

Radiative lifetimes of  $s$  and  $d$  states of potassium

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The radiative lifetimes of the  $7s$ – $11s$  and  $5d$ – $9d$  states of potassium have been measured by means of a time- and wavelength-resolved laser-induced-fluorescence approach. The observed lifetimes (in  $\mu\text{sec}$ ), measured at a temperature of 355 K, of the  $7s$ – $11s$  states are 0.165(12), 0.260(14), 0.441(38), 0.60(13), and 0.91(12). The observed lifetimes (in  $\mu\text{sec}$ ) of the  $5d$ – $9d$  states are 0.61(9), 0.89(6), 1.21(10), 1.59(13), and 2.04(30). The measured  $s$ -state lifetimes are roughly a factor of 2 shorter than the hydrogenic ones, and the measured  $d$ -state lifetimes are roughly a factor of 10 longer than the hydrogenic ones. The  $d$ -state lifetimes are reduced from the 0-K radiative lifetimes by as much as 20% by stimulated emission and absorption induced by blackbody radiation. For both  $s$  and  $d$  states the calculated and observed values of 355-K lifetimes agree to within 10%.

The radiative lifetimes of excited states in general are of interest for several reasons. They afford one of the more straightforward checks of the accuracy of calculated radial matrix elements.<sup>1</sup> In addition, reasonably accurate values of the radiative lifetimes are essential for the interpretation of fluorescence-yield collision experiments involving excited atoms.<sup>2</sup> The radiative lifetimes of the K  $s$  and  $d$  states are of particular interest since the K  $d$ -state lifetimes appear to be anomalous among the alkali-metal atoms. For all the other alkali metals the calculated  $s$  and  $d$  lifetimes are roughly comparable to the hydrogenic states of the same binding energy, an intuitively appealing result. However, the K  $d$ -state lifetimes are calculated<sup>3</sup> to be an order of magnitude longer than those of H. Both as a check of the calculated values and as the start of the investigation of excited-state collision processes, we have measured the radiative lifetimes of a series of  $s$  and  $d$  states of K which we report here.

The basic idea of the experiment is to use two pulsed tunable dye lasers to excite K atoms in two steps from  $4s_{1/2} \rightarrow 4p_{3/2}$  and then from  $4p_{3/2} \rightarrow ns_{1/2}$  or  $4p_{3/2} \rightarrow nd_{5/2}$ , and observe the time resolved  $ns \rightarrow 4p$  or  $nd \rightarrow 4p$  fluorescence as shown in Fig. 1.

Both dye lasers are simultaneously pumped by the same Quanta Ray Q-switched Nd:YAG laser-harmonic generator system. The laser provides up to 200 mJ of 1.064  $\mu\text{m}$  light in an 8-ns pulse which can be converted to up to 80 mJ of second harmonic at 5320  $\text{\AA}$  and 35 mJ of third harmonic at 3577  $\text{\AA}$  using the KDP harmonic generator. In these experiments, though, we only used  $\sim 3$  mJ of the second or third harmonic of the laser to pump the dye lasers. The resonance-line ( $4s \rightarrow 4p$ ) laser at 7666  $\text{\AA}$  is pumped by the second harmonic of the Nd:YAG laser and is operated with a mixture of DOTC (3, 3'-diethyl-2, 2'-oxatricarbocya-

nine iodide) and cresyl violet dyes yielding conversion efficiencies of  $\sim 5\%$ . The second dye laser operating in the 4800–5800- $\text{\AA}$  range is pumped by the second harmonic of the Nd:YAG laser to populate the K  $5d$  and  $7s$  states and by the third harmonic to populate the higher states.

The fluorescence is observed using an EMI 9558 photomultiplier and either a small monochromator or a filter. For the  $5d$  and  $7s$  states we used a monochromator with a bandwidth of 150  $\text{\AA}$  (FWHM); for the  $6d$  and  $8s$  states we used a filter combination with a bandwidth of 200  $\text{\AA}$  passing radiation from only the state under study; and for the higher states we used a filter to block the fluorescence from states lying below  $7d$ , that is, at wavelengths longer than 5200  $\text{\AA}$ . For the

