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INFRARED SPECTROSCOPY OF A DENSE POTASSIUM VAPOR JET

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In this paper we report the development of new apparatus for the containment and study of dense alkali metal vapors, and the use of the apparatus to study the infrared spectra of potassium vapor. The apparatus is the first to employ aerodynamic confinement of a dense alkali vapor. We have recorded absorption spectra, thermal emission spectra, and laser-induced emission spectra of dense potassium vapor. These techniques all reveal a spectral feature near 1.1 μm which we believe originates in $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transitions of the K_2 molecule.

In this paper we present a qualitatively new approach to the confinement of dense metal vapors for spectroscopic study. We report the development of apparatus which employs aerodynamic confinement of a flowing hot metal vapor column (1 cm diameter) by a concentric annular sheath of flowing inert buffer gas. We have tested this device in investigations of alkali metal vapors at pressures of up to 260 Torr and temperatures of up to 700°C for potassium and 850°C for sodium. Laser-induced emission, thermal emission, and absorption experiments have all revealed new information about the near-infrared spectra of potassium, as well as several previously observed band structures.

In the past, alkali vapors have been studied in glass cells, stainless steel cells with sapphire windows, discharge tubes, and heat pipe ovens. Our device provides advantages over all of these techniques, especially for the study of optical emission from dense vapors. The high temperatures required for the generation of alkali vapor pressures greater than a few torr, and the corrosive nature of the vapor, limit the use of glass cells. Stainless steeel cells with sapphire windows provide some improvement, but the sapphire to stainless steel seals are not effective at temperatures much above 500°C or alkali densities above a few torr.

Denser vapors can be contained in heat pipe ovens which were first used in spectroscopic studies in the late 1960's [1]. The long, well-defined column of clean, uniform temperature metal vapor is ideally suited for absorption experiments. Heat pipes are, however, of more limited use in fluorescence experiments. The poor geometry of heat pipes for such fluorescence experiments has been improved with the development of heat pipes in a crossed or "T" configuration, but this arrangement is still not ideal for the study of laser excited vapors. This is especially true if the vapor is optically thick at the wavelength of either the excitation or fluorescence. In such a configuration the laser light must traverse a long, vapor-filled arm of the oven before reaching the observation region, and only a limited amount of the laser's energy can be deposited in the region visible to a detector. Likewise, any fluorescence emerging from the laser excited region of the vapor and the cooler boundary layer where the metal vapor and the buffer gas meet, and the fluorescent radiation is subject to absorption in both of these regions. Heat pipes are also limited to operation at saturated vapor pressures, and independent control of temperature and pressure is not possible in most designs. Finally, stable heat pipe conditions are ultimately limited in temperature and pressure by the generation of turbulence at the boundary layer between the cool buffer gas and the hot metal vapor. The subsequent mixing of the two vapors results in the formation of metal

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fogs which limit the spectroscopic uses of the instrument.

In order to overcome the difficulties presented by high temperature metal vapors, we isolate a large (1 cm diameter) flowing isothermal stream, or jet, of hot alkali vapor from the cool windows with argon gas flowing alongside the hot alkali, rather than using a static region of buffer gas as is done in heat pipes. A well defined boundary between the two vapors exists as long as laminar flow can be maintained.

After extensive testing of the properties of flowing gases in various pyrex constructions using water vapor to model the alkali metal and argon as a buffer gas, we arrived at the configuration displayed in fig. 1. The body of the apparatus is constructed of welded 304L stainless steel. The metal is heated to boiling in the cylindrical boiler (A) and the vapor flows up the vertical chimney (B). The cross-sectional area of the chimney is reduced to smooth the flow before the vapor emerges from the nozzle (C) into the flowing stream of argon. The argon has been preheated in the serpentine tubing (D) by the same heating elements which heat the boiler. The argon enters the chimney at (E). The observation windows (F) and laser entry ports (G) are set back 13 cm from the vertical chimny on stainless steel arms, and we bleed a small flow of argon buffer gas into the arms at (H) in order to maintain a slight positive pressure of buffer gas in the arms with respect to the pressure in the vertical column.

