We describe a series of measurements of absorption and laser induced fluorescence on gas cells containing cesium and rubidium and a rare gas: He, Ar, Kr, or Xe. These studies show strong blue wing absorption to the short wavelength side of the alkali atom D_2 lines due to collisionally formed Cs- or Rb-rare gas excimers. We also have observed an efficient two photon excitation of higher lying states in Cs and Rb that produces both intense blue emission and IR atomic emission in the 1.3 to 3.8 µm spectral region. We discuss sub-Doppler absorption and gain spectroscopy for Rb and Cs, and results from preliminary measurements of optical gain for Cs.

I. Introduction

There has been a long standing interest in developing optically pumped alkali atom lasers. Krupke and coworkers demonstrated that excitation of the slightly higher energy ^2P_{3/2} level followed by rapid collisional energy transfer to the ^2P_{1/2} level could provide the basis of an efficient three level laser. This initial work used a CW Ti:S laser at 760 nm to excite the ^2P_{3/2} state in Rb. Ethane in the Cs cell provided efficient energy transfer to the ^2P_{1/2} level and laser oscillation was observed on the Rb D_1 line (5^2P_{1/2} -> 5^2S_{1/2}) at 794 nm. Diode laser pumped alkali lasers (DPAL) hold considerable promise for efficient, scalable lasers in the 760 to 894 nm range for K, Rb, and Cs.

High power diode lasers and laser arrays typically are spectrally much broader than the D_1 absorption lines in alkali atoms, and this can significantly reduce the efficiency of the optical excitation process. Collisional broadening of the alkali atom absorption lines and spectral narrowing of the diode laser output using Bragg gratings are two approaches being pursued to improve the spectral overlap of the pump laser and the alkali atoms absorption lines. Very recently Readle et al. described a novel approach that eliminates this concern by exciting the D lines of alkali atoms via broad-band absorption on rare gas-alkali atom molecular complexes. They used the blue-wing satellite of the Cs D_2 line in an Ar bath to absorb pulsed dye laser pulses covering the spectral region ~840 to 852 nm. Photons in this range can be absorbed by CsAr(X^2Σ_{1/2}^+) collision pairs to produce CsAr(B^2Σ_{1/2}^+), an unstable complex which rapidly dissociates into the Cs(4^2P_{3/2}) upper state of the D_2 transition. In this experiment, the Cs ^2P_{3/2} atoms were collisionally relaxed by ethane to the ^2P_{1/2} level and laser oscillation on the D_1 line was observed. The broad absorption wing of the Cs-Ar excimer provides a path for using spectrally broad high power diode lasers to produce alkali atom D-line lasers. These investigators have also recently demonstrated a Cs atom laser based upon Cs-Kr molecular absorption, as well as lasing directly on the D_2 transition in the absence of ethane. Additional details on the theoretical basis and performance modeling for the exciplex-assisted optically pumped alkali laser system (XPAL) are given in other papers presented as part of this conference.

In this paper we describe spectroscopic studies of Rb- and Cs- absorption using both white light and tunable Ti:S laser radiation in order to further assess these systems as possible efficient gas phase optically pumped laser systems. We also discuss preliminary results for sub-Doppler absorption and gain measurements on Cs and Rb.
II. DESCRIPTION OF EXPERIMENTAL SETUP

Our experimental test bed is shown in Fig. 1. The oven allows us to insert sealed Pyrex cells that contain alkali species buffered with a rare gas. The cell chamber includes four cartridge heaters that have the capability for operating the cells from room temperature to over 250°C. The oven chamber also contains ports that allow both optical absorption and fluorescence measurements.

For these experiments we used a Schwartz Electro Optic “Titan” Ti:S laser for our excitation source. This device can be operated in both a stable cavity and ring configuration, and provides tunable, CW output covering the range from 750 to nearly 900 nm. The Ti:S laser is pumped by a Coherent Verdi diode laser-pumped, frequency-doubled Nd:YAG laser that produces 5 W of 532 nm output. We also have used a single-mode optical fiber-coupled white light excitation source for absorption studies. This device provides a collimated beam convenient for absorption studies using the heated alkali atom cells. We used an optical multi-channel analyzer (OMA) to detect the white light absorption and laser induced fluorescence (LIF) spectra from the alkali atom cells. The heart of this detection system is a Princeton Instruments, liquid nitrogen cooled, Si-CCD array that provides low dark count detection ideal for CW measurements. We used several 5 cm long, 2.5 cm diameter cells, each containing Cs or Rb and buffered with 500 Torr of a rare gas species (Kr, Xe, Ar). Some cells also contained 75 Torr of ethane.

