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NaK Chemiluminescence*

J.J. Wright and L.C. Balling

Department of Physics

University of New Hampshire

Durham, NH 03824

Abstract

The gas phase reaction between a mixture of K and Na and CBr_4 produces, under low density conditions, emission from high-lying vibrational levels ($v' > 9$) of the $B^1\Pi$ state of NaK.



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As part of a study of the chemiluminescent reactions between alkali vapor and carbon tetrahalides, we investigated the reaction of potassium vapor, containing about 0.05% sodium as an impurity, and CBr_4 . In addition to the previously observed alkali atom emission and C_2 Swan band emission [1,2], we observed chemiluminescence which we have identified as being due to the $\text{B}^1\Pi \rightarrow \text{X}^1\Sigma$ transition of NaK. Aside from its possible applications to chemical lasers, the chemiluminescence is interesting because the excited NaK molecules appear to be formed as the result of a chemical vibrational-electronic energy transfer reaction between vibrationally excited NaBr and K_2 .

In our experiment, potassium metal, containing about 0.05% sodium as an impurity, was heated in a 500 ml Pyrex cell connected to a vacuum-gas-handling system. A vial containing CBr_4 crystals was heated to 90°C in order to melt the crystals and produce a CBr_4 vapor pressure of 40 torr. CBr_4 vapor was admitted to the reaction cell by means of a Teflon valve. If the cell temperature exceeded 200°C , i.e. the potassium vapor pressure was $> 10^{-3}$ torr, C_2 Swan band and alkali atom emissions dominated the visible spectrum. At lower cell temperatures the diffusion flame completely changed character and exhibited a uniform yellow chemiluminescent glow. Fig. 1 shows a typical spectrum of this yellow flame, recorded with an optical multichannel analyser (OMA) with a resolution of 0.14 nm/channel. Except for the potassium D lines at 766.5 and 769.9 nm, we observed no

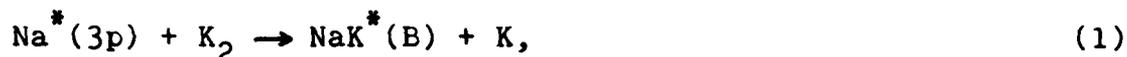
other emission in the range 380 - 800 nm. The ratio of K to Na did not appear to be important. For the case of equal (mass) amounts of K and Na in the reaction cell, we observed the same NaK spectrum as with trace amounts of Na.

Using the NaK spectroscopic constants of Allegrini et al [3], the emission can be correlated with transitions from vibrational levels of the $B^1\Pi$ state with $v' > 9$. (Prior to 1978, the state of NaK correlating with $Na(3^2S)$ and $K(4^2P)$ was designated as the $C^1\Pi$ state. Recent papers [4,5] have alphabetized the states of NaK in the order of increasing energies. The state previously designated as $C^1\Pi$ is now designated as the $B^1\Pi$ state.) One sequence of bands near 570 nm corresponds to transitions from $v' > 9$ to $v'' = 0-3$ and the other sequence near 585 nm corresponds to transitions from the same v' levels to $v'' = 4-8$. These emission intensities are consistent with available NaK Franck-Condon factors [4]. Values of v' from 9 to 22 fit the observed spectrum. Unfortunately, because of the overlap of wavelengths, we could not determine which of these possible transitions produce the chemiluminescence. The fact that we do not observe $v' < 9$ may be due to a perturbation at $v' = 8$ [6,7].

In considering the mechanisms which might be responsible for the production of NaK molecules in the $B^1\Pi$ state, the most striking aspect of the observed chemiluminescence spectra was the absence of either K_2 or Na emission. The lack of K_2 emission rules out the possibility that the

excited NaK molecules are formed by simple collisional energy transfer to pre-existing NaK ground state molecules, as the same process would necessarily apply to K_2 .

The absence of Na emission also argues against the formation of NaK in the reaction:



although such a process is energetically possible.

The observation that K atom emission accompanied the NaK emission suggested the possibility of NaK^* formation from three body recombination:



If this were the case, one would expect the addition of He gas to enhance the effect [8]. However, the addition of even less than one torr of He gas to the reaction cell completely altered the reaction dynamics and produced chemiluminescence similar to that at higher potassium densities, i.e. K, Na, and C_2 emission. Hence, NaK^* formation does not appear to be the result of three body recombination. This is also consistent with the absence of K_2 emission.

Since the reaction of Na and K with CBr_4 produces NaBr, KBr, and CBr_n radicals ($n < 4$), it is reasonable to assume that further reactions involving these products are responsible for the chemiluminescence. We suggest that the

selective excitation of NaK molecules is the result of the chemical-exchange process:



and that this reactive process has a much greater cross-section than that for a non-reactive vibrational-electronic energy transfer process such as,



Our assumption that the reactive vibrational-electronic energy exchange process (3) is much greater than that for the non-reactive exchange process (4) is based on the molecular beam studies of Moulton and Herschbach [9]. They showed that the cross-section for the reactive energy exchange process,



is more than an order of magnitude greater than that for the non-reactive exchange process,



It seems reasonable to assume that this also holds true for vibrational-electronic energy transfer to alkali dimers.

