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UNIVERSITY OF SOUTH FLORIDA TAMPA DEPT OF CHEMISTRY F/G 20/5
PHOSPHORUS CHEMILUMINESCENCE FEASIBILITY STUDIES FOR AN ULTRAVI--ETC(U)
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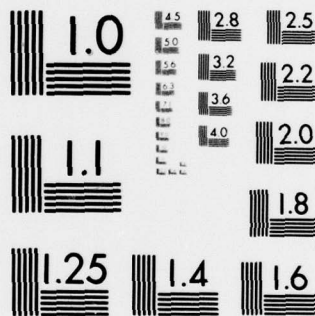
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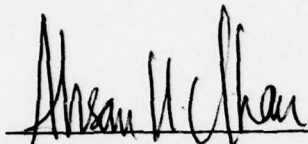
COMPLETED PROJECT SUMMARY

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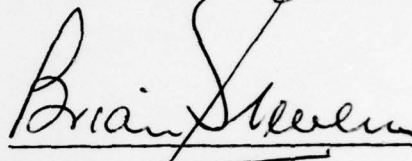
1. TITLE: Phosphorus Chemiluminescence Feasibility Studies for an Ultraviolet and Visible Chemical Laser

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6. SENIOR RESEARCH PERSONNEL:

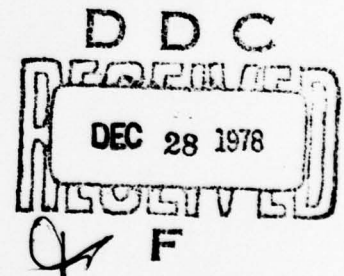
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8. OBJECTIVES AND ACCOMPLISHMENTS:

Feasibility studies for the development of an electronic chemical laser from phosphorus chemiluminescence. Phosphorus chemiluminescence is very unusual in that the metal vapor reacts with oxygen under atmospheric conditions without any increase in temperature. A large number of electronic excited species have been identified as flame components, states of HPO , PO , and PO excimer. Some of these electronically excited states are at energy levels in the vacuum uv region. The aim of this project was to explore whether an inverted population of electronically excited species either, 1) exists among the intermediates of the phosphorus chemiluminescence reaction or, 2) can be generated by excitation of atomic and molecular species added to the flame. The project was divided into two sections:

i) Electronic excitation of Na, K and NaK by an oxygen-deficient white phosphorus chemiluminescence. Several apparatus were designed and constructed using university facilities to provide for the addition of a stream of Na and K and the intermetallic alloy NaK carried by an inert gas into a reaction vessel containing the phosphorus chemiluminescence. The table summarizes the experimental results:

OBSERVED λ_A	ASSUMED CHEMICAL SPECIES	TENTATIVE ASSIGNMENT	COMMENT
5765.3	NaK	$B^1\Pi \longrightarrow x^1\Sigma$	Very strong, approx. 10 ³ over P-chemiluminescence
5787.6	K	$(7s)^2S_{1/2} \longrightarrow (4p)^2P_{1/2}^\circ$	Identification of both chemical species and the transition is assumed positive.
5806.0	K	$(7s)^2S_{1/2} \longrightarrow (4p)^2P_{1/2}^\circ$	
5920	Na	$(3P) \left\{ \begin{array}{l} 2P_{1/2}^\circ \\ 2P_{1/2}^\circ \end{array} \right\} \longrightarrow (3s)^2S_{1/2}$	Positive assignment
7670	K	$(4p) \left\{ \begin{array}{l} 2P_{1/2}^\circ \\ 2P_{1/2}^\circ \end{array} \right\} \longrightarrow (4s)^2S_{1/2}$	Positive assignment

ii) An investigation of laser light amplification on traversing phosphorus chemiluminescent flames using light in the 280-500 nm region. The experimental set-up used the frequency doubled output of a Molectron DL 200 tunable