For sub-Doppler scans of absorption and gain on the Cs and Rb D-lines, we use a distributed-feedback, tunable diode laser in a dual-beam configuration. The probe laser beam is split into reference and probe beams, and the probe beam is co-aligned along the axis of the Ti:S pump beam. In measurements to date, the probe beam samples the D1 transition while the pump beam is tuned near or onto the D2 transition. A series of two diffraction gratings separates the probe beam from the pump beam and directs it to the detector. The reference and transmitted probe beams are sampled by a balanced ratiometric noise cancellation detection system. The probe laser wavelength is rapidly and repeatedly scanned through the D1 hyperfine multiplet to produce a signal-averaged spectral scan for a given condition. Scans with the pump laser off measure atomic absorption by the ground 2S1/2 state for a given cell temperature (alkali vapor concentration). Scans with the pump laser on measure the modification of the ground-state concentration by the optical pumping effect, and optical gain in the event of an inversion on the D1 transition.

III. RESULTS AND DISCUSSION

Exciplex Absorption and Laser-Induced Fluorescence Spectroscopy

One of our Cs cells contained enough Rb that we could observe both species simultaneously via white-light absorption with the OMA equipped with a low dispersion grating (300 grooves/mm). Figure 2 shows absorption from the Rb-Kr excimer and from both D lines (780 and 794 nm) and part of the CsKr exciplex. Note that for the Cs-Kr case the grating dispersion is not sufficient to display the Cs D1 line at ~895 nm simultaneously with the Rb lines. These data clearly show the excimer formation as the alkali vapor pressure is increased by increasing the cell...
temperature. We also performed measurements using a Rb-He-ethane cell and saw minimal blue wing absorption that implies a much smaller excimer concentration as shown in Fig. 3. This is expected since He is much less polarizable than the larger rare gas atoms, and its interaction potentials with the alkali metal atoms are essentially purely repulsive.

Figures 4 through 7 show the absorption spectra as a function of Cs number density for the Cs/Kr/ethane; Cs/Ar/ethane, Cs/Ar; and Cs/Xe cells. Note that the Cs number densities were calculated using vapor pressure curves assuming that the Cs vapor is in equilibrium with the solid.

![Figure 2](image1.png)

**Figure 2.** White light absorption of the Rb-Kr and Cs-Kr exciplex systems as a function of cell temperature

![Figure 3](image2.png)

**Figure 3.** Absorption spectrum of Rb cell containing 500 Torr of He and 75 Torr of ethane
Figure 4. Absorption spectrum of Cs cell containing 500 Torr of Kr and 75 Torr of ethane

Figure 5. Absorption spectrum of Cs cell containing 500 Torr of Ar and 75 Torr of ethane
We have normalized all of the spectra to zero intensity where the D₁ and D₂ lines appear to be opaque. The data clearly show the formation of blue satellite wings at 837 nm for the CsAr excimer, and 841 nm for CsKr and CsXe. We also observed that ethane has a pronounced effect on the exciplex formation. Figure 8 shows a comparison of the CsAr excimer formation with (black trace) and without (dashed trace) ethane buffer gas in the cell. Both spectra were recorded at a cell temperature of 448 K ([Cs] = 6.75 x 10¹⁴ cm⁻³). The blue wing peak and origin appear in the same location in both spectra, however the exciplex formation is greatly enhanced in the Cs/Ar/ethane cell as compared to the Cs/Ar cell. In addition, there is significant exciplex absorption to the red of the D₁ line that was not detectable in the absence of ethane. We observed a similar enhancement in the Cs/Kr/ethane system. We do not

Figure 6. Absorption spectrum of Cs cell containing 500 Torr of Ar

Figure 7. Absorption spectrum of Cs cell containing 500 Torr of Xe
know the mechanism for this effect, however it could potentially be turned to advantage to increase the absorption by the ground-state collision pair.