Although process (4) is obviously non-reactive, the analogous process involving the more abundant KBr,



can proceed via a chemical reaction, by virtue of charge exchange. However, reaction (3) differs significantly from reaction (7). The latter is not exothermic, whereas the former has an exothermicity of $1330 \pm 700 \text{ cm}^{-1}$ [10], which is 4-5 times greater than kT . This difference in reaction exoergicity could make the cross section for process (7) orders of magnitude smaller than that for process (3) and account for the absence of K_2 emission.

Because reaction (3) is exothermic, the NaBr would need less than $15,500 \text{ cm}^{-1}$ of vibrational energy to produce NaK in the observed v' levels. This is half the dissociation energy of NaBr, which has a vibrational spacing of 315 cm^{-1} . However, the B state potential well of NaK is only 1030 cm^{-1} deep so vibrational relaxation of the NaBr could account for the quenching of NaK^* formation observed when He gas was added to the reaction chamber.

In conclusion, the reaction of $\text{K} + \text{Na} + \text{CBr}_4$ produces $\text{NaK}^*(B^1\Pi)$ molecules with an inverted vibrational population. Since the emission spectrum does not overlap any strong absorption bands of K_2 or Na_2 , the system is a potential candidate for a visible chemical laser. In addition, a specific process for the formation of $\text{NaK}(B)$ is proposed which is consistent with all experimental observations.

Figure Captions

Fig. 1 The chemiluminescence spectrum of NaK from the reaction of $K + Na + CBr_4$. The v', v'' numbers shown are representative only, and do not include all possible transitions.

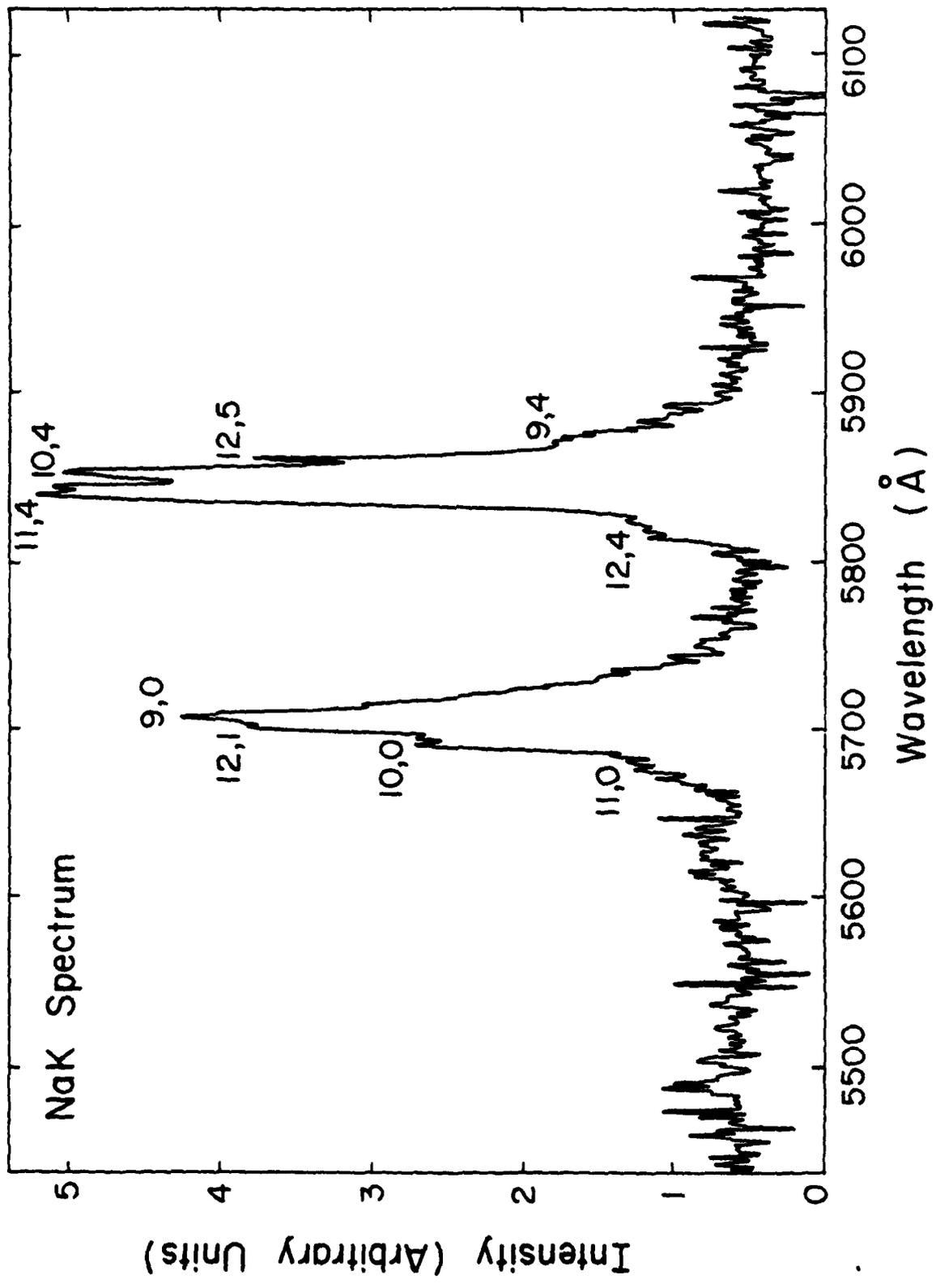


Fig. 1

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