dye laser, pumped by a UV 400 Nitrogen Laser, directed through a beam splitter. The main beam traverses one hundred phosphorus flames, and the intensities of the two beams are measured with two photomultipliers and a dual channel Boxcar Averager PAR 162 with plugins, Sampled Integrator Model 163 and Gated Integrator Model 164 with Sampling Head Model S-5. The ratio was taken and the output was recorded on an XY plotter. An identical ratio of the outputs of the laser beam was recorded with no phosphorus flame. The intensities of the normalized laser beam with and without the phosphorus flame was compared. Under room temperature and atmospheric pressure, scattering from the interfaces of the flames was the dominant effect. We estimate a flux of 3×10^{10} photons per pulse at 290 nm through an intersection of 4×10^9 P₄ molecules, so that we are at the detectability limit of the experiment. It appears with the present experimental set-up under certain conditions there is suggestion of amplification but because of the scattering at the interfaces no definite conclusion can be drawn. Initial attempts were also made to obtain laser induced fluorescence from components of a single phosphorus flame both at atmospheric and reduced pressure conditions.

iii) Conclusion. In the case of the light amplification studies the conclusion is to dispense with the multiple flame design and thereby eliminate light scattering at the interfaces. The obvious solution is to enclose the flame in a heat pipe oven where pressure, temperature, and the concentration of the reactants can be regulated. In the chemi-excitation experiments of Section i) the two emission lines at 5787 and 5806 Å which we have tentatively assigned as excited state - excited state transitions of K are good candidates for lasing. The other emissions, the 5765.3 Å emission tentatively assigned to NaK and the Na and K doublets have lasing potential depending on the mechanism of excitation. The phosphorus flame and the atomic and molecular composition of the NaK stream are extremely susceptible to pressure and temperature changes and, as in the light amplification studies, the obvious next step is to confine the system in a heat pipe oven where these variables can be strictly controlled. Considering the broader aspects, the project has achieved chemi-excitation of atomic and molecular species by interaction with phosphorus flame components. This interaction can be extremely efficient judging from the very strong intensity of the 5765 Å NaK emission. Also there appears to be a preferential excitation of selected electronic transitions, depending on the experimental conditions of the system studied.

APP. 55-14 for	
5	White Section ☒
6	Buff Section ☐
7	Grey Section ☐
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Appendix

CHEMI-EXCITATION EXPERIMENTS

I. Experimental Section

The experiment consists of monitoring the emission associated i) with phosphorus chemiluminescence and ii) with the interaction of an Ar stream carrying NaK into an oxygen-deficient phosphorus glow.

Experimental conditions: The temperature of the NaK stream is about 140°C and the temperature of the phosphorus stream is about 40°C. The phosphorus-nitrogen stream and the NaK-Ar stream are both driven by a pressure higher than atmospheric pressure.

Experimental Apparatus: The reaction vessel consists of a 2-inch diameter glass tube, 24 inches long, held vertically with the top end narrowing down to a tube connected via tygon tubing to an aspirator. The bottom is sealed with a rubber stopper. Through a central hole in the stopper, a 10 mm glass tube with a needle valve connects the reaction vessel to a 50 ml flask containing white phosphorus. A side arm of the 50 ml flask is connected through another needle valve to a nitrogen tank via a water bubbler. A by-pass loop of glass tubing with two stopcocks is provided to allow the moist N₂ stream to enter the reaction vessel without transit through the phosphorus flask, if desired. Through a second hole in the rubber stopper in the reaction vessel, a second glass tube provides entrance to the atmosphere which can be closed off with a rubber tubing and a clamp. A metallic nozzle, one inch in diameter with a 1 mm hole in the middle, is inserted into the side of the cylindrical reaction vessel at a height 2 inches above the glass tube which directs the phosphorus-nitrogen flow. This nozzle terminates a brass cartridge of about 8 inches in length 1½ inches in diameter, which is connected by a 10 mm brass tubing to an argon tank. The intermetallic alloy, NaK, is inside the cartridge, and the outside of the cartridge is wrapped up by an electric heater made by winding heating wire between two layers of asbestos. The heater is connected to a Variac which allows control of the temperature.