We have also used the OMA spectrometer to observe the side fluorescence when the pump laser is tuned through the exciplex absorption region. Spectral data are shown in Fig. 9 for Cs buffered with 500 Torr of Kr at 473 K. The four traces show fluorescence spectra for a succession of pump wavelengths. In the top trace, the pump laser is set to 870.1 nm, in between the $D_2$ (852.1 nm) and $D_1$ (894.3 nm) lines. Both lines are observed in fluorescence. The absorption in this region appears to occur through the $X(2\Sigma^+_{1/2}) \rightarrow B(2\Sigma^+_{1/2})$ transition of CsKr, via the high-velocity component of ground-state Cs-Kr collision pairs, and results in prompt dissociation of the B-state to form Cs($2P_{3/2}$) and the corresponding $D_2$ fluorescence. In the second scan, the pump laser is essentially in resonance with $D_2$ and directly exciting Cs($2P_{3/2}$). Interestingly, we also observe fluorescence from the excited-state CsKr pair, the shoulder between 840 and 848 nm. This is surprising in view of the expected short lifetime of the CsKr(B) state. In the third scan, the pump laser is tuned into the exciplex blue wing, directly pumping the CsKr(B) state, and we observe $D_2$ and $D_1$ fluorescence. Finally, in the bottom scan, the pump laser is tuned off of the exciplex band, and there is no observable fluorescence. These experiments demonstrate how laser-induced fluorescence can be used to trace the state-to-state interactions, and establish the connection between the excited-state exciplex and $D_2$ excitation. We also note that $D_1$ fluorescence is consistently produced as well, however we have not yet identified a direct path to Cs($2P_{1/2}$) excitation for this case.

Figure 8. Comparison of CsAr excimer formation with (black trace) and without (red trace) ethane buffer gas present in the cell

We have also used the OMA spectrometer to observe the side fluorescence when the pump laser is tuned through the exciplex absorption region. Spectral data are shown in Fig. 9 for Cs buffered with 500 Torr of Kr at 473 K. The four traces show fluorescence spectra for a succession of pump wavelengths. In the top trace, the pump laser is set to 870.1 nm, in between the $D_2$ (852.1 nm) and $D_1$ (894.3 nm) lines. Both lines are observed in fluorescence. The absorption in this region appears to occur through the $X(2\Sigma^+_{1/2}) \rightarrow B(2\Sigma^+_{1/2})$ transition of CsKr, via the high-velocity component of ground-state Cs-Kr collision pairs, and results in prompt dissociation of the B-state to form Cs($2P_{3/2}$) and the corresponding $D_2$ fluorescence. In the second scan, the pump laser is essentially in resonance with $D_2$ and directly exciting Cs($2P_{3/2}$). Interestingly, we also observe fluorescence from the excited-state CsKr pair, the shoulder between 840 and 848 nm. This is surprising in view of the expected short lifetime of the CsKr(B) state. In the third scan, the pump laser is tuned into the exciplex blue wing, directly pumping the CsKr(B) state, and we observe $D_2$ and $D_1$ fluorescence. Finally, in the bottom scan, the pump laser is tuned off of the exciplex band, and there is no observable fluorescence. These experiments demonstrate how laser-induced fluorescence can be used to trace the state-to-state interactions, and establish the connection between the excited-state exciplex and $D_2$ excitation. We also note that $D_1$ fluorescence is consistently produced as well, however we have not yet identified a direct path to Cs($2P_{1/2}$) excitation for this case.
Multiphoton Excitation of Alkali Atom Emission

We have observed an intense blue beam in Cs-Kr and Rb-Kr cells when exciting with the Ti:S laser in the exciplex band to the short wavelength side of the D$_2$ absorption line. The laser-induced fluorescence spectra are shown in Fig. 10. The blue emission is due to transitions from the higher states of the alkali atoms, $^7$P$_{3/2,1/2}$ for Cs and $^6$P$_{3/2,1/2}$ for Rb, to the respective ground states. We have also observed transitions in the 1.3 to 3.8 $\mu$m region as shown in Figures 11 and 12. This is similar to observations of Sharma et al. who observed mirrorless, CW lasing from many transitions in both Cs and Rb when the same manifolds that we observed were excited directly with a CW dye laser tuned to the blue lines. These laser transitions varied in wavelength from 1.32 to 3.09 $\mu$m. The energy levels and laser transitions observed by Sharma et al. are shown in Fig. 13. The emission lines that we observed must be formed by two-photon absorption, however a two-photon transition on the atoms would pump a virtual state some 1517 cm$^{-1}$ above the blue-emitting states. We observe these emissions with very low pump laser power, ~0.1 W, and with the pump wavelength tuned well to the blue of the atomic D$_2$ transition. This suggests that the excitation mechanism involves very efficient, sequential pumping through real, excited states of the alkali-Kr complex, resulting in direct dissociation into the upper atomic state of the radiative cascade sequence. We are continuing a more detailed investigation of this phenomenon.

