

INVESTIGATION OF ABSORPTION SPECTRA OF PURE DENSE POTASSIUM VAPOUR

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The absorption spectra of potassium vapour in visible range, with primary interest on diffuse band at about 575.0 nm, were investigated. In addition to main maximum, weaker ones were observed at 571.3 nm, 557.6 nm and 561.5 nm. Comparison with previously reported position of the band obtained in emission shows that the main band maximum in absorption occurs at longer wavelength.

The first observation of diffuse band at about 577.0 nm in absorption spectra of potassium vapour was reported by Walter and Barratt¹⁾ in 1928. About forty years later Rebbeck and Vaughan²⁾ observed this band at 572.5 nm in low power discharge. They report peculiar behaviour compared with other part of spectrum. In addition to previous observation they measured maxima at 568.5 nm, 565.0 nm, and possibly at 562.5 nm, and 560.5 nm. Recently, Korchevoi et al.³⁾ proposed that the relevant excitation process could be the intensive photorecombination of two resonant excited potassium atoms. The lack of any typical band structure leads to assumption that the lower state is $^3\Sigma_u$ state. The upper state from which that diffuse band arises was not identified. It could be one of the states which correspond to $4S + 3D$ or $4S + 5S$ states of the dissociated molecule. But there are not accurate potential curves and problem cannot be solved yet. The only available potential curves were recently reported by Valance and Nguyen⁴⁾ for the Σ_u states which correspond to $4S + 4S$, $4S + 4P$, and $4S + 5S$ states of the dissociated K_2 molecule.

We have undertaken an investigation of the absorption spectra in order to determine other band maxima in absorption not previously reported¹⁾ and to collect additional experimental data about these bands under conditions of high potassium vapour pressure.

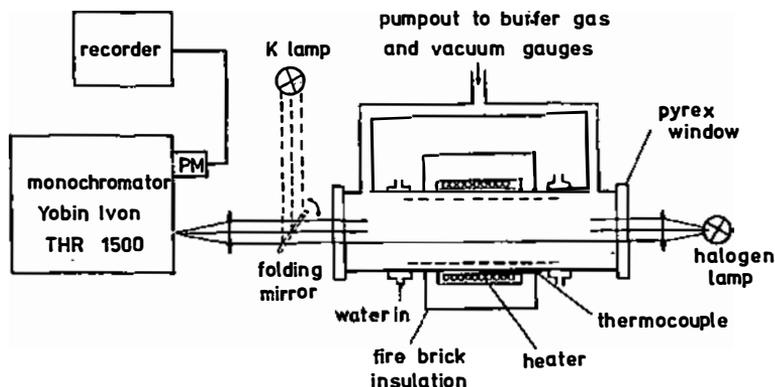


Fig. 1: Schematic diagram of experimental arrangement.

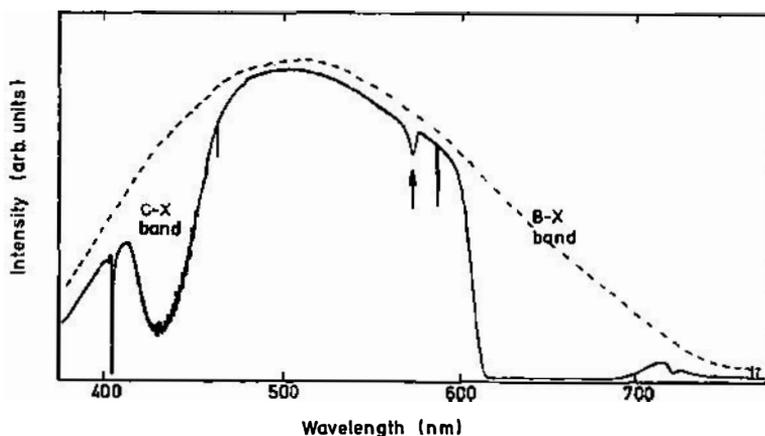


Fig. 2: Absorption spectrum for pure potassium in the range from 380.0 nm to 770.0 nm. The pressure of potassium vapour was of about 3 mbar. Ar was used as a buffer gas.

The experimental arrangement used was the same as that described in Ref. 5. For convenience a schematic diagram is shown in Figure 1. We have used standard heat-pipe oven with heating region of about 10 cm in order to produce high pressure of pure potassium vapour. The buffer gases used were He, Ar and Kr. As was discovered earlier^{6,7)}, heavier noble gases (Ne, Ar, Kr and Xe) are found to produce dense clouds of alkali-metal fog near the condensation region in the heat-pipe at gas pressures above 400 mbar. In order to obtain larger vapour pressures we had to use He as buffer gas which was found to be free of that problem.

In Figure 2 we show one typical scan of the absorption spectra in visible region (from 380 nm to 770 nm). The dashed curve represents continuum spectrum from halogen lamp. The full curve shows absorption of pure potassium vapour (heat-pipe regime with Ar as buffer gas*) with diffuse band at about 575.0 nm. We measured additional weaker absorption maxima at 571.3 nm and 557.6 nm. The major features of the potassium atomic and dimer molecular spectra may be also clearly seen: The first and the second resonant doublets with satellite bands in the blue wing of shorter wavelength component⁵⁾; forbidden transition $4S - 3D$ at 464.2 nm; $B-X$ and $C-X$ band systems of the K_2 . We also report occurrence of the satellite at about 480.0 nm on red side of $C-X$ band. This satellite of the molecular band is usually called head of heads. Sodium D -lines were present as impurity. We note that, with increasing potassium vapour pressure, the forbidden transition appear in spectra before the diffuse band. Figure 3 shows three absorption spectra with He as buffer gas at pressure of 978 mbar. This curves A, B, C , were obtained at higher heating powers, respectively, so that each corresponds to approximately one order of magnitude larger pressure of the potassium vapour. Note the strong increase of the main absorption maximum with the appearance of weaker maxima at (561.5 ± 1.5) nm and at (518.0 ± 1.5) nm.