The oxygen-deficient white phosphorus glow is obtained in the reaction vessel by establishing an equilibrium between the nitrogen stream carrying the phosphorus from the flask underneath and the suction by the aspirator from the top. The NaK emission is obtained by raising the temperature of the cartridge while the argon pressure is adjusted; so that a jet of NaK is injected into the reaction vessel, impinging on the whitish phosphorus glow resulting in an intensely glowing jet. With the needle valve leading to the phosphorus flask, the intensity of the metal glow can be adjusted. Using the by-pass loop, the phosphorus flow and the accompanying luminescence, both of the phosphorus and of the NaK, can be completely shut off. Alternatively, by cooling the cartridge the NaK glow can be completely extinguished without affecting the phosphorus glow.

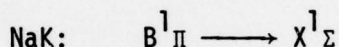
Spectra were taken using either a f2.5 Jarrell-Ash Monochromator and RCA 1P28 photomultiplier or a 0.5 m McPherson Monochromator and an EMI 9558 QB Photomultiplier.

II. Results

A. Intense Emission Band at 5765.3 Å

Figure 1 is a spectrum of the glowing metallic jet surrounded by an oxygen-deficient whitish phosphorus glow. Figure 2 is obtained by letting the temperature of the cartridge cool down to about room temperature, other conditions remained the same as those of Figure 1. The experimental conditions for recording Figure 3 are exactly the same as for Figure 1, except a less sensitive setting was used to bring the peak position down within the range of the chart paper. These three spectra were taken with the Jarrel-Ash monochromator.

Figure 1 scans the spectral range of 3000-8000 Å. There are two distinct features of the spectrum: i) a broad weak emission identified as the oxygen-deficient white phosphorus chemiluminescence (compare Figure 2) and, ii) an intense emission band at 5765.3 Å (see also Figure 3). The intense emission is tentatively identified as



based on: i) spectral position ($17,345 \text{ cm}^{-1}$), ii) bandwidth at half maximum intensity (365.3 cm^{-1}), iii) probable chemical species and, iv) comparison with known atomic and molecular transitions in this spectral region (see Table).

CHEMICAL SPECIES	TRANSITION	λ_A	$\Delta\lambda$ error
Na	$(3p)^2P_{1/2}^\circ \longrightarrow (3s)^2S_{1/2}$	5897.5	132.2
	$(3p)^2P_{1/2}^\circ \longrightarrow (3s)^2S_{1/2}$	5891.6	126.3
	$(4d)^2D_{1/2} \longrightarrow (3p)^2P_{1/2}^\circ$	5689.7	75.6
	$(4d)^2D_{1/2} \longrightarrow (3p)^2P_{1/2}^\circ$	5684.2	81.1
NaK	$B^1\Pi \longrightarrow X^1\Sigma$	5970-5650	

YELLOW SYSTEM

Intensity	$v' \quad v''$		
7	4,0	5802.6	37.3
6	5,0	5783.0	17.7
7	6,0	5763.4	1.9
9	7,0	5745.4	19.0
10	8,0	5728.2	37.1
9	9,0	5711.7	53.6

B. Atomic Transitions at 5787.6 and 5806.0 Å

Figure 4 is a spectrum of a glowing metallic jet surrounded by an extremely weak whitish oxygen-deficient phosphorus glow. In Figure 4 the spectrum covers the range 5700-6000 Å. There are two distinct types of emissions, i) a broad emission around 5900 Å, not identified, and, ii) three distinct sharp lines. Two of these lines, the lines at 5787.6 and 5806 Å, are tentatively assigned to neutral potassium atomic excited state-excited state transitions:

OBSERVED λ Å	ASSUMED CHEMICAL SPECIES	TRANSITION	λ Å	$\Delta\lambda$ error
5787.6	K	$(7s) \ 2S_{1/2} \longrightarrow (4p) \ 2P_{1/2}^{\circ}$	5783.99	3.61
5806.0	K	$(7s) \ 2S_{1/2} \longrightarrow (4p) \ 2P_{1/2}^{\circ}$	5803.36	2.64

The spectrum was taken with the 0.5 m McPherson Monochromator with both the exit and entrance slit wide open (2 mm).