Figure 9. Laser excitation spectra of Cs($^3$P) fluorescence via CsKr exciplex absorption: Cs in 500 Torr Kr, 473 K. (a) Pump laser wavelength 870.1 nm, between Cs D$_1$ and D$_2$ lines; (b) Pump laser wavelength 852.0 nm, near resonance with D$_2$ line; (c) Pump laser wavelength 841.1 nm, in exciplex blue-wing region; (d) Pump laser wavelength 833.9 nm, no exciplex absorption
Figure 10. Laser-induced fluorescence spectra illustrating two-photon excitation: (a) Cs in 500 Torr Kr, 473 K, pump laser wavelength = 852.0 nm; (b) Rb in 500 Torr Kr, 473 K, pump laser wavelength = 776 nm.
Figure 11. Near-IR emission from Cs following two photon excitation near the 852 nm D₂ line; 500 Torr Xe, 393 K

Figure 12. Shortwave IR emission observed subsequent to two photon excitation of Cs near the 852 nm D₂ line; 500 Torr Xe, 393 K
Sub-Doppler Absorption and Gain Spectroscopy

As described above, we use narrow-band tunable diode lasers to scan through the Cs and Rb hyperfine multiplets comprising the D\textsubscript{1} transitions at 894 and 795 nm, respectively. The probe laser beam is co-aligned with the pump laser beam, so that we can observe absorption by the fully populated ground state in the absence of optical pumping, and depletion of the ground-state population and/or optical gain when the pump laser is turned on. This type of measurement provides a direct probe of the dynamics of the population inversion as a function of pump laser power, and aids in the design of optical resonators. Extensions of the technique can be used to examine spatial variations in the gain, e.g. for side-pumped systems.

The spectroscopy of alkali atom absorption near room temperature and low bath-gas pressures is straightforward and well understood through some five decades of research. However, the measurements are more complex to interpret at the elevated temperatures and pressures required for DPAL and XPAL operation, due to extensive collisional broadening and overlap of the lines. To guide this interpretation, we compute the absorption spectra from first principles, using well-established equations and spectroscopic constants available in the literature. The calculations treat the effects of spin-orbit coupling, and the coupling of the nuclear spin I to the electron angular momentum J to give the total angular momentum quantum number F and the hyperfine structure.\textsuperscript{13} In the case of Rb, there are two significant isotopes, $^{85}\text{Rb}$ and $^{87}\text{Rb}$, with corresponding isotopic shifts in the hyperfine energy levels. The $^{2}\text{S}_{1/2}$ and $^{2}\text{P}_{1/2}$ states each have two hyperfine components: $F = 2,3$ for $^{85}\text{Rb}$ (I = 5/2), $F = 1,2$ for $^{87}\text{Rb}$ (I = 3/2), and $F = 3,4$ for $^{133}\text{Cs}$ (I = 7/2). This results in four allowed D\textsubscript{1} transitions for each atom. Computed absorbance spectra for Rb and Cs in the Doppler-broadened limit are shown in Fig. 14, and illustrate the separation of the hyperfine components at low pressure. Calculations for elevated bath-gas pressures must include the effects of collisional broadening using the Voigt line shape expression, as well as collision-induced shifts of the transition frequencies. Computed absorbance spectra for Rb and Cs at elevated pressures are shown in Fig. 15. The calculations illustrate the broadening into a single unresolved feature, with Lorentzian wings extending far from the line center. This greatly extends the required scan range of the probe laser, in order to encompass the full line shape and determine the baseline signal level. In addition, the absorbance becomes highly optically thick for ground state atom concentrations characteristic of DPAL and XPAL operating conditions. Thus comparisons of the computed and observed spectra are essential for interpreting the experimental results.

