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TOPICS IN LASER SPECTROSCOPY

The radiative lifetimes of the potassium 5*P*, 6*P* and 7*P* states*

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Abstract—The radiative lifetimes of the fine-structure components of the 5*P*, 6*P* and 7*P* states in potassium were determined using techniques of laser-induced fluorescence. Potassium vapour in a quartz cell was irradiated with pulses of dye laser light which selectively excited each fine structure (fs) state. The time-evolution of the resulting fluorescence was registered with a transient digitizer and analyzed to yield the following lifetimes (in ns). $5P_{1/2}$, 137 ± 2; $5P_{3/2}$, 134 ± 2; $6P_{1/2}$, 344 ± 3; $6P_{3/2}$, 333 ± 3; $7P_{1/2}$, 623 ± 6; $7P_{3/2}$, 592 ± 6.

1. INTRODUCTION

THE PRECISE determinations of the lifetimes of excited states in alkali atoms are of continuing interest to both experimenters and theoreticians as they provide a useful vehicle for comparison of experimental data with increasingly accurate calculations. The *S* and *D* states in potassium have recently been investigated by HART and ATKINSON [1]. Although the *P* states in potassium can be relatively easily excited using laser techniques, separate measurements of the lifetimes of the fine-structure (fs) components have only been made for the 4*P* states [2] though lifetimes of the $5P_{3/2}$ and $6P_{3/2}$ states have been measured using level-crossing methods [3]. A recent calculation of alkali lifetimes by THEODOSIOU [4] distinguishes between the 5*P*, 6*P* and 7*P* fs substates, providing a useful comparison with the results of this investigation, in which methods of time-resolved laser spectroscopy were used to determine the lifetimes of the $5P_{1/2}$, $5P_{3/2}$, $6P_{1/2}$, $6P_{3/2}$, $7P_{1/2}$ and $7P_{3/2}$ states.

2. EXPERIMENTAL DETAILS

2.1. *Description of the apparatus*

The arrangement of the apparatus, which is similar to that described by HART and ATKINSON [1], is shown in Fig. 1. The output of a N_2 laser-pumped dye laser was focused in a Pyrex cell containing potassium vapor, to selectively excite one of the 5*P*, 6*P*, or 7*P* fs states. The fluorescence resulting from the decay to the 4*S* ground state was monitored at right angles to the direction of excitation and registered with a monochromator and photomultiplier whose signal was amplified and analyzed with a transient digitizer (TD) interfaced to a computer, which produced a time-evolution spectrum of the fluorescence.

The N_2 laser and dye laser were both manufactured in-house. The N_2 laser produced 2 mJ per pulse and was operated at 12 Hz. The dye laser incorporated two holographic 1800 l/mm gratings in a Littman grazing incidence configuration and a double-prism beam expander. Fine tuning was accomplished with the aid of a piezoelectric transducer. The dye laser output spanned 3–4 modes and had an effective band width of 4 GHz. A saturated solution of DPS in p-dioxane was used for the excitation of the 5*P* state, 10^{-3} M Nile Blue in ethanol was used for the 6*P* state (the 689 nm radiation was frequency-doubled), and the 7*P* state was excited using the frequency-doubled 643 nm output produced by 2×10^{-2} M solution of R640 in ethanol.

The dye-laser output, after frequency doubling (if required), was made incident on a Pellin–Broca prism where the u.v. and visible components were separated. The diameter of the laser beam was

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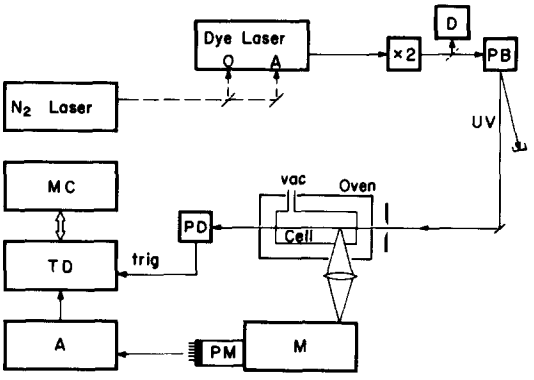

Fig. 1. Schematic diagram of the apparatus. D, thermionic diode; PB, Pellin–Broca prism; PD, photodiode; M, monochromator; A, amplifiers; TD, transient digitizer; MC, computer

sufficiently small that tight focusing in the cell was not necessary, thus greatly reducing photoionization of the potassium atoms which takes place at high power densities.

The cylindrical fluorescence cell was 10 cm long and 5 cm in diameter, with plane end-windows perpendicular to the cell axis. It was fitted with a 7-cm long side-arm 1 cm in diameter, which contained a few grams of potassium. The cell was connected by a narrow-bore tube (2 mm inside diameter) and a magnetically operated greaseless stopcock to the vacuum system which produced a vacuum of 5×10^{-7} torr. During the experiments, the cell was continuously pumped through the incompletely closed stopcock to remove any gaseous impurities desorbed from the glass surfaces without, however, causing any noticeable removal of potassium. The cell and side-arm was mounted in a 2-compartment electrically heated oven and was separated from the heating elements by a stainless steel enclosure. The temperature was measured with four copper–constantan thermocouples attached at various points to the cell and side-arm which was kept at a temperature 20 K below that of the cell to avoid condensation of the metal on the windows. The whole oven assembly was located at the centre of Helmholtz coils whose purpose was to eliminate Zeeman quantum beats from the fluorescence decay spectrum.