C. Intense Transitions at 5900 and 7670 Å

Figure 5 is another spectrum of the glowing metallic jet and of an extremely weak envelope of whitish oxygen-deficient phosphorus glow. The spectrum was recorded with the 0.5 m McPherson Monochromator with the exit and entrance slits wide open (2 mm). The spectral range covered about 4700-9000 Å.

OBSERVED λ Å	ASSUMED CHEMICAL SPECIES	TRANSITION	λ Å	$\Delta\lambda$ error
5920	Na	$(3p) \left\{ \begin{array}{l} 2p_{1/2}^{\circ} \\ 2p_{1/2}^{\circ} \end{array} \right\} \longrightarrow (3s) \ 2S_{1/2}$	5897.5	22.5
			5891.5	28.5
7670	K	$(4p) \left\{ \begin{array}{l} 2p_{1/2}^{\circ} \\ 2p_{1/2}^{\circ} \end{array} \right\} \longrightarrow (4s) \ 2S_{1/2}$	7701.1	31.0
			7667.0	3.0

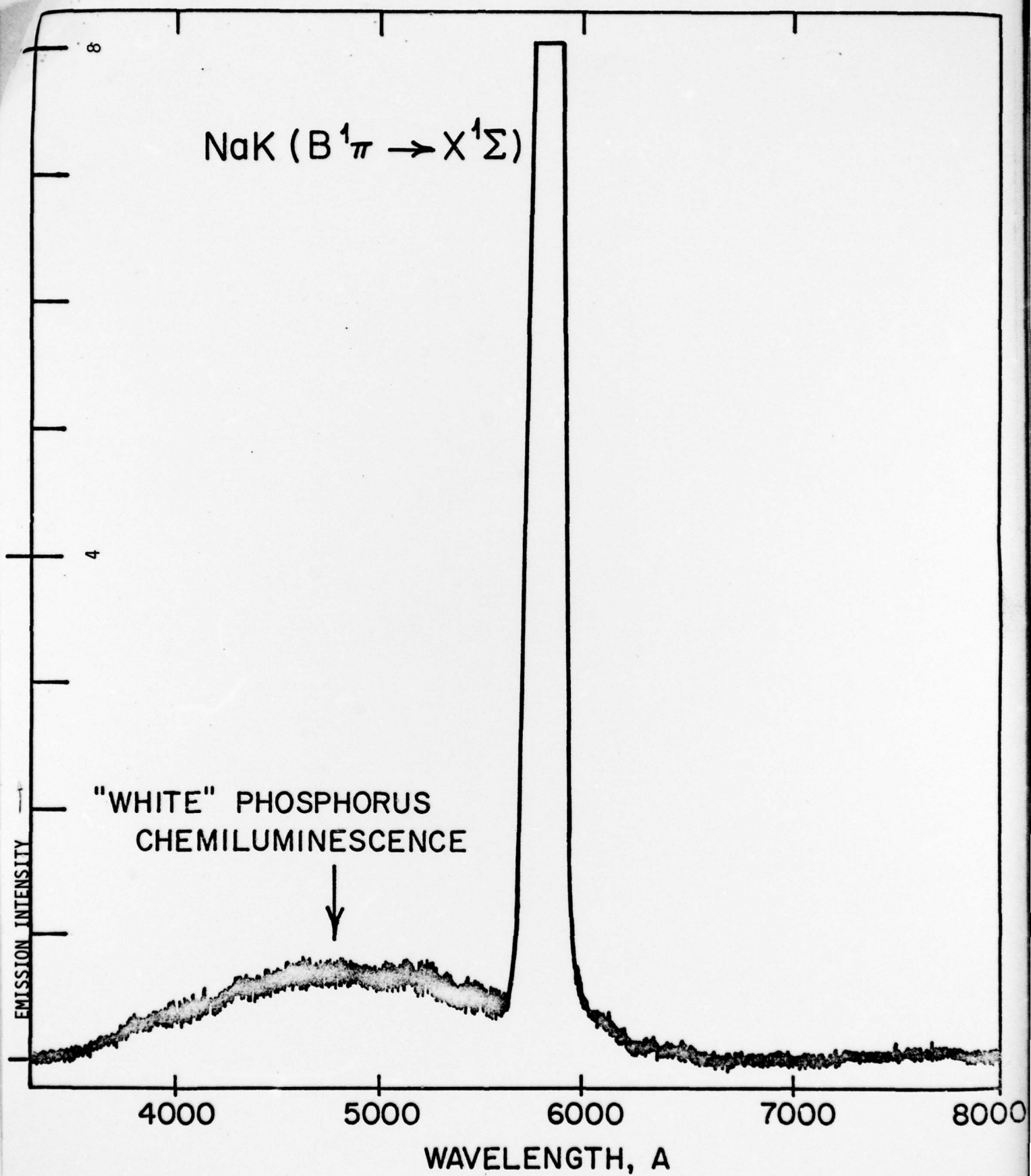


FIGURE 1

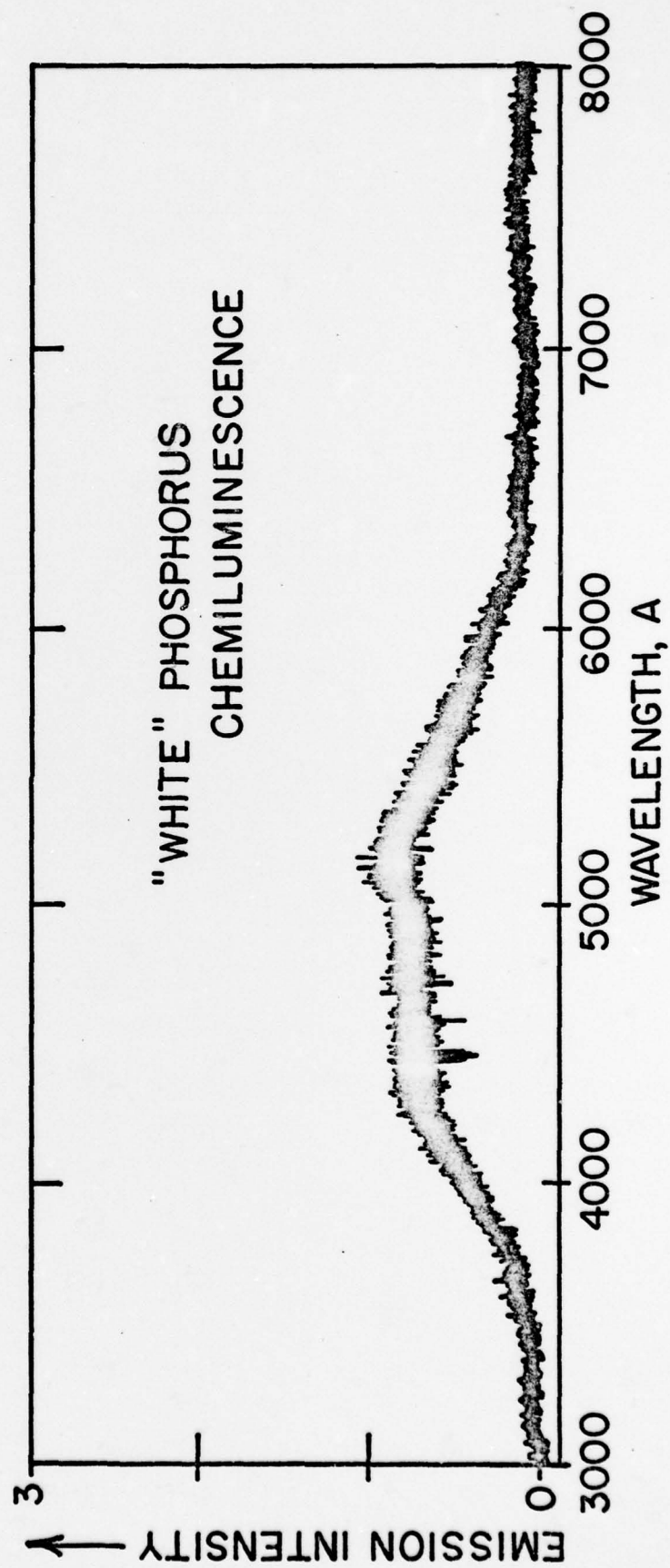


FIGURE 2

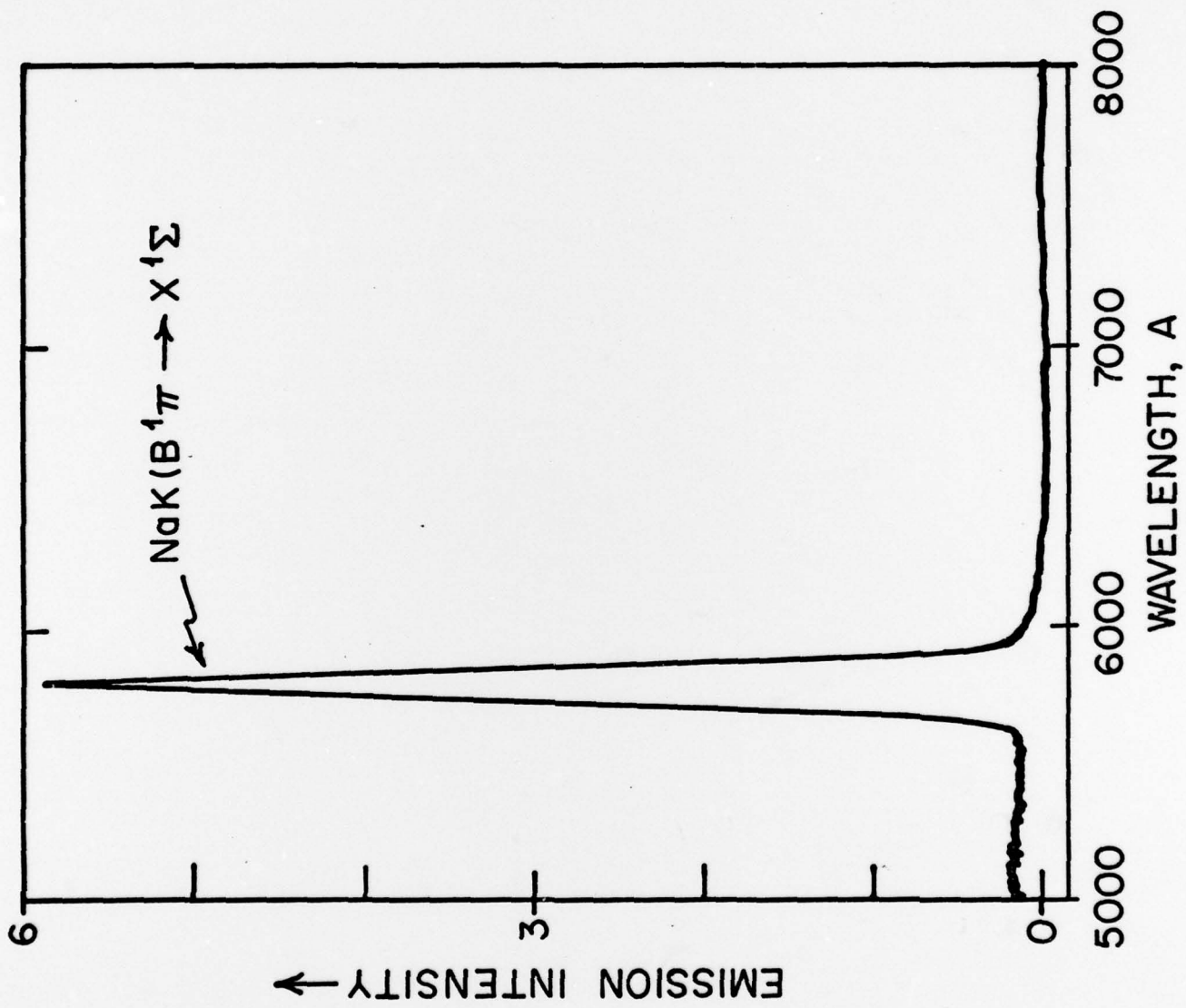


FIGURE 3