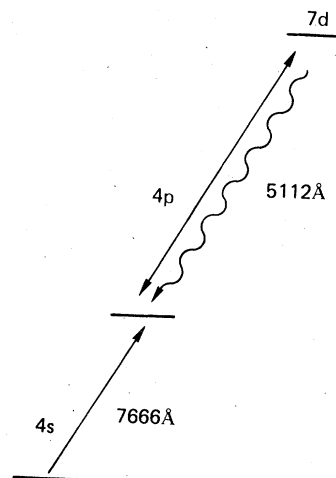


FIG. 1. Level diagram for the measurement of the K  $7d$  lifetime. The straight arrows up indicate the laser pumping steps  $4s \rightarrow 4p$  and  $4p \rightarrow 7d$ . The wavy arrow down indicates the observed  $7d \rightarrow 4p$  fluorescence.

higher states the branching ratios to nearby states which would eventually lead to observable fluorescence is very small.<sup>3</sup> We estimate that the errors introduced by such cascade processes to be negligible,  $\leq 4\%$ .

The fluorescence-decay curves are recorded using a PAR 162 analog boxcar averager which is controlled by a laboratory computer.<sup>4</sup> The observed decay curves are then fit by single exponentials by the computer yielding the radiative lifetimes.

The cell is a Pyrex cylinder 2.5 cm in diameter and 10 cm long which is connected to an external vacuum system with a base pressure of  $10^{-6}$  Torr. The typical operating temperature of the cell is  $80^\circ\text{C}$  corresponding to a K vapor pressure of  $2 \times 10^{-6}$  Torr. To check that there were no effects due to collisions with ground-state K atoms we observed the K  $6d$  lifetime is a function of cell temperature. The temperature was varied from  $80$  to  $125^\circ\text{C}$ , a variation in the K pressure from  $2 \times 10^{-6}$  to  $6 \times 10^{-5}$  Torr, and no systematic effect on the  $6d$  lifetime was observed.

Because of the long radiative lifetimes  $\tau$  of the K  $d$  states the blackbody-induced stimulated emission and absorption lead to noticeably shorter effective lifetimes  $\tau^*$ .<sup>5</sup> In Table I we give the values of  $\tau$  calculated by Lindgard and Nielsen<sup>3</sup> using the Bates-Damgaard method, the values of  $\tau^*$  calculated using the method of Ref. 5, and the observed values of  $\tau^*$ . To examine the  $n$  dependence it is convenient to introduce the effective principal quantum number  $n^*$  by the relation  $W = -1/(2n^{*2})$ , where  $W$  is the binding energy (in a.u.). The quantum defect  $\delta$ , links the principal quantum number  $n$  to  $n^*$  via the relation  $n^* = n - \delta$ . For K the  $s$ -,  $p$ -, and  $d$ -state quantum defects are 2.17, 1.70, and 0.27, respectively.<sup>6</sup> In Fig. 2 we plot  $n^*$  versus the observed values of  $\tau^*$  for the K  $s$  and  $d$  states as well as the calculated values of  $\tau$  and  $\tau^*$ . For comparison we have plotted the values of  $\tau$  for the H  $s$  and  $d$  states as well. For H the quantum defects are zero, and  $n^* = n$ . However, here we shall express

TABLE I. K  $s$  and  $d$  state lifetimes.

	$\tau_{\text{calc}}^a$	$\tau_{\text{calc}}^{*b}$	$\tau_{\text{obs}}^*$		$\tau_{\text{calc}}^a$	$\tau_{\text{calc}}^{*b}$	$\tau_{\text{obs}}^*$
$ns$	( $\mu\text{s}$ )	( $\mu\text{s}$ )	( $\mu\text{s}$ )	$nd$	( $\mu\text{s}$ )	( $\mu\text{s}$ )	( $\mu\text{s}$ )
7s	0.160	0.158	0.165(12)	5d	0.720	0.70	0.61(9)
8s	0.269	0.262	0.260(14)	6d	1.066	1.00	0.89(6)
9s	0.423	0.402	0.441(18)	7d	1.416	1.28	1.21(10)
10s	0.628	0.582	0.60(13)	8d	1.844	1.60	1.59(13)
11s	0.895	0.810	0.91(12)	9d	2.332	1.99	2.04(30)

<sup>a</sup>See Reference 3.

<sup>b</sup>See Reference 5.

the H principal quantum number in terms of  $n^*$  both for ease of comparison to K and to stress the connection with the binding energy. As shown by Fig. 2 the difference between  $\tau$  and  $\tau^*$  is most pronounced for the long-lived K  $d$  states, and is in the most extreme case a 20% effect. From both Table I and Fig. 2 it is apparent that the agreement between the calculated and measured values of  $\tau^*$  is quite good.