The fluorescence emitted by the vapor was focused on the entrance slit of an ISA Mod. HR-320 grating monochromator fitted with an 1800 l/mm holographic grating and a stepper motor drive for wavelength scanning. The entrance and exit slits were set to produce an 8 nm band pass. The radiation passing through the exit slit was focused onto the photocathode of a refrigerated RCA 31034 photomultiplier tube whose signal was amplified by fast Ortec 9301 (10 ×) and 9302 (20 ×) amplifiers acting in tandem, and was applied to a Biomation 6500, 1024 channel TD which was triggered by a fast photodiode and was interfaced with a Commodore Pet 2001 computer. The time resolution of the TD was set at 2 ns/channel for the $5P$ and $6P$ states, and at 5 ns/channel for the $7P$ states.

2.2. *Experimental procedure*

Before commencing the experiments, the fluorescence cell and side-arm were baked under vacuum for 2 days and then the potassium was vacuum-distilled into the side-arm. During the experiments the main oven maintained the cell at the operating temperature but the side-arm was allowed to cool down between the experimental runs, while the system was continuously pumped through the narrow-bore tube with the magnetic stopcock open. When the side-arm oven was turned on, the system required about 2 h to reach equilibrium. During this time, the lasers were stabilized, the tuning of the dye laser was calibrated with a potassium thermionic diode or a Fizeau wavemeter, and the Pellin–Broca prism, frequency doubling crystal and monochromator were set for the appropriate wavelength. The oven and side-arm temperatures were checked periodically during the experiment and were found to remain stable within ± 0.5 K over the average run of 4 h.

The initially recorded spectra exhibited modulation components, even though the earth's magnetic field had been cancelled to within $\pm 2 \times 10^{-3}$ gauss using the Helmholtz coils to suppress the Zeeman beats. To suppress quantum (hfs) beats, a linear polarizer was first inserted between the cell and monochromator at the "magic angle" of 54.7° to the laser polarization axis, at which the quantum beats disappear [5]. Although the modulation was suppressed, the presence of the polarizer also caused a reduction in the signal-to-noise (S/N) ratio. An alternative and more successful device for suppression of the quantum beats was then applied, by setting the Helmholtz coils to produce a field of 25 gauss at the cell, thus shifting the frequency of the modulation to a range which was not detectable

by the transient digitizer. At this field, the Zeeman splitting of the fs P states was still only 10% of the laser bandwidth, ensuring uniform excitation of the broadened fs state. The main advantage of this method was found to be the good reproducibility of the data and high S/N ratio of the fluorescence signals.

3. Calculation of Lifetimes from Experimental Data

The populations of the excited states were assumed to obey the relation:

$$N(t) = N_0 e^{-t/\tau} \tag{1}$$

where τ is the mean radiative lifetime of the excited state (we assumed stimulated emission and quenching to be absent). The experimental data (corrected for constant background) were fitted by the method of weighted least squares to a single exponential using a weighting factor proportional to the inverse number of counts per channel [6].

A typical semilogarithmic plot of the recorded time-decay spectrum for the $7P_{1/2}$ state is shown in Fig. 2. This was the most difficult of all the decays to observe, as the transition has the smallest oscillator strength and the $7P$ atoms are easily photoionized because of the short wavelength of the laser light. It may be seen that the spectrum is free of modulation (on the average, the S/N ratio exceeded 200). The correction for background did not affect the slope of this plot (and thus the lifetime), but allowed for easier data manipulation. The lifetime was determined from the slopes of the semilogarithmic plots at various locations on the plots. Each value was calculated with an associated χ^2 fit and the most linear fits corresponding to the largest time-span of the data were chosen as the most reliable. The uncertainty in each lifetime was estimated from the scatter among various sections of the plot. As may be seen in Fig. 2, the first 30 TD channels (0.15 μs) show a small non-linearity attributed to a photoionization cascade which could not be completely eliminated. The lifetimes were calculated from the data recorded in time segments where these effects were negligible. For each fs state, several (4–16) experimental runs were carried out to test the consistency of the data and probe the temperature and pressure dependence of the lifetimes.