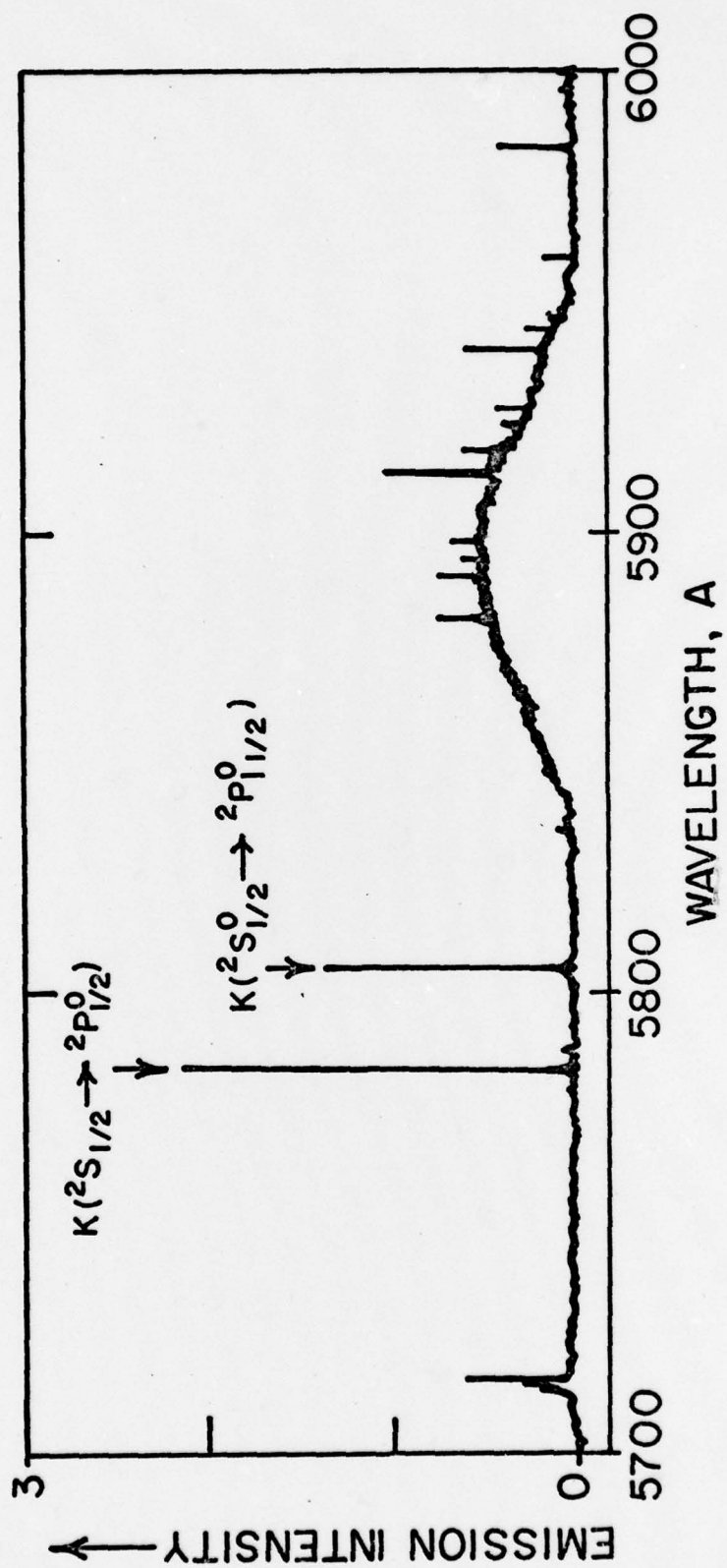
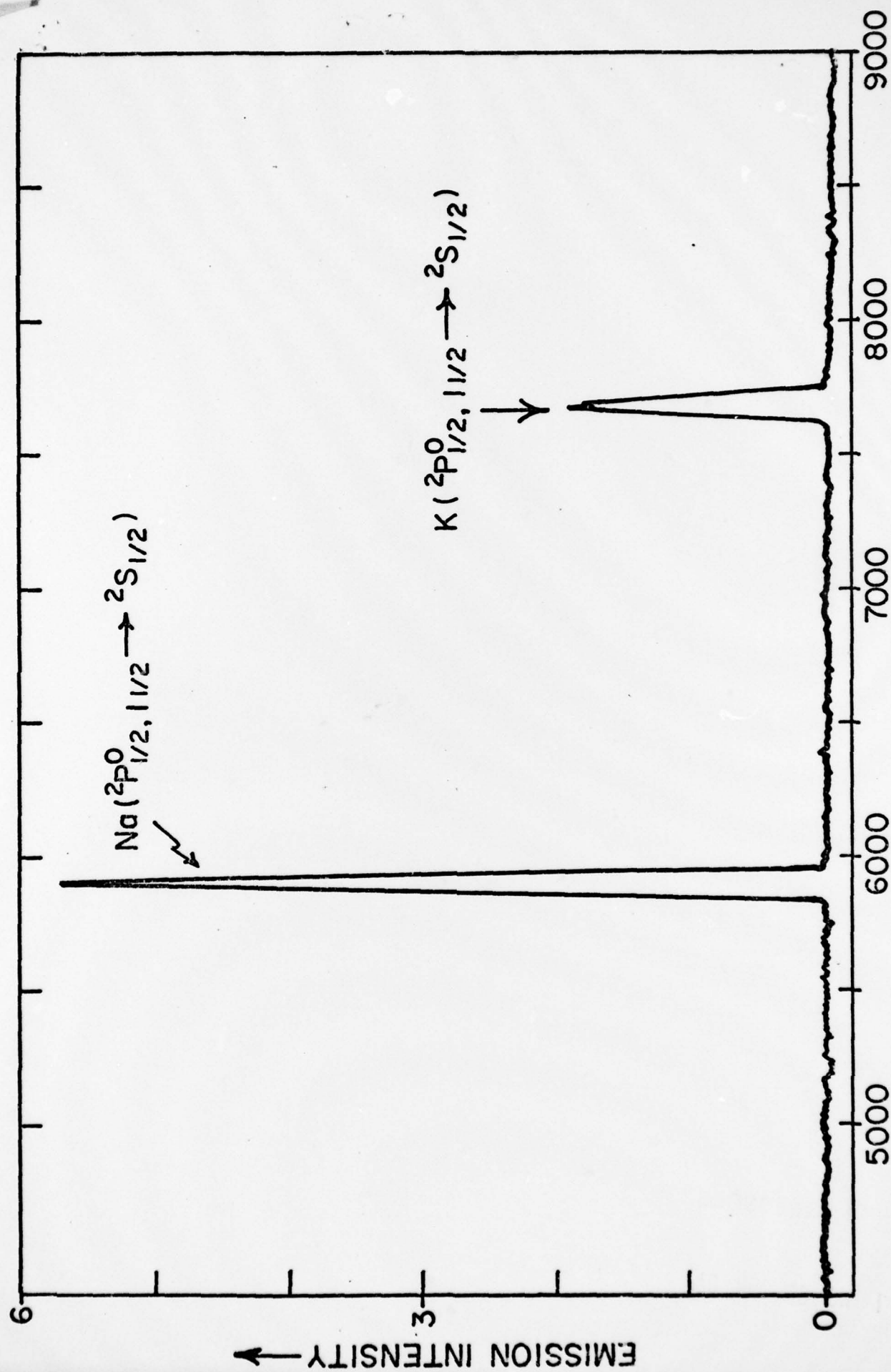


FIGURE 4



WAVELENGTH, Å

FIGURE 5

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20. ABSTRACT

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