alpha and N II 1085 were measured.

These data were combined with the known theoretical lifetimes of the H $2p$ and H $3d$ states (1.6 and 15.6 nsec, respectively) and used in the cascade fit process described below to obtain the value of the N II 1085 lifetime.

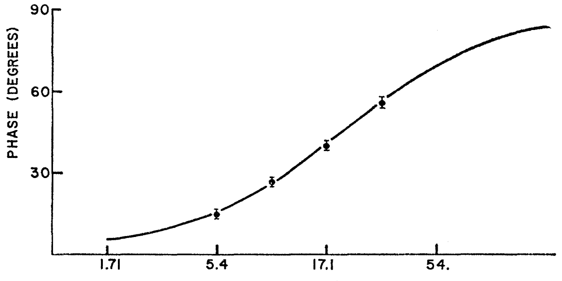

FIG. 1. Absolute phase delay versus frequency for the cascade-free transition of C I 1560. Solid curve is plot of $\theta=\tan^{-1}\omega\tau$ for $\tau=8.0$ nsec which gives least-squares fit to experimental data.

Theoretical. In analyzing the phase-delay process with complications such as cascading, we have found it useful to think of an excited state as a transfer function between the "incoming" excitation modulation and the "outgoing" modulation of the photon flux. For example, the case of no cascading, in which the state population delays exponentially after removal of excitation, is characterized by a transfer function

$$\text{signal out/signal in}=(1+i\omega\tau)^{-1}, \qquad (1)$$

where ω is the angular frequency of modulation, and τ is the mean lifetime. This transfer function shows a phase delay given by

$$\theta=\tan^{-1}\omega\tau. \qquad (2)$$

One then measures θ versus ω to determine τ.

A study of the experimental results and of the energy-level diagrams allows a division of the observations into two groups, the cascade-free lines and those lines which contain cascading. The C I 1560 and C I 1657 transitions are examples of these two situations, respectively. The 1560 multiplet involves the excitation of an "inner" ($2s$) electron and any possible cascading terms are above the ionization limit of the atom. The experimental phase shifts are seen to follow the $\tan^{-1}\omega\tau$ relation of Eq. (2) as illustrated in Fig. 1. The C I 1657 transition, however, does not have a simple exponential decay and requires a more involved analysis. Figure 2 shows the transitions

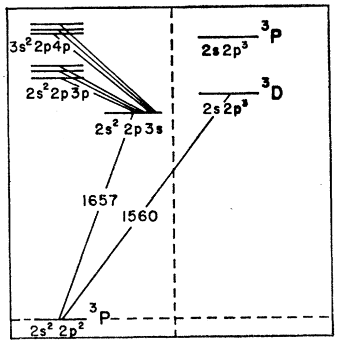

FIG. 2. Relevant terms of carbon I triplet system. The 1657-Å line is subject to cascading while the 1560-Å line is cascade free. The term diagram is not to scale.

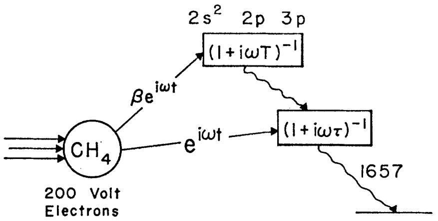

FIG. 3. Schematic diagram of the major cascade process into C I 1657. The energy levels are treated as transfer functions for the sinusoidal modulation. The excitation of the amount β into the cascading state with lifetime T produces an additional cascading phase as given by Eq. (5).

of interest in the triplet system of carbon. The upper state of the 1657 multiplet is seen to be at least partially populated by cascading transitions from terms of the $3s^22p3p$ and $3s^22p4p$ configurations. The terms involved have lifetimes calculated with the Coulomb approximation[4] of 35 to 50 nsec for the $3p$ terms and 600 to 1500 nsec for the $4p$ terms. The Coulomb approximation should give 30% or so accuracy for such transitions as they are between excited states. As we shall see this accuracy is sufficient to perform the cascade correction. The upper state of C I 1657 has a lifetime of 3.1 nsec, i.e., more than ten times smaller than the shortest cascading lifetime. This separation of values is typical and makes the cascade correction possible. Figure 3 illustrates the concepts involved in the analysis required to correct for cascading. Start with one cascading state with lifetime T. Let β be the rate of excitation through cascading relative to unit direct excitation of the upper state in question. From Fig. 3 one can write down the transfer function for the case of *several* one-step cascades.

