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ALKALI ATOM - SBCL(5) REACTIONS: BLUE-GREEN
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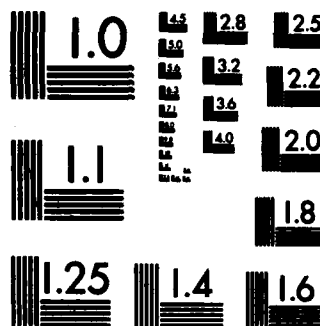
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Alkali Atom-SbCl₅ Reactions: Blue-Green Chemiluminescence
from an Inverted Population in SbCl^{*}

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Abstract

The gas phase reaction between alkali atoms and SbCl₅ produces SbCl ($A_1 \rightarrow X_1$) chemiluminescence from $v' > 4$ to $v'' > 6$.

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In this Letter we report on the observation of visible emission from the $A_1 \rightarrow X_1$ transition of the $SbCl$ free radical produced in alkali atom- $SbCl_5$ reactions. All of the identifiable emission bands are from $v' \geq 4$ to $v'' \geq 6$, making the system a potential blue-green chemical laser candidate.

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In our experiments, K or Cs metal was distilled into a 300 ml Pyrex cell connected to a vacuum-gas-handling system. The cell was heated to produce an alkali atom vapor pressure in the range 10^{-3} - 1 torr. $SbCl_5$ vapor was admitted to the cell by means of a Teflon valve. Chemiluminescence was observed and recorded with an optical multichannel analyser with a spectral range of 380-700 nm.

Fig. 1 shows a low resolution (0.55 nm/channel) spectrum from the $K + SbCl_5$ reaction and Fig. 2 shows a higher resolution (0.14 nm/channel) spectrum from the $Cs + SbCl_5$ reaction. The observed molecular spectra were independent of the alkali atom (K or Cs) reactant. We have identified $SbCl$ radicals as the source of the chemiluminescence, which originates from the A_1 state. The vibrational analysis and classification of the $SbCl$ A_1 state is uncertain [1,2]. Ferguson and Hudes [3] fit the wavenumbers of the transitions they observed to $\nu = 22395 + 244.4v' - 2.28v'^2 - 368.0v'' + 0.84v''^2$ while the best fit to the data of Avasthi [4] was $\nu = 22109 + 236v' - 1.5v'^2 - 369v'' + 0.75v''^2 + 0.025v''^3$. Both polynomials fit our spectrum, but with different vibrational quantum numbers.

Using the data of Ferguson and Hudes, the most intense bands we observe are from $v' = 6$ to $v'' = 10-15$, the next set of bands from $v' = 5$ to $v'' = 6-13$ and the weakest discernible bands are from $v' = 4$ to $v'' = 7-12$. The data of Avasthi reproduces the same spectrum but with $v' = 7, 6$, and 5 rather than $v' = 6, 5$, and 4 . In either case, the vibrational distribution in the excited state is highly inverted.

It seems evident that the SbCl is produced from sequential alkali atom stripping reactions,



where $2 \leq n \leq 5$. We propose that this sequence of reactions is responsible for the selective electronic excitation of the SbCl .

The mean Sb-Cl bond energy for SbCl_5 is 60.4 kcal/mole, the SbCl dimer bond energy is 83.6 kcal/mole, [5] and the KCl or CsCl bond energy is 102 kcal/mole [6]. Therefore, on average, the excess energy per alkali atom reaction is less than 48 kcal/mole. In order to produce SbCl in the A_1 state ($T_e > 63$ kcal/mole), excess reaction energy must remain in the Sb-Cl bonds of the the original reactant rather than in the K-Cl or Cs-Cl bonds of the alkali halide product. This is similar to the observations of Engelke and Zare [7] in $\text{Ba} + \text{S}_2\text{Cl}_2$ reactions, where the energy excess appeared in the S-S bond.

Two separate experiments confirm that energy pooling is responsible for the excitation of the SbCl . In the first experiment, we added He gas to the reaction $\text{K} + \text{SbCl}_5$ in order to thermalize the energy distribution among the various reaction products. While the reaction was not inhibited, there was no visible chemiluminescence when less than 1 torr of He gas was added to the reaction cell.

In an attempt to further verify that energy pooling is responsible for the electronic excitation of SbCl , we reacted Cs and SbCl_3 . The mean Sb-Cl bond energy for SbCl_3 (74.8 kcal/mole) [5] is greater than that for SbCl_5 and so only 63 kcal/mole is liberated from the stripping of two Cl atoms. If all of this energy remained in the SbCl radical, it would not be enough to excite even the $v' = 0$ level of the A_1 state. If, on the other hand, the SbCl was excited by collisional energy transfer, one might expect to observe $A_1 \rightarrow X$ chemiluminescence since SbCl_3 is an intermediate reaction product from the stripping of SbCl_5 . The Cs reacted readily with the SbCl_3 but there was no visible chemiluminescence.

This result and the result from adding He gas to the SbCl_5 reaction provide convincing evidence that each successive stripping reaction is adding to the internal energy of the remaining SbCl_n molecule.