4. Discussion of the Results

The experimentally determined lifetimes of the $5P$, $6P$ and $7P$ fs states are compared in Table 1 with experimental and theoretical values reported elsewhere, though no experimental values are available for the $5P_{1/2}$, $6P_{1/2}$, $7P_{1/2}$ and $7P_{3/2}$ states. The stated limits of error represent the standard deviations ($\Delta\tau$) of the measured values calculated from the several (n) experimental runs. Our lifetimes for the $5^2P_{3/2}$ and $6^2P_{3/2}$ states are in good agreement with the measurements of Svanberg [3] who employed the Hanle effect to measure the lifetimes as well as the hyperfine (hf) coupling constants for these states. We

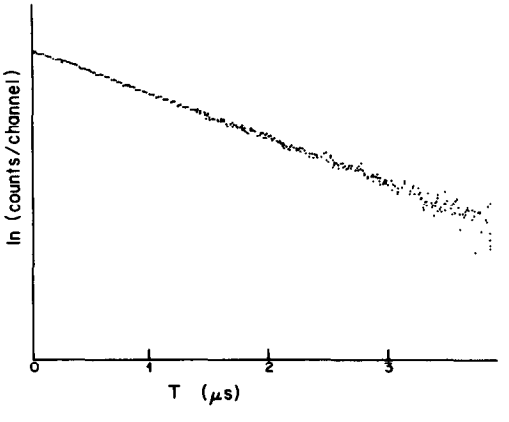

Fig. 2. A semilogarithmic plot showing the decay of the $7P_{1/2}$ state.

Table 1. Lifetimes τ of the $5P$, $6P$ and $7P$ states

State	n	$\tau \pm \Delta\tau$ (ns)	T(K)	Source
$5^2P_{1/2}$	10	137 ± 2	372	This work
		130	0	Theor. [7]
		127.06	0	Theor. [4]
		127.05	355	Theor. [4]
		126.86	600	Theor. [4]
		138	0	Theor. [8]
		123.15		Theor. [11]
$5^2P_{3/2}$	12	134 ± 2	372	This work
		133 ± 3	353	Exp. [3]
		130	0	Theor. [7]
		124.02	0	Theor. [4]
		124.02	355	Theor. [4]
		123.82	600	Theor. [4]
		120 ± 4	363	Exp. [9]
		140.8 ± 4	n.a	Exp. [10]
		135	0	Theor. [8]
		120		Theor. [11]
$6^2P_{1/2}$	8	344 ± 3	432; 378; 355	This work
		320	0	Theor. [7]
		321.67	0	Theor. [4]
		319.86	355	Theor. [4]
		306.33	600	Theor. [4]
		298	0	Theor. [11]
$6^2P_{3/2}$	15	333 ± 3	432; 369; 355	This work
		310 ± 15	403	Exp. [3]
		315	0	Theor. [7]
		312.77	0	Theor. [4]
		311.04	355	Theor. [4]
		298.21	600	Theor. [4]
		300	0	Theor. [11]
$7^2P_{1/2}$	4	626 ± 6	431	This work
		620	0	Theor. [7]
		619.47	0	Theor. [4]
		590.93	355	Theor. [4]
		523.75	600	Theor. [4]
$7^2P_{3/2}$	7	595 ± 6	431	This work
		600	0	Theor. [7]
		601.8	0	Theor. [4]
		574.8	355	Theor. [4]
		511.19	600	Theor. [4]

have not been able to detect any variation in the measured lifetimes with temperature; as may be seen in Table 1, the lifetimes of the $6P$ fs states do not appear to vary over the relatively small temperature range.

Changes in the temperature and density of the fluorescing vapor can produce accompanying changes in the measured values of the lifetimes through various mechanisms. At sufficiently high vapor densities, the excited atoms can be deexcited by quenching collisions with ground-state atoms, and this would tend to decrease the effective lifetime; on the other hand, reabsorption and trapping of the fluorescence would tend to increase the effective lifetime. At the relatively high temperatures, at which the measurements were carried out, black-body radiation might be expected to cause depopulation of the excited states by stimulated emission, which would again result in a shorter measured lifetime. That no temperature effects could be detected in this investigation may well indicate the absence of

quenching and trapping at the relatively low vapor densities that were employed, or the mutual cancellation of these effects. No temperature effects were noted by HART and ATKINSON [1] in their measurements of S and D lifetimes in potassium, though there is no possibility of radiation trapping of these states since they are not radiatively connected to the ground state. It is also possible that, in the present case, the temperature range (355–432 K) was too small to observe the effects of black-body radiation.

In most cases the trends of the theoretically determined lifetimes (none of which indicates limits of error) agree with those found experimentally. The theoretical calculations employed a variety of methods. GRUDZEV *et al.* [7] performed a semi-empirical numerical Coulomb approximation (NCA) calculation, an approach which was also used by WIESE *et al.* [8] who determined the transition probabilities whose sum yielded the appropriate lifetimes. THEODOSIOU [4] employed the Bates–Damgaard approximation with corrections for core polarization, spin-orbit interaction and blackbody radiation at various temperatures. There is, on the whole, satisfactory agreement between our experimental values and those calculated by Theodosiou.

5. CONCLUSIONS

The lifetimes of the fs $5P$, $6P$ and $7P$ states of potassium were measured using techniques of time-resolved laser spectroscopy. The measurements were carried out with sufficient accuracy to distinguish between the lifetimes of the $P_{1/2}$ and $P_{3/2}$ fs components and the lifetimes, which are listed in Table 1, were found to be in satisfactory agreement with some recent experimental and theoretical values.

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