From Fig. 2 it is apparent that the lifetimes of the K  $s$  states are comparable to those of the H  $s$  states of the same  $n^*$ , which is what we would expect intuitively. To be more precise, the K  $s$ -state lifetimes are a factor of 2 shorter than those of H. It is true of all the alkali metals that the  $s$ -state lifetimes are shorter than those of H, which can be understood qualitatively in the following way. Assuming that a one-electron model is adequate for the alkali metal atoms, we may apply the one-electron sum rules.<sup>7</sup> The sum over  $n'$  of the oscillator strengths from  $ns$  to  $n'p$  is 1, from  $np$  to  $n's$  the sum is  $-\frac{1}{3}$ , and from  $np$  to  $n'd$  it is  $\frac{10}{9}$ . For all the alkali-metal atoms the oscillator strength of the resonance line ( $4s - 4p$  for K) is  $\sim 1$ . Thus for K the  $4p - 4s$  oscillator strength is  $\sim -\frac{1}{3}$  and the sum of the  $4p - ns$ ,  $n \geq 5$  oscillator strengths must be  $\frac{2}{3}$ , an order of magnitude greater than the value for the analogous  $2p$  state of H. Thus we expect the radiative lifetimes of the K  $s$  states to be shorter than those of H.

Note also that for both K and H  $s$  states the lifetimes increase as  $n^{*3}$  which is expected in the

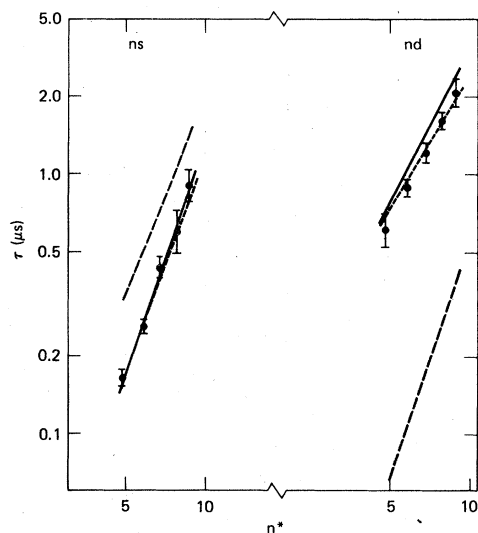


FIG. 2. Observed ( $\bullet$ ) K  $s$  and  $d$  radiative lifetimes vs  $n^*$ . Solid and short-dashed curves indicate the calculated values of  $\tau$  and  $\tau^*$ , respectively, for K. The long-dashed curve indicates calculated values of  $\tau$  for H.

limit of high  $n^*$  where the dominant channel for radiative decay is to the lowest-lying states. Since the wavelengths of these transitions do not change noticeably with  $n^*$ , the only important variation is the magnitude of the dipole matrix elements which, because of the spatial overlap of the high- $n$  and low- $n$  states, should lead to a  $n^{*3}$  dependence of the lifetime. In fact the K states are calculated to have large branching ratios to the  $4p$  state, and the  $n^*$  dependence we observe is  $n^{*2.9(2)}$ .

From Fig. 2 it is clear that the K  $d$ -state lifetimes are an order of magnitude longer than the H  $d$ -state lifetimes and do not exhibit an  $n^{*3}$  dependence but an  $n^{*1.7(2)}$  dependence. Both these effects are due to the fact that the oscillator strengths (and hence the branching ratios) of the K  $nd \rightarrow 4p$  transitions are small for  $n \geq 5$ . In this regard the behavior of the K  $d$  states is exactly analogous to that observed in all the alkali-metal-atom principal series. In the alkali-metal-atom principal series the oscillator strength of the resonance line is typically  $\sim 1$  leaving very little oscillator strength from the ground  $s$  state to the higher  $p$  states, resulting in the long lifetimes of

the high  $p$  states of the alkali metals. Similarly the oscillator strength of the K  $4p \rightarrow 3d$  transition is 0.83, leaving relatively little oscillator strength (0.3) for the  $4p \rightarrow nd$  transitions for higher  $n$  states. This results in the two effects mentioned above, the small  $nd \rightarrow 4p$  branching ratios and the long radiative lifetimes of the  $nd$  states.

Although it is tempting to assume that the radiative lifetimes of excited alkali-metal  $s$  and  $d$  states are hydrogenic, these measurements, particularly those of the K  $d$  state lifetimes, underscore the danger of such an assumption. In addition, as we have seen here it is necessary to consider the effect of stimulated emission and absorption induced by blackbody radiation on the radiative lifetimes of long-lived states.

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