$$\text{signal out/signal in} = (1+i\omega\tau)^{-1}[1+\textstyle\sum_n \beta_n(1+i\omega T_n)^{-1}]. \quad (3)$$

The sum is taken over the cascading states with cascading fractions β_n and lifetimes T_n. In the cases reported here $T_n \gg \tau$, so that at high frequencies the effect of cascading becomes relatively small. In this high-frequency limit the transfer function with cascading becomes

$$[1-i\omega^{-1}\textstyle\sum_n(\beta_n/T_n)](1+i\omega\tau)^{-1}, \quad (4)$$

so that at high frequencies the additional effect of cascading can be expressed by one parameter, $\sum_n \beta_n/T_n$. In practice, a single value of T was assigned to (3) and the experimental phases were made to fit this equation by varying β and τ in a manner which weights the high-frequency points most heavily. The phase given by (3) with only one value of T is

$$\theta = \tan^{-1}\omega\tau + \tan^{-1}\omega T - \tan^{-1}[\omega T/(1+\beta)]. \quad (5)$$

Some algebraic manipulation of this equation leads to the form

$$F(\theta,\omega T) \equiv \frac{\omega T[1+(\omega T)\tan\theta]}{\omega T - \tan\theta} = (\omega T)^2\frac{bc}{b-c} + \frac{1}{b-c}, \quad (6)$$

where $c=\tau/T$ and $b=1/(1+\beta)$. Thus if the function F of the experimental phases and the assigned T is plotted versus $(\omega T)^2$ a straight line should result. The parameters β and τ can be obtained as functions of the slope and intercept of the best straight-line fit. A computer program making use of a least-squares fit was used to do this. Figure 4 illustrates such a fit for the C I 1657 line. Figure 5 shows the same fit in the form of phase versus frequency as described by Eq. (5).

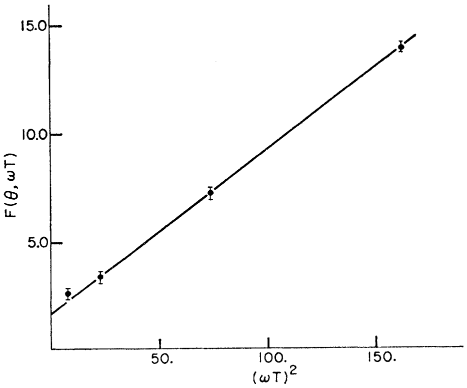

FIG. 4. F versus $(\omega T)^2$ for C I 1657. Least-squares fit made to upper three frequencies. β and τ are obtained as function of slope and intercept as seen in Eq. (6). $T=40$ nsec.

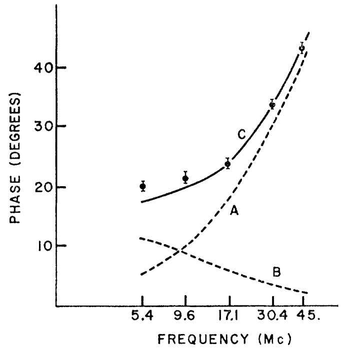

FIG. 5. Absolute phase shift versus frequency for C I 1657. (A) $\tan^{-1}\omega\tau$ with $\tau=3.1$ nsec; (B) Cascading phase; (C) Curve is sum of curves A and B, points are experimental.

The nominal value of T for the purpose of the fit is chosen near the theoretical value of the smallest T_n. The appropriate theoretical values of T_n were all calculated in the Coulomb approximation.[4] This choice of T fails to fit at frequencies lower than about $\omega=1/T$ because it ignores the spread in T values. Hence the fit must be made at the highest frequencies where Eq. (4) is valid. We have found that variation of T about the nominal value has little effect on the determined values of τ and β/T. This is illustrated in Fig. 6. A two-step cascade process can be shown to contribute a cascading phase shift which goes to zero as $1/\omega^2$ at high frequencies. Neglecting these higher order effects, β/T found by the

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[4] D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. (London) **A242**, 101 (1949).

