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Radiative lifetimes of the *S* and *D* Rydberg levels of Na[†]

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We have determined the radiative lifetimes of the $n = 5$–13, *s* and *d* states of Na by pumping the desired level with two resonant photons derived from two dye lasers excited by the same N_2 laser. The lifetimes increase approximately as the cube of the effective quantum number, and are in good agreement with a Coulomb-approximation calculation.

Atoms in high-lying or Rydberg states behave quite differently than atoms in the ground or lower excited states. The differences stem from the fact that in a Rydberg state, the electron is in a large, loosely bound orbit. For example, in $n=11$, $l=3$, the average value of the orbital radius is ~100 Å, while the binding energy is only 0.12 eV. Therefore, one expects atoms in Rydberg states to be highly polarizable and to exhibit large cross sections for collision processes. In addition, the large orbit of the electron has a poor overlap with the radial wave functions of the lower states, giving rise to a very long radiative lifetime. As a first step in understanding the properties of atoms in Rydberg states, we have measured the radiative lifetimes of the highly excited ($n=5$–13) *s* and *d* states of sodium. In principle, the electronic properties of the Rydberg states of all atoms are identical to the extent that the electron remains far away from the ionic core. Consequently, measuring the properties of the *d* states of Na should suffice for all atoms. The *s* states penetrate the ion core, but the "hydrogenic" nature of the levels can be preserved by using a quantum defect characteristic of the particular atoms to give an effective quantum number n^*, where n^* is defined by

$$E_n = -\mathcal{R}/(n^*)^2 \qquad (1)$$

with E_n the energy of the nth state and $\mathcal{R}$ the Rydberg constant. Quantum-defect theory also predicts that the lifetime of a state should be proportional to $(n^*)^3$, which can be checked by our measurements.

To excite the Rydberg levels, we used two synchronized, pulsed dye lasers to pump the sodium atoms in two steps: first, from the $3s$ ground state to the $3p$ state, and then from the $3p$ state to a high-lying *s* or *d* state. We monitored the decay of the $ns \rightarrow 3p$ or $nd \rightarrow 3p$ fluorescence to determine the radiative lifetime directly. The lifetime of the $4d$ state of sodium has been measured previously[1] in this way, giving a lifetime of 57 nsec. Lifetime measurements could be distorted by cascade population from higher levels or the observation of photons from lower levels which have longer lifetimes. Cascading from higher states is eliminated since only one state is pumped. By using filters which restrict the observed photons to the range from 4000 to 5000 Å we eliminated most of the radiation from lower states. The branching ratios calculated by Tsekeris and Happer[2] indicate that only 1% of the observed light can be coming from states other than the one of interest. This is experimentally confirmed by our observations of only a single exponential decay. The effects of diffusion out of the viewing region were not serious since the diffusion time is at least an order of magnitude greater than the longest observed lifetime.

The experimental configuration shown in Fig. 1 was basically the same as that used by Haroche *et al.*[3] to measure the fine structure of the 10 and $11d$ states of Na. A nitrogen laser of the design of Basting *et al.*[4] pumped two dye lasers of the Hänsch design.[5] To pump the Na resonance line at 5890 Å, we used Rhodamine 6*G* in the "yellow" laser. In the "blue" laser we have used 4-diethylamino-4-methyl-coumarin, coumarin 120, coumarin 102, and popop to pump the $3p \rightarrow ns$, nd transition. We chose to use the $P_{3/2}$ level so that in the second step we could pump to the $D_{5/2}$ level as well as the $D_{3/2}$ level. The two dye-

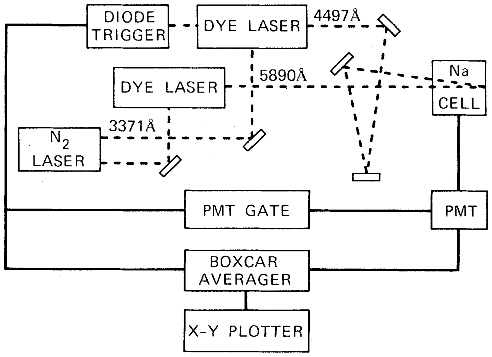

FIG. 1. Schematic diagram of the apparatus with the lasers tuned to pump the $7d$ level via the $3p_{3/2}$ level.

TABLE I. Lifetimes of sodium *s* and *d* states.

State	n^* Effective quantum number	Number of runs	Calculated lifetime (nsec) [a]	Calculated lifetime (nsec) [b]	Observed lifetime (nsec)
7*s*	5.647	18	292	262	276(14)
8*s*	6.650	28	476	419	465(40)
9*s*	7.638	16	730	634	713(76)
10*s*	8.638	11	1063	909	1024(49)
11*s*	9.641	29	1428	1211	1270(130)
13*s*	11.64	3		2004	2270(170)
5*d*	4.985	9	110	107	120(14)
6*d*	5.987	16	196	190	206(24)
7*d*	6.982	18	317	306	324(32)
8*d*	7.985	7	477	460	502(39)
9*d*	8.981	33	685	673	720(67)
10*d*	9.985	5	943	947	971(35)
12*d*	12.01	10		1578	1650(150)
13*d*	12.99	10		2087	2120(400)

[a] See Reference 2.