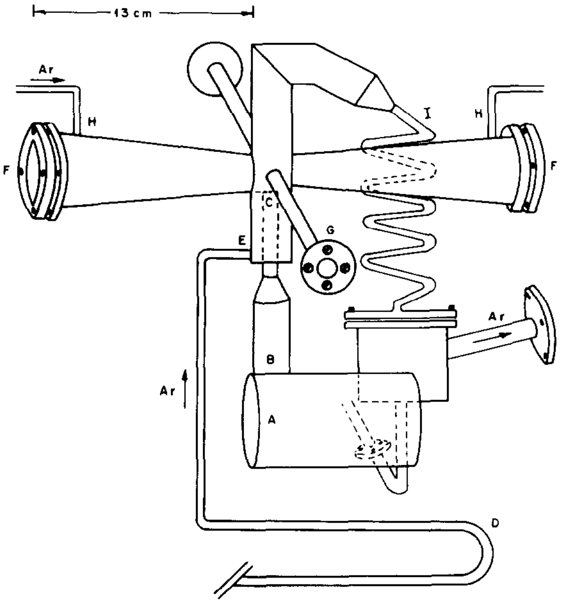

Fig. 1. Apparatus for the generation of the dense metal vapor jet.

The windows are attached to the arms with stainless steel flanges and Viton O-rings. The windows are cooled by water flowing through copper tubing soldered to the stainless steel arms immediately behind the flanges. The observation arms are tapered to provide a large solid angle for the gathering of fluorescence from the vapor. It should be noted that each of the windows faces another window. The laser entry windows are paired in order to allow all unabsorbed laser light to escape the central viewing region and thus avoid scattered laser light within the body of the apparatus. The observation windows are paired so that any detector views a cool window as a background rather than the hot stainless steel walls of the chimney. At the temperatures required to generate dense metal vapors the thermal radiation of the stainless steel is considerable.

After passing the windows, the laminar boundaries eventually break down and the mixture of the metal vapor and the buffer gas passes into the condensing region (I), where the metal vapor and the buffer gas are separated. Most of the metal condenses and is collected in the receptacle at the base of the condensing section before flowing back into the boiler under the influence of gravity. The condensate receptacle is attached to the rest of the device with copper O-ring sealed flanges and is removable for ease in cleaning the apparatus.

The stainless steel assembly is mounted in a steel box containing high temperature insulation. We used stainless steel sheet to create two cylindrical cavities: one around the boiler and another around the vertical chimney. The cavities are independently heated by resistive silicon carbide heating rods. Temperatures at various points on the boiler and along the vertical chimney are monitored by chromel-alumel thermocouples spot-welded to the stainless steel body of the apparatus. The thermocouples are shielded from direct radiation with ceramic cement.

The closed-loop argon circulation system is illustrated in fig. 2. The boiling point of the metal in the boiler is determined by the pressure of the argon in this loop. After leaving the stainless steel "cell" de-

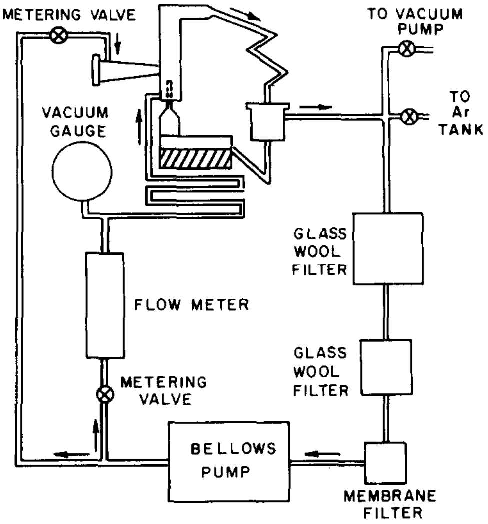

Fig. 2. Diagram of the argon circulation loop for the alkali vapor jet apparatus.

scribed above, the argon is filtered to remove the residual metal entrained in the argon flow. The argon is circulated by a non-contaminating stainless steel bellows pump. Downstream from the pump the flow rate is measured with a rotameter and the pressure is monitored before the argon flows back into the preheating section. The flow rate is controlled by a metering valve at the base of the flowmeter. The pressure gradient developed across this valve drives the small flow of argon into the window arms of the apparatus.