In a discharge containing SbCl_3 and active nitrogen [3,4], SbCl exhibits two emission band systems, $A_1 \rightarrow X$ and

$A_2 \rightarrow X$, with $T_e = 22178 \text{ cm}^{-1}$ and 25906 cm^{-1} , respectively [2]. The strongest transitions observed in a discharge from both systems are from $v' = 0$ and 1. The fact that we do not observe emission from the A_2 state is consistent with the fact that the highest v' level of the A_1 state that we observe is only 23700 cm^{-1} (68 kcal/mole) above the $v'' = 0$ of the X_1 state. This suggests that the selective excitation of SbCl is due to a specific internal energy distribution resulting from the stripping reactions since, in a discharge, A_1 state excitation does not appear to be favored over A_2 state excitation.

The selective excitation of SbCl to $v'=6,5$, and 4 can be qualitatively explained by assuming that the average energy liberated per stripping reaction (47.5 kcal/mole) is successively redistributed between the reaction products according to their vibrational degrees of freedom. After four stripping reactions, the remaining SbCl would then have 70 kcal/mole of internal energy. The $v'=6$ level of the A_1 state is 68 kcal/mole above the ground state. This is probably a fortuitous coincidence since the problem has been over simplified by assuming that each stripping reaction liberates the same amount of energy, which we know is not the case since the average Sb-Cl bond energy for SbCl_3 is not the same as that for SbCl_5 . However, the model does provide a simple and plausible explanation for how the SbCl radical might be selectively excited and is consistent with all of the experimental observations.

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➤ In conclusion, alkali atom-SbCl₅ reactions produce chemiluminescence from a vibrationally inverted population distribution in the A₁ of SbCl. A simple model has been proposed to account for this selective excitation. Since the excited SbCl is a primary reaction product and is produced with an inverted population, this system appears to be a viable candidate for a blue-green chemical laser.

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Figure Captions

- Figure 1. Low resolution spectrum of SbCl emission from the reaction $K + SbCl_5$.
- Figure 2. High resolution spectrum of SbCl emission from the reaction $Cs + SbCl_5$.

