Radiative lifetimes of excited *p* states of Na†

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Using a laser-cascade fluorescence technique, we have measured the radiative lifetimes of the $n = 4$ to 7 p states of Na. The $(4\text{-}7)p$ lifetimes are 125(12) nsec, 345(43) nsec, 0.89(9) μsec, and 1.45(10) μsec. These results are in qualitative agreement with calculated values.

Although the properties of the $3p$ state of sodium have been well characterized,[1] the higher p states have hardly been investigated at all. This is due mostly to the fact that resonance lamps, which are perfectly adequate for populating the $3p$ state, are not satisfactory for experiments with the higher p states. We report here laser fluorescence measurements of the radiative lifetimes of Na p states from $n=4$ to 7, using a technique which is an extension of the method we previously used to measure Na s and d radiative lifetimes.[2]

Experimental values of these radiative lifetimes are useful for several reasons. Measurements of the collisional properties of an excited state depend critically on the knowledge of the radiative lifetime of the state. In addition, the existence of accurate experimental lifetime data offers a good way of checking theoretical atomic structure calculations.

The method is best understood by considering a specific example, the measurement of the $6p$ radiative lifetime. As shown in Fig. 1, we use two synchronized pulsed dye lasers at 4890 and 4669 Å to selectively excite the atoms from the $3s$ to the $3p$ state and then from the $3p$ to $6d$ state. The initially populated $6d$ state decays with its radiative lifetime of ~200 nsec.[2] About 10% of atoms decay to the $6p$ state.[3] The atoms in the $6p$ state then decay with the much longer $6p$ radiative lifetime of ~900 nsec.[3] About 30% of the atoms in the $6p$ state decay to the $6s$ state.[3] Atoms in the $6s$ state decay with the $6s$ radiative lifetime of ~160 nsec,[3] and we observe the time resolved $6s \rightarrow 3p$ fluorescence at 5154 Å. As shown by the inset of Fig. 1, the cascade $6d \rightarrow 6p \rightarrow 6s$ is the only way that atoms initially excited to the $6d$ state can cascade from the $6d$ state to the $6s$ state; so when we observe $6s$-$3p$ fluorescence, we know that the fluorescing atoms have followed the cascade $6d \rightarrow 6p \rightarrow 6s$ and no other route. Actually, there is one other possible cascade sequence, $6d \rightarrow 5f \rightarrow 5d \rightarrow 5p \rightarrow 6s$, but since the branching ratios indicate that less than one in 10^8 atoms initially excited to the $6d$ state will follow this cascade path, we have ignored this cascade.[3] Since the cascade involves the $6s$, $6p$ and $6d$ states, the time dependence of the fluorescence is a function of all of their lifetimes. As shown in Table I the $6p$ lifetime is much longer than either the $6s$ or $6d$ lifetime and is the rate limiting step in the $6s$-$3p$ fluorescence. It is straightforward to show that for times more than one $6p$ lifetime after the laser pulses the $6s$-$3p$ fluorescence decays with the $6p$ radiative lifetime. An example of $6s$-$3p$ fluorescence decay is shown in Fig. 2. Note that although there is an initial buildup, the decay is a single exponential at later times.

The $5p$ and $7p$ lifetimes are measured in an analogous fashion. To measure the $4p$ lifetime, we observed the $4p \rightarrow 3s$ fluorescence at 3303 Å rather than the $4s$-$3p$ fluorescence, eliminating one step of the cascade.

Since this cascade method for measuring p state lifetimes depends critically on the relative values of the s, p, and d lifetimes of each n state, we have listed in Table I the values of the relevant s, p, and d lifetimes calculated by Tsekeris and Happer using a Coulomb approximation.[3] We have included the $4s$ lifetime for completeness although, as we have pointed out, it is not part of the cascade used to measure the $4p$ lifetime.

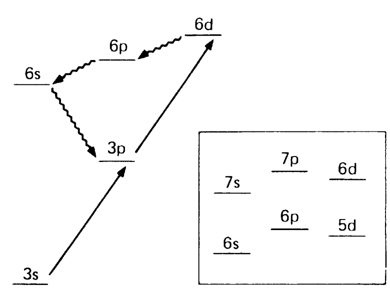

FIG. 1. Energy-level diagram showing the relevant levels for the measurement of the $6p$ radiative lifetime. The straight arrows show the laser pumping steps, and the wavy arrows indicate the fluorescent decays. The inset shows the relative positions of the s, p, and d energy levels near $n=6$.

TABLE I. Calculated lifetimes of Na *s*, *p*, and *d* states.[a]

	Lifetimes (nsec)		
n	*s*	*p*	*d*
4	40	97	53
5	84	317	110
6	165	749	196
7	292	1457	317

[a]See Ref. 3.

TABLE II. Calculated and observed Na *p*-state lifetimes.

n	No. of Runs	τ_{obs} (μsec)	τ_{calc}[a] (μsec)	τ_{calc}[b] (μsec)
4	12	0.125(10)	0.097	0.103
5	14	0.345(43)	0.317	0.351
6	14	0.89(9)	0.749	0.864
7	7	1.45(10)	1.457	1.750

[a]See Ref. 3.
[b]See Ref. 5.