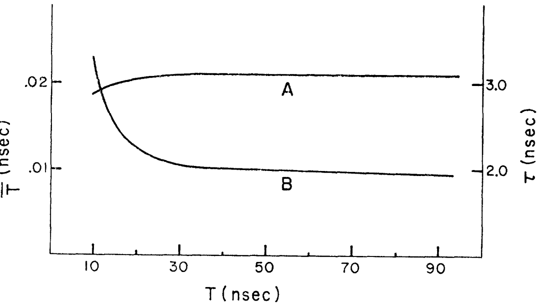

FIG. 6. Variation of τ (curve A) and β/T (curve B) with T for C I 1657. Nominal value of T is 40 nsec. Best fit is found near $T=40$ nsec.

straight-line fitting process is probably a good approximation to $\sum_n \beta_n/T_n$. These values are listed in Table II. By multiplying the values of β/T by the nominal T, one can see that the values of β are on the order of unity. Such values of β have meaning only within factors of 2 or 3.

The cascade fit process was also applied to the phase data for the cascade-free lines of Table I. The results yield an upper limit for β of approximately 0.03.

In most cases the cascade correction changes τ on the order of 30% from what would be obtained without the correction, using only the highest frequency phase measurement.

III. DISCUSSION

The recent NBS compilation of atomic transition probabilities[5] lists "best" values, selected and compiled for most major transitions in the first ten elements. The critical selection and a bibliography have been made by Wiese and the NBS data center staff from available theoretical and experimental values.

Assuming *L-S* coupling,[6] the quantity A in Tables I and II is the total (multiplet) transition probability. This is a sum over lower levels (J). It is given by $1/\tau$ times the fraction of transitions going to the lower term of the multiplet in question. That is, the branching fraction$=A\tau$. This fraction, where less than unity, was obtained from the relative values of data in the NBS compilation mentioned above. The NBS values used to obtain branching fractions are theoretical except for N I which are from Labuhn's[7] measurements.

In column 7 of the tables are listed for comparison a few values of A from other sources, mostly from the NBS compilation. The experimental values which are derived from the arc intensity method of Boldt[8] and Labuhn[7] are expected to be more accurate on a relative scale than in absolute scale. Boldt gives an absolute scale error estimate of 25%. The comparison shows agreement within 5% on a relative scale. To produce agreement on an absolute scale, Boldt's C I f values can be multiplied by 0.8 and Labuhn's N I values by 0.75.

All of the transitions listed in Tables I and II, except B II 1624, are to the configuration of the ground state. Theoretical calculation of such transition probabilities is difficult because of the high degree of electron interaction in the ground state, especially with nearly half-filled shells. For example, the analytical Hartree-Fock procedure of Kelly and Armstrong[9] yields an A value of 1.5×10^8 sec^{-1} for the N I 1200 transition, lower by a factor of 3 than Labuhn's or our values. The f values given by Varsavsky[10] for some of the transitions in Table I are larger than the ones our lifetimes yield by factors of 2 or 3.

The self-consistent-field calculation of Weiss[11] for B II 1624 perhaps may be expected to and does give agreement with our value because the transition is between excited states of a light ion.

The estimated error in our values is generally the greater of 10% or 0.2 nsec for the cascade-free lines or 15% or 0.3 nsec for the lines with cascading. The uncertainties are due to a combination of zero phase reference inaccuracy, phase meter error, approximations in the cascade correction, photomultiplier delay change with wavelength, and spectral impurities in the emissions studied.

IV. ACKNOWLEDGMENTS

Thanks are due to Kurt Dressler for encouragement and useful discussions. W. L. Wiese was very kind in providing the NBS values prior to publication.

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[5] B. M. Glennon, M. W. Smith, and W. L. Wiese, *Atomic Transition Probabilities H to Ne* (U. S. Government Printing Office, Washington, D. C., 1965) Vol. I.

[6] For allowed transitions in *L-S* coupling, all states (M values) of a given upper term (L value) have the same radiative lifetime. This should apply within a few percent to the transitions reported here.

[7] F. Labuhn, Z. Naturforsch. (to be published).

[8] G. Boldt, Z. Naturforsch. **18a**, 1107 (1963).

[9] P. S. Kelly and B. H. Armstrong, Phys. Rev. Letters **9**, 426 (1962).

[10] C. M. Varsavsky, Astrophys. J. Suppl. Ser. **53**, 75 (1961).

[11] A. W. Weiss (private communication); see also Ref. 5.