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We have been conducting a series of experimental and theoretical investigations of the optical absorption and emission spectra of alkali atoms trapped in rare-gas matrices[1-6] in an attempt to understand the observed spectra in terms of the matrix perturbation of the alkali energy levels in various trapping sites. For our first attempt to identify absorption and emission bands associated with energy levels above the first excited state (np), we chose to work with matrix-isolated Cs and Rb. In these atoms the $(n+1)p$ and $(n-1)d$ states are easily reached by direct laser excitation from the ground state and the energy separation between these two excited states is greater than in the lighter alkalis. We prepared lightly-doped, well annealed samples to eliminate confusion due to multiple trapping sites. We report here the results of our initial experiments on Cs and Rb trapped in Ar at 10 K. We have identified the absorption bands associated with transitions from the ground state to the lowest d state and to the second-excited p state, and the emission band due to radiative transitions from the d state back to the ground state.

The apparatus used in this experiment was essentially the same as that described in Refs. 1–4. White light scans were used to monitor sample growth and to identify the strong absorption bands. To detect weaker absorption bands, a dye laser was scanned over the wavelength range 3800–7900 Å and the fluorescence was observed.

For both Cs and Rb a strong absorption band near the free-atom D lines was observed, along with a weaker, blue-shifted band attributed to another trapping site, as is typical of matrix-isolated alkalis. For Rb, both bands had a triplet structure, and the peaks occurred in the same positions reported by Kupferman and Pipkin.[7]

In the case of Cs, Weyhmann and Pipkin[8] reported only the unshifted band, which in their experiment had a triplet structure. In our experiment, the third peak is missing; we observed a doublet with peaks at 8450 and 8220 Å. We conclude that the third peak reported in Ref. 8 was due to another overlapping band from a similar trapping site. The weaker, blue-shifted band we observed for Cs was also a doublet with peaks at 7520 and 7260 Å.

In this experiment, we confined ourselves to a study of the laser-induced fluorescence from atoms trapped in sites which produced the unshifted absorption band associated with the free-atom D lines. The results for Cs are summarized in Table I.

Excitation of the absorption doublet in Cs produced broad red-shifted emission peaked at 9700 Å due to the matrix-perturbed $6p - 6s$ transition.

Two weak absorption bands due to transitions to states above the $6p$ level were observed: a band extending from 4400–5200 Å and a band from 6100–6700 Å. Laser excitation of either band produced the same fluorescence: an emission band coinciding with the 9700 Å emission and a second emission band peaked at 7620 Å.

These results are readily understood by referring to the Cs energy-level diagram in Fig. 1, where the fine-structure splitting has been suppressed by presenting weighted averages of the fine-structure levels.

The (6100–6700 Å) absorption and the emission peaked at 7620 Å are clearly due to $6s - 5d$ transitions. The emission at 9700 Å is due to population of the $6p$ level by radiative cascade from the $5d$ level. The 4400–5200 Å band is due to $6s - 7p$ transitions, and the observed emission bands are a result of radiative cascades to the $5d$ and $6p$ levels. We were unable to detect fluorescence from the direct $7p - 6s$ radiative transition, which is consistent with the free-atom branching ratio for the decay of the $7p$ state.

The observation of the 9700 Å fluorescence provides confirmation that the weak absorption bands are due to transitions to higher Cs levels in the trapping site associated with the unshifted white-light absorption.

Results quite similar to the case of Cs were obtained for Rb and are summarized in Table I. Excitation of the unshifted white-light absorption band $(5s - 5p)$ produced broad emission peaked at 8300 Å. Because the $6p$ and $5d$ energy levels in Rb are closer together than is the case for Cs, $5s - 6p$ and $5s - 4d$ transitions gave rise to one broad absorption band extending from 4200–5400 Å. Laser excitation in this region produced the $5p - 5s$ emission at 8300 Å and emission peaked at 6300 Å which we attributed to the $4d - 5s$ transition.