As the apparatus has already been described in detail elsewhere,[2] we only outline the main features here. The sodium vapor is contained in a cylindrical Pyrex vapor cell which was kept at a temperature of 145°C. This provides a sodium vapor pressure of 4×10^{-6} Torr and a number density of 10^{11} cm^{-3}. No buffer gas was added in order to avoid any possible complications due to angular momentum mixing of the *nd* state.[4] The laser beams pass through the cell along its axis, and we detect the fluorescence emitted in the direction perpendicular to the cell axis.

The 4*p*-3*s* 3303-Å fluorescence was selectively detected by using a uv filter, and the signal was averaged using a PAR boxcar averager. The *ns*-3*p* fluorescence from $n = 5$ to 7 was selectively detected with a *f* 5.6 Bausch and Lomb monochromator, and an Ortec digital boxcar was used for signal averaging.

Although radiation trapping of the $np \rightarrow 3s$ radiation is possible for $n \geq 4$, it is much less likely to be trapped than the 3*p*-3*s* radiation which we observed to be only slightly trapped (decay times of ~30 nsec). Nonetheless, we checked the variation of the 4*p* lifetime as we varied the cell temperature from 130 to 170°C, a variation in sodium density of 5×10^{10} to 2×10^{12} cm^{-3}, and saw no significant effect. If the 4*p* state is not trapped, then none of the higher *p* states will be.

The *p* lifetimes we measured, and those calculated by Tsekeris and Happer[3] and Anderson and Zilitis[5] are given in Table II. Since we checked

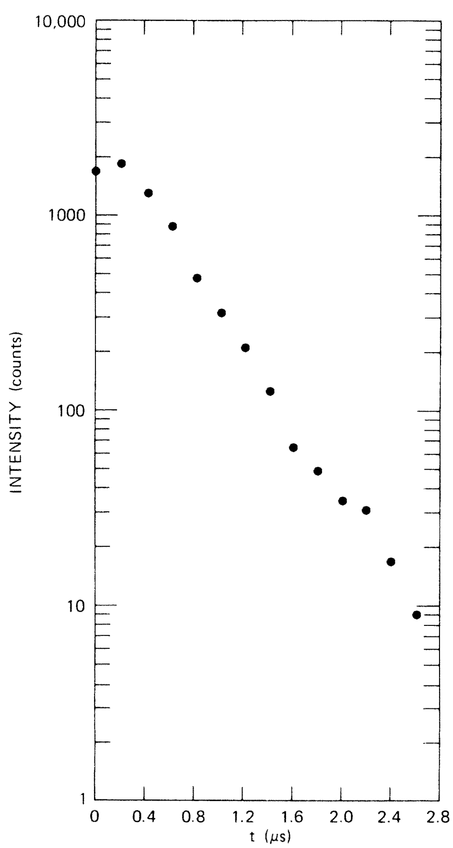

FIG. 2. Semilogarithmic plot of the 6*s*-3*p* fluorescence decay. The initial points of the curve show the buildup of population in the 6*p* state, and the later points show a single exponential decay reflecting the 6*p* radiative lifetime.

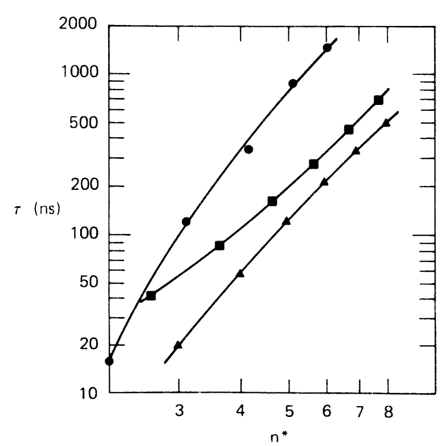

FIG. 3. Log-log plot of Na 4*s*-9*s* (■), 3*p*-7*p* (●), and 3*d*-8*d* (▲) radiative lifetimes vs n^*. The 7-9*s* and 5-8*d* lifetimes are from Ref. 2. The 3*p* and lower *s* and *d* lifetimes are from Ref. 3.

the most likely sources of systematic errors, we feel that the uncertainties are mainly statistical. Consequently, the reported uncertainties for each lifetime is the standard deviation for the number of runs indicated in Table II. For low n our data seem to agree with the calculations of Anderson and Zilitis[4] and cross over to the value of Tsekeris and Happer[3] at $n = 7$. In Fig. 3 the lifetimes of the s, p, and d states are plotted vs n^*, where n^* is the effective principal quantum number, that is $n^* = n - \delta$ where n and δ are the principal quantum number and quantum defect ($\delta = 1.35$, 0.85, and 0.014 for s, p, and d, respectively). It has been shown previously that for higher n the s and d lifetimes increase as n^{*3} as does hydrogen. Figure 3 suggests that this may well be true for the higher Na p states as well.

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[5]E. M. Anderson and V. A. Zilitis, Opt. Spektrosk. 16, 177 (1964) [Opt. Spectrosc. 16, 99 (1964)].