We have so far successfully operated this device with potassium and sodium metal. We have worked with potassium at pressures of up to 260 torr and temperatures of up to 700°C, and sodium at pressures of up to 150 torr and temperatures of up to 850°C. At these pressure the vapors are strongly colored when illuminated from behind due to molecular absorption bands in the visible region of the spectrum. The potassium is a deep green while the sodium is deep violet. The vapors also exhibit strong thermal emission which is visible to the naked eye in a darkened room. The contrast between the deeply colored vapor and the transparent argon provides a clear demonstration of the well defined boundary between the two gases. The measured argon flow velocity for the maintenance of the laminar flow conditions is about 50 cm/s.

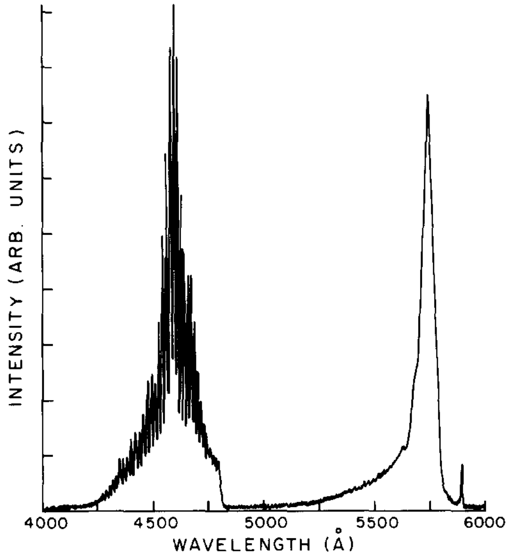

Fig. 3. Potassium emission induced by the 457.9 nm line of a cw argon ion laser and recorded by an S-20 photomultiplier (Temperature 665°C, density 230 torr, spectral resolution 0.5 nm). The emission centered about the laser is from C → X transitions of K_2. The diffuse emission centered near 573 nm has been discussed by several authors (see ref. [10]).

We have successfully maintained stable flow for up to 10 hours with this apparatus. The low level of noise detected during the recording of several previously observed bands attests to the stability of the vapor flow in the device (see fig. 3). We are, at present, limited in running time by the loss of metal from the circulating loop as it accumulates in the filters. The problem occurs because the hot metal vapor condenses as a fine mist or fog when it reaches the condensing section, and some of the small mist particles are entrained in the argon flow rather than coalescing into large droplets which can "rain" out of the argon in the condensing section of the apparatus. We are currently redesigning this portion of the apparatus in order to extend the running time of a single load of metal. Additional details of the design, construction and operation of this apparatus can be found in ref. [2].

Our initial goal with this apparatus was to look for emission bands in the alkali vapors beyond 1 μm corresponding to the recently observed weak absorption bands at these wavelengths [3]. Bhaskar et al. [3] attributed the absorption between 1.1 and 1.6 μm in potassium to transitions out of the lowest triplet state