TABLE I. A summary of observed absorption and emission bands of Rb and Cs atoms trapped in an Ar matrix of 10 K. Each free-atom state is actually a fine structure doublet. The wavelengths listed are a weighted average for each doublet.

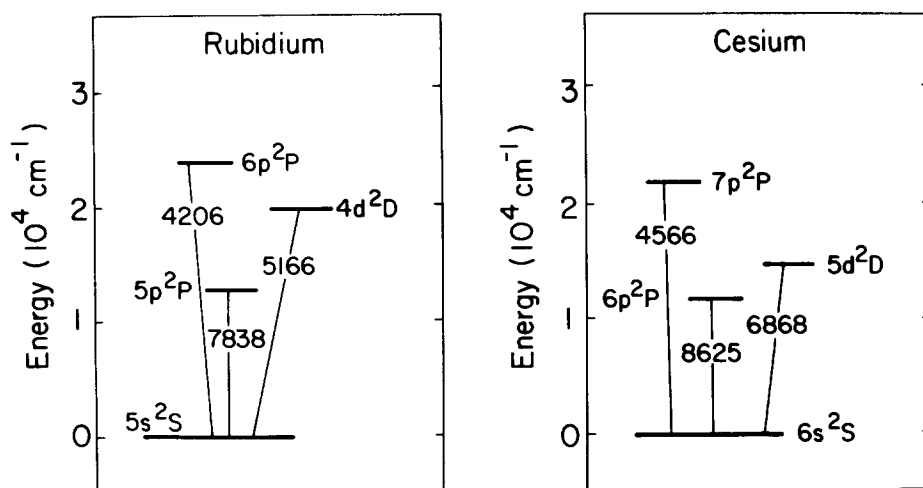| Atomic transition	Free-atom wavelength (Å)	Absorption band (Å)	Emission peak (Å)	Emission width (Å)
$5s-5p$	7840	7980 (peak)	8300	400
		7760 (peak)	8300	400
		7550 (peak)	8300	400
$5s-5p$	4205	[4200–5400]		
$5s-5d$	5165		6300	900
$6s-6p$	8625	8450 (peak)	9700	750
		8220 (peak)	9700	900
$6s-7p$	4565	4400–5200		
$6s-5d$	6870	6100–6700	7620	500

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FIG. 1. Grotian diagrams showing the relevant energy levels of Rb and Cs. The wavelengths labeling the transitions are in angstroms and are a weighted average for each doublet.

In our Rb measurements we were able to observe the lifetimes associated with the laser-induced fluorescence. When the $5p$ state was excited directly, the 8300 Å emission decayed with a lifetime ~20 ns, consistent with a free-atom lifetime of 27 ns.[9] Excitation in the range 4200–5400 Å, however, produced emission at 6300 and 8300 Å with lifetimes ~100 ns, consistent with a free-atom $4d$ lifetime of 87 ns[10] and with the interpretation of the 8300 Å as being the result of radiative cascading to the $5p$ state.

In summary, we have observed absorption and emission spectra associated with the np, $(n+1)p$, and $(n-1)d$ states of Cs and Rb atoms trapped in an Ar matrix. As might be expected, the matrix perturbation of the higher lying levels is greater than that for the lowest p state, although it is not obvious why the energy of the $(n+1)p$ state is lowered to produce a red-shifted absorption band. The blue shift of the absorption band associated with $ns - (n-1)d$ transition is consistent with the gas-phase perturbations observed by Moe et al.[11] The red-shifted, broad emissions from both the np and $(n-1)d$ states demonstrate that motion of the trapped atom and deformation of the matrix site relax the system to a new equilibrium configuration before the excited state decays.

Although it is possible that measurements can be extended to even higher energy levels, positive identification of the levels will be increasingly difficult because of the number of excited states of different configurations which have nearly the same energy.

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