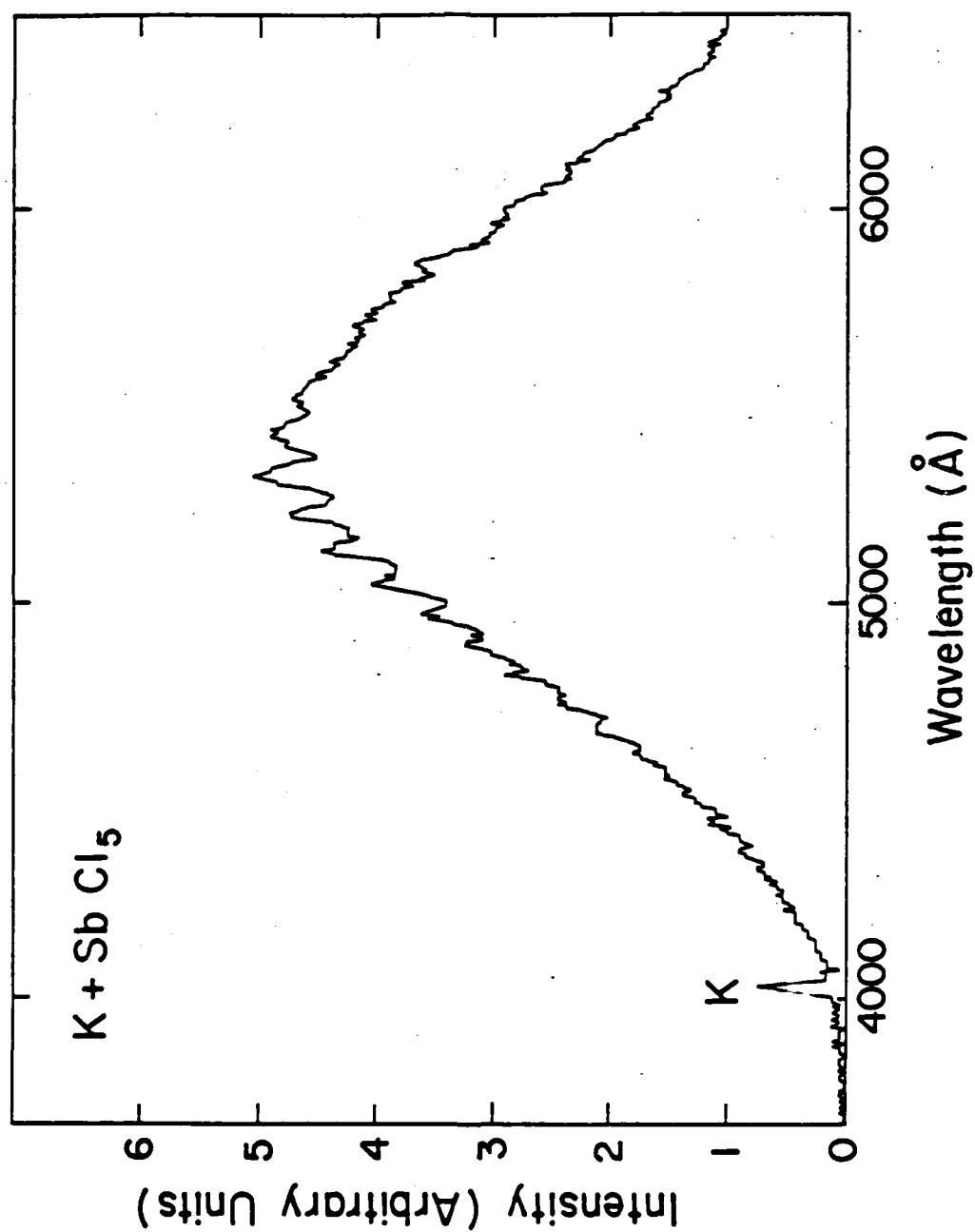


Fig. 1

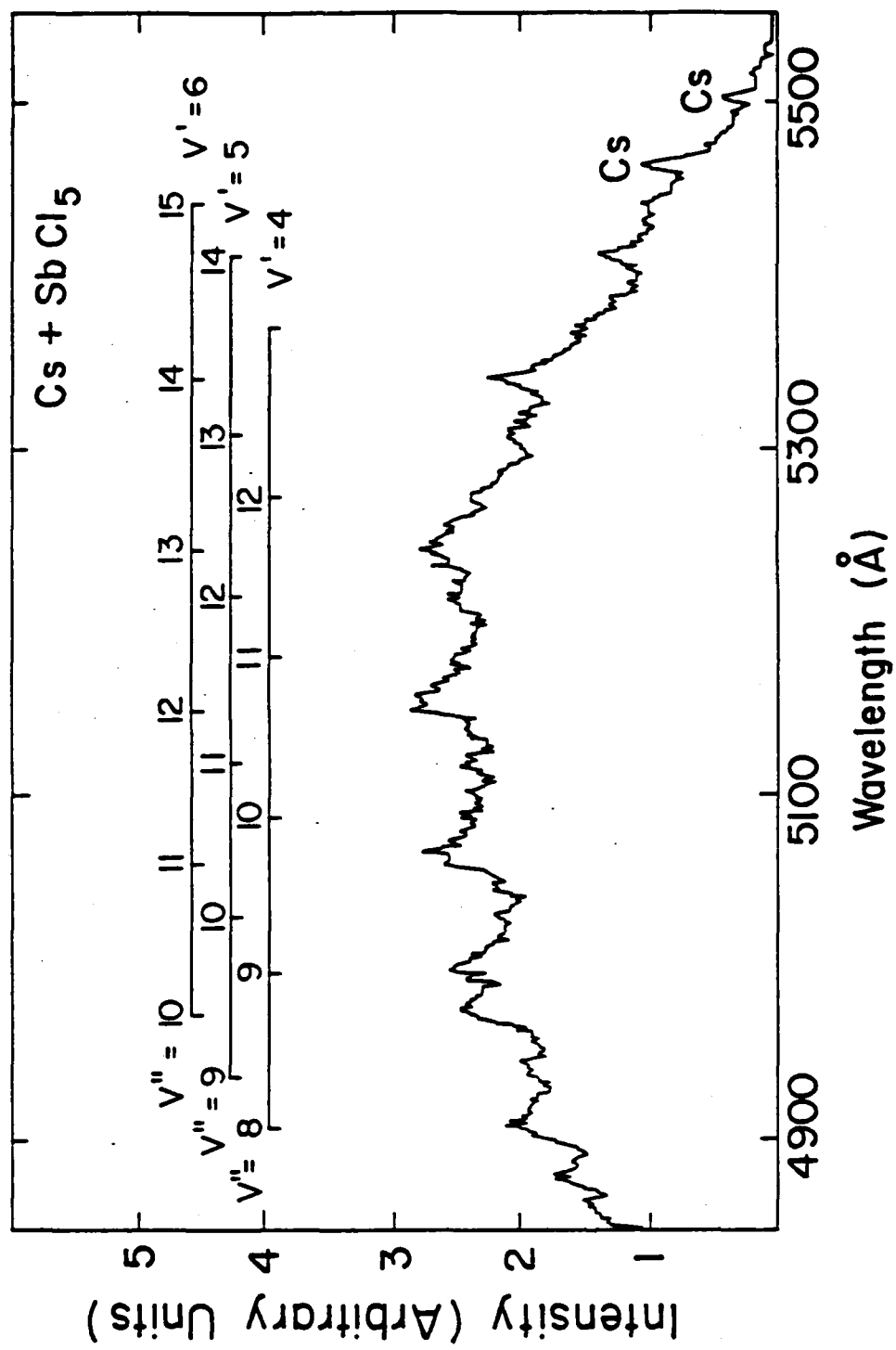


Fig. 2

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