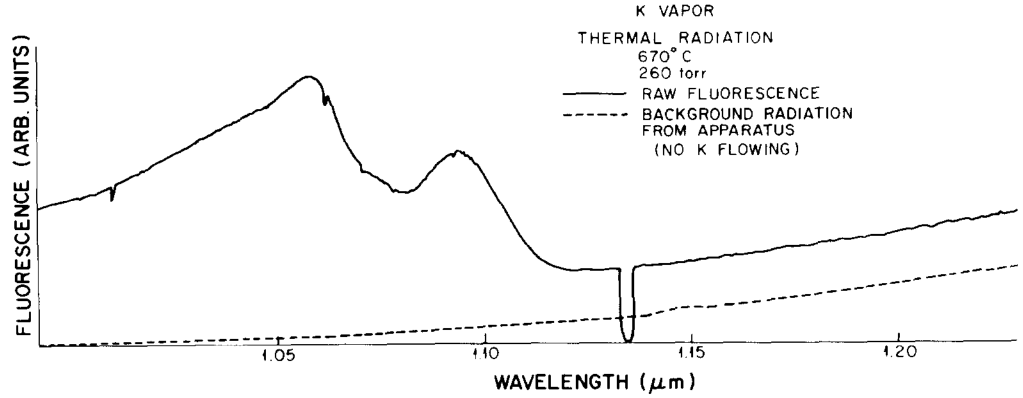

Fig. 4. Thermal emission of potassium vapor recorded by a PbS photoconductive detector. The temperature of the vapor was 670°C the pressure was 260 torr and the spectral resolution was ~5 nm. The figure has not been corrected for the response of the detector or the rest of the optical system. The signal was deliberately blocked at ~1.135 μm to obtain the zero level.

of K_2 molecules, $^3\Sigma_u^+$, which is primarily repulsive, to the bound $^3\Sigma_g^+$ state. The reverse transition would be analogous to the strong and well studied ultraviolet continuum of H_2 which appears in almost any hydrogen discharge [4]. This transition in the diatomic alkali molecules has been suggested as a candidate for a powerful excimer-like lasing transition in the near-infrared [5].

In fig. 4 we present the thermal emission of 260 torr potassium vapor at 670°C. The peak in the spectrum just beyond 1.05 μm corresponds to the red edge of the $A\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ band [6]. Further into the infrared is a peak centered at 1.095 μm. A similar feature was reported by Sorokin and Lankard [7], who recorded the emission spectrum of a potassium discharge contained in a heat pipe oven. They suggested that this feature might be due to the 5F–3D transition of the potassium atom. The presence of this feature in our thermal emission spectra rules out this interpretation. We suggest that the structure at 1.095 μm corresponds to the red satellite of the $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transition. Support for this interpretation is given by a recent calculation by Konowalow and Rosenkrantz which indicates that the peak of this transition should occur near 1.10 μm in potassium [8]. In making this prediction, they used potential energy curves for K_2 that were scaled from accurate ab initio potential energy curves for Li_2 and Na_2.

We have also recorded the emission spectrum of the potassium vapor after excitation by the 1.06 μm line of a pulsed Nd : YAG laser. Measured rate coefficients for the collisional transfer of electronic energy between diatomic alkali molecules and alkali atoms [9] suggest that, at the densities of our experiments, the excitation of any molecular state will result in the rapid population of all other molecular states with similar energies before an appreciable amount of radiation is emitted. When we excite potassium vapor (175 torr, 630°C) with the 1.06 μm line of the Nd : YAG laser we directly populate the $A\,^1\Sigma_u^+$ state [6], and we do detect emission from many collisionally populated excited molecular states. The vapor emits strongly over the entire range of the $B\,^1\Pi_u \rightarrow X\,^1\Sigma_g^+$ transition (690–760 nm), as well as the entire range of the $A\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ transition (780–1060 nm). A previously observed diffuse band centered at 573 nm [10] is also readily observed under these conditions (see fig. 3 where this band is clearly visible for 457.9 nm cw Ar^+ laser excitation). We also see the emission band which peaks at 1.095 μm that was observed in the thermal emission spectrum displayed in fig. 4. We do not, however, see strong emission at the longer wavelengths where the absorption, which was attributed to the $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transition by Bhaskar et al. [3], was observed. The $^3\Sigma_g^+$ state must surely be populated under the conditions of our experiment, and lack of any strong emission at longer wavelengths supports our conclusion that the emission at 1.095 μm is from the $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transition. Similar structure was also observed in absorption experiments as well as emission induced by the fixed frequency lines of an argon ion laser.

We are now investigating sodium vapor. We will compare our results for sodium with predictions made using the accurate ab initio potential curves available for Na_2 [11] and we will do the same for the potassium data as such curves become available for K_2. We also plan to investigate the origin of the absorption at longer wavelengths which was previously attributed to the $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transition.

We have demonstrated the value of aerodynamic confinement as a tool for the investigation of dense metal vapors, and have successfully employed such techniques in the construction of apparatus for the study of alkali metal vapors. Our initial studies using this apparatus have shed new light on spectral features of potassium in the infrared. We believe that the emission and absorption observed at 1.095 μm is due to the triplet transition $^3\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$.

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