Figure 13. Energy level diagrams for Cs and Rb showing the ground $^{2}\text{S}_{1/2}$ state and several excited states relevant to alkali atom lasers (from Reference 12)
For a given gas cell composition, pressure, and temperature, we scan the D1 absorption spectrum and then introduce the excitation laser beam. The Ti:S laser excitation laser is tuned to various frequencies within the D2 multiplet and in the neighboring exciplex band, and its intensity is varied systematically by adjusting the power of the Nd:YAG laser that pumps it. As the excitation intensity increases, the ground state concentration is depleted as population is moved to the upper states. For example, in preliminary experiments with Rb in 100 Torr of He (no hydrocarbon), we have observed depletion of the 2S1/2 population for excitation intensities as low as ~3 W/cm². In this case, the optical excitation populates the 2P3/2 state, but there is no rapid route to the 2P1/2 state to produce gain on D1. When a hydrocarbon such as ethane is added to the gas mixture to promote the transfer of population from 2P3/2 to 2P1/2, the system functions as a conventional DPAL configuration, and large optical gain is easily observed.

Figure 14. Computed Doppler-broadened D1 absorbance spectra for (a) Rb, 331 K, and (b) Cs, 300 K

Figure 15. Computed collisionally broadened D1 absorbance spectra for (a) Rb, 500 Torr He, 423 K, and (b) Cs, 500 Torr Kr and 75 Torr C₂H₆, 295 K

For a given gas cell composition, pressure, and temperature, we scan the D1 absorption spectrum and then introduce the excitation laser beam. The Ti:S laser excitation laser is tuned to various frequencies within the D2 multiplet and in the neighboring exciplex band, and its intensity is varied systematically by adjusting the power of the Nd:YAG laser that pumps it. As the excitation intensity increases, the ground state concentration is depleted as population is moved to the upper states. For example, in preliminary experiments with Rb in 100 Torr of He (no hydrocarbon), we have observed depletion of the 2S1/2 population for excitation intensities as low as ~3 W/cm². In this case, the optical excitation populates the 2P3/2 state, but there is no rapid route to the 2P1/2 state to produce gain on D1. When a hydrocarbon such as ethane is added to the gas mixture to promote the transfer of population from 2P3/2 to 2P1/2, the system functions as a conventional DPAL configuration, and large optical gain is easily observed. Figure 16 shows an example for Cs in 500 Torr Kr, 75 Torr C₂H₆ at 338 K. At present, our probe laser can only scan over about 60 GHz, so the wings of the lines are cut off by the baseline subtraction procedure. However, this is a small correction (<10%, cf. Fig. 15b), and the plot illustrates the development of the ground-state population inversion as the excitation intensity is increased. In this case, the inversion appears to occur on the F” = 4 transitions (cf. Fig. 14b). More detailed work is in progress, including measurements of gain in Cs and Rb as a function of hyperfine state excitation and exciplex excitation, for various temperatures (alkali concentration) and rare gas conditions.
IV. SUMMARY

The results of these preliminary investigations illustrate the spectroscopy and dynamics of alkali-rare gas complexes and show how these species can be used to optically excite both the resonant $^2P_{1/2}$ and $^2P_{3/2}$ levels and higher lying levels in the alkali energy level manifold. These exciplex species provide broad-band absorption features with spectral bandwidths of several nm, consistent with the use of commercially available high-power diode lasers. The XPAL system is inherently very simple, in that it can be operated with only two gas-phase atomic species at moderate pressures and temperatures. We have also observed an apparent enhancement of the exciplex absorption by the presence of ethane in the mixture; elucidation of the mechanism for this effect could offer a means to improve the efficiency of the optical excitation process. In addition, efficient two photon absorption may produce a host of excited states that could serve as the upper levels of several laser transitions in the near to mid-IR spectral region. Finally, we have demonstrated preliminary optical gain measurements on the D$_1$ transition for optical pumping on D$_2$. We plan to examine these phenomena in continuing investigations.

V. ACKNOWLEDGEMENTS

This work was supported under a Multi-disciplinary Research Initiative program sponsored by the High Energy Laser Joint Technology Office and administered through the Air Force Office of Scientific Research. We are grateful for numerous technical discussions with M. Heaven of Emory University, D. Carroll and J. Verdeyen of CUAerospace, and G. Eden of the University of Illinois Urbana Champaign.

References


Figure 16. Absorption and gain spectra for Cs (D$_1$) as a function of D$_2$ pump intensity. Cell conditions: Cs in 500 Torr Kr and 75 Torr C$_2$H$_6$, 338 K