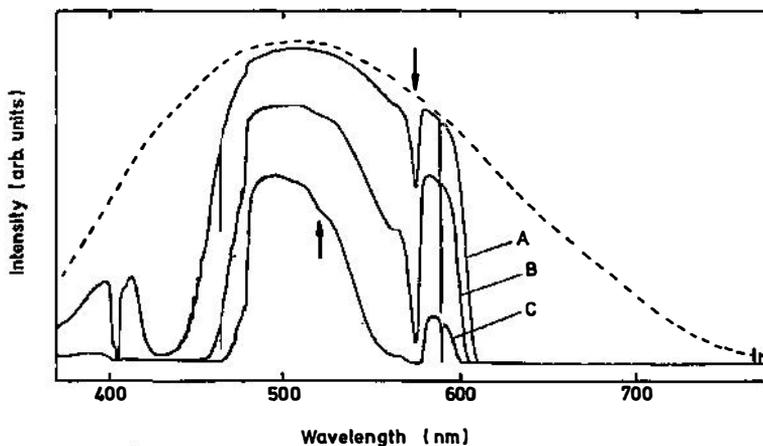


Fig. 3: Absorption spectrum for potassium with He present as a buffer gas. Approximate potassium pressures: Curve A : 6 mbar, Curve B : 40 mbar, Curve C : 270 mbar.

There is no observable shift of the main band maximum with increasing potassium vapour pressure up to about 300 mbar, which is the feature of the absorption measurement.

We report here the weak band at 518 nm. We are not sure whether it originates from K_2 or from KHe molecule since both types of molecules are present in the oven. The interaction with He is visible via KHe satellite band in the blue wing of the second potassium resonance doublet as shown in Figure 3 (Curve A). The presence of the helium as a buffer gas in potassium heat-pipe oven experiment, can be easier detected by observing the relevant blue satellite at second resonance

* One additional indication of heat-pipe regime was the absence of KAr satellites in spectra.

doublet which is only 178.3 cm^{-1} away from 404.4 nm line. The corresponding blue satellite band of the first resonance doublet is about 1130 cm^{-1} away from the 766.5 nm line and therefore requires much larger concentration of He and K particle for the threshold of visibility. By increasing K particle concentration one also increases the $B-X$ band system, which precludes the observation of the blue satellite at 705.4 nm .

The weak band at 518.0 nm is 1722 cm^{-1} close to $4S + 5S$ forbidden transition indicating that it possibly belongs to K_2 spectrum. Calculations by Pascale and Vanderplanque⁸⁾ and experiments with Ar, Kr and Xe by Tam et al.⁹⁾ indicate that possible KHe band should be at smaller distances (below 1355 cm^{-1}) from forbidden $4S - 5S$ transition. Similar band in other potassium-noble gas combinations have not been observed in our experiments presumably because of the alkali fog at elevated noble gas pressures in the oven. Since alkali fog is most probably connected with condensation region in the heat-pipe the final conclusions about the origin of 518.0 nm band can be met in closed absorption cell experiments at high pressures. As is known to us from literature, there have been no observation of KHe bands in visible or infrared regions neither in emission nor absorption¹⁰⁾.

In spite of above mentioned facts and conclusions we believe that the configuration interaction calculations of the adiabatic $1,3\Sigma_u$ potentials for K_2 ⁴⁾ may possibly serve to explain the origin of the 518 nm band. By inspection of their results, and forming all available difference potential curves we obtained that the difference $1\Sigma_u(4S + 5S) - X\ 1\Sigma_u(4S + 4S)$ has a minimum at 522.0 nm and maximum at 457.0 nm . The latter could hardly be observable because of strong $C-X$ band. The minimum at 522 nm is very close to the band 518 nm indicating the possible mutual connection. The difference between experiment and calculations is about 7%. The accuracy of the configuration interaction calculations at large internuclear separations (the minimum is at 15 atomic units) is certainly not smaller than 10%. This may indicate that the band at 518 nm stems from the $1\Sigma_u$ state which dissociates into $4S + 5S$ states. If it is true, this would be the first observation of the bands that are connected with $4S + 5S$ dissociating level for the homonuclear alkali dimer systems.

We continue to study peculiar diffuse bands of K_2 spectra and we intend to expand the measurements to similar bands of other alkali spectra especially the sodium case.

Acknowledgments

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ISTRAŽIVANJE APSORPCIONIH SPEKTARA GUSTIH KALIJEVIH PARA

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Istraživani su apsorpcioni spektri kalijevih para u vidljivom području, s posebnim osvrtom na difuzne vrpce kod 575 nm. Pored glavnog maksimuma opažene su i slabije vrpce kod 571,3 nm, 557,6 nm i 561,5 nm. Ustanovljeno je da se u emisijom spektru glavni maksimum pojavljuje na kraćoj valnoj dužini, kod 572,5 nm. Raspravljena je pojava slabe vrpce kod 518 nm i dan je prikaz za njeno moguće objašnjenje.