[b] See Reference 7.

laser beams are merged in the sodium cell at a slight angle. The blue dye-laser pulse is delayed by 4 nsec relative to the yellow laser pulse to ensure full population of the 3p level for the second pumping step. The radiative lifetime of the $3\,^2P_{3/2}$ state is 16 nsec, so that negligible decay of this state occurs before the second laser pulse, but essentially none remains during observation of the *ns*, *nd* fluorescence.

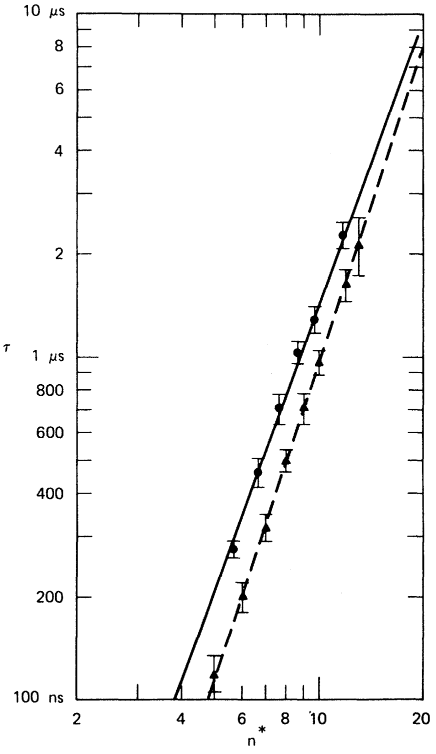

FIG. 2. Log-log plots of the lifetimes of the *s* and *d* states of sodium vs n^*. The measured *s*-state lifetimes and errors are denoted by (●) and the solid line. The *d* states are denoted by (▲) and the broken line.

The sodium cell is a Pyrex cylinder 22 mm in diameter and 10 cm long, connected to a glass vacuum system through a magnetically activated ground glass seal. The base pressure of the cell was less than 10^{-5} torr. An EMI 9558A photomultiplier tube, at right angles to the laser beams, monitored the fluorescence from the upper *s* or *d* state back to the 3p state. The high quantum efficiencies of phototubes in this wavelength range, the branching ratios of the transitions from the excited state, the absence of cascade problems, and the ease with which the resonance line can be discriminated against make this the most attractive transition to monitor, even though it coincides with the pumping laser wavelength. In measuring the longer lifetimes, we had to amplify the weak fluorescence signals, and the pulse produced by photons scattered from the blue laser overloaded the boxcar averager. This problem was eliminated by gating the photomultiplier on 300 nsec after the laser pulses. Signal averaging was done with a Princeton Applied Research 162 boxcar averager, or a Tektronix R7912 transient digitizer for some of the higher states.

The cell was operated at 135±10 °C corresponding to a sodium vapor pressure of 2.5×10^{-6} torr. We checked for possible quenching or radiation trapping by the sodium by measuring the lifetime of the 8s state from 115–190 °C corresponding to sodium vapor pressures from 9×10^{-7} to 6×10^{-5} torr and found no significant variation.

The lifetimes given in Table I are the averages of many experimental runs. The figures in parentheses are standard deviations. The effective quantum numbers are calculated using the term energies of Moore[6] and Eq. (1). The theoretical lifetimes calculated by Tsekeris and Happer[2] using the Bates-Damgaard method, as well as those calculated from the oscillator-strength tables of Anderson and Zilitis,[7] are given in Table I. The *s*-state lifetimes calculated by a self-consistent-field method[7] do not seem to give as good agreement, particularly at high n, as the Coulomb-approximation calculations.

These lifetimes, plotted against the effective quantum number, are shown in a log-log plot in Fig. 2. The straight lines are least-squares fits to the experimental points for the *s* and *d* lifetimes, given by the expression

$$\tau = \tau_0 (n^*)^B , \tag{2}$$

with the parameters: for *s* states, $\tau_0 = 1.99(33)$ nsec, $B = 2.87(8)$; and for *d* states, $\tau_0 = 0.965(39)$ nsec, $B = 3.00(2)$. The 4*d*-state lifetime, measured previously by Gornik *et al.*[1] also fits this expression. Within two standard deviations, the exponent for both *s* and *d* states is equal to 3, the prediction of quantum-defect theory. The agreement between the experimental results, Tsekeris and Happer's calculations (Table I), and the quantum-defect prediction [Eq. (2)], indicates that at least for Na the lifetimes of the Rydberg levels can be calculated with confidence.

We now hope to determine cross sections for energy transfer and for transfer between Rydberg levels with various collision partners.

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