CHEMILUMINESCENCE STUDIES OF LITHIUM ATOM REACTIONS WITH HALOGEN GASES (Cl_2, Br_2) AND HALOGENATED GASES (SF_6, CH_2Cl_2, CF_2Cl_2).

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ABSTRACT

Chemiluminescence spectra from Li-Cl_2 and Li-SF_6 reactions were investigated. The intense atomic excitation of Li is discussed. A band structure in the 700-800 nm region was resolved and may be associated to A-X transitions of Li_2. Fluctuation bands from electronically excited Li halides did not appear.

1. INTRODUCTION

Chemiluminescence produced in reactions of the alkali metals Na....Rb with halogen gases has thoroughly been investigated by Polanyi et.al. (1), Herschbach et.al. (2,3), Zare et.al. (4) and many other authors. As a result of their experiments the processes yielding an intense excitation of the alkali atoms are well understood. Moreover, several types of molecular spectra from the electronically excited states of the alkali halides (KCl, RbCl, CsBr) were identified (4). But only a few results on the chemiluminescence of reactions of Li with halogen gases are found in the literature. In the following some studies of this type which were performed in our laboratory are described and compared with the results of the corresponding experiments quoted above.

2. APPARATUS

In one apparatus used here (6,7) a Li atomic beam from a steel furnace at about 1000 K is directed into a reaction chamber containing the halogen gas at pressures of 10^{-4} to 10^{-1} mb. Li_2 molecules are present in the beam with one to several percent, depending on the temperature of the oven. In a second apparatus the oven room and the reaction chamber were separated and differentially pumped. The spectroscopic results from both of the devices were nearly the same.

The spectra were registered with a 1 m -scanning spectrograph (McPherson) using a 600/mm or a 1200/mm blazed grid and a cooled EMI 9558 QB photomultiplier.

3. EXPERIMENTS AND RESULTS

Referring to the interpretation of the earlier investigations on the alkali-halogen reactions (1-5) the following processes must primarily be taken into account (M and X denoting alkali and halogen atoms):

[1] $M+X_2 \longrightarrow MX^+ + X$

[2] $MX^+ + M \longrightarrow MX + M^*$

[3] $M_2 + X \longrightarrow MX + M^*$

[4] $M_2 + X \longrightarrow MX^+ + M$

[5] $M_2 + X_2 \longrightarrow MX + MX$

[6] $M_2 + X_2 \longrightarrow M + MX + X$

These processes may depend in a more or less complex way on the components in the reaction chamber.

In the $Li+Cl_2$ reactions the luminescence is dominated by the red 2p-2s line (670,8 nm) of the excited Li atoms. The excitation of n = 3 levels is also relatively intense (fig. 1), but the higher levels are much less populated as this has been reported in (8). In the case of $Li+SF_6$ levels up to nearly the ionisation limit of Li have been observed.

In the $Li+Cl_2$ reaction the excitation by the process [1] followed by [2] yields an energy of 2,4 eV which is sufficient for the D line of Li (1,84 eV). Taking $D(Li_2) \approx 1{,}1$ eV (9) and considering a thermal energy of about 0,1 eV the reactions [1] and [3] can deliver the energy necessary for the excitations up to the 3d level (3,88 eV). The same energy is delivered by a mechanism following the reactions [1] , [4] , and [2] . In this way the excitation of Li up to the 3d level is well understood. As the n=3 levels partially decay via the 2p level the Li D line is appearing with a high intensity. Using $D(LiF) \approx 6$ eV it is obvious that in the SF_6-reaction higher levels can be populated. In the mechanisms quoted a vibrational excitation of LiF^+ of 4,9 eV can occur. To explain still higher levels a process [5] followed by [2] can be taken into account as this has been pointed out by Oldenborg et.al. (4) and by Struve et.al. (3).

The situation is more complicated in the processes $Li+CH_2Cl_2$ and CF_2Cl_2. Here a contribution of a sequence of reactions is necessary to explain the excitation of Li levels. With $D(CH_2Cl\text{-}Cl) \approx 3{,}6$ eV the reaction [1] only retains 1,3 eV in $LiCl^+$, which is below the 2p energy of Li. Reactions with Li_2 can yield Cl atoms so that [3] and [4] can occur furtheron.

As is shown in fig. 2 in the $Li+SF_6$-reaction (and less intense in $Li+Cl_2$) a band structure in the 700-800 nm range rapidly growing with the gas pressure in the reaction chamber has been found here. It may be associated to the known Li_2-A-X-system (10,11,12). The most intense bands can be recognized as the 1,0; 0,0-0,4; and 1,1-1,5 transitions. As can be seen from fig. 3 the bands are only weakly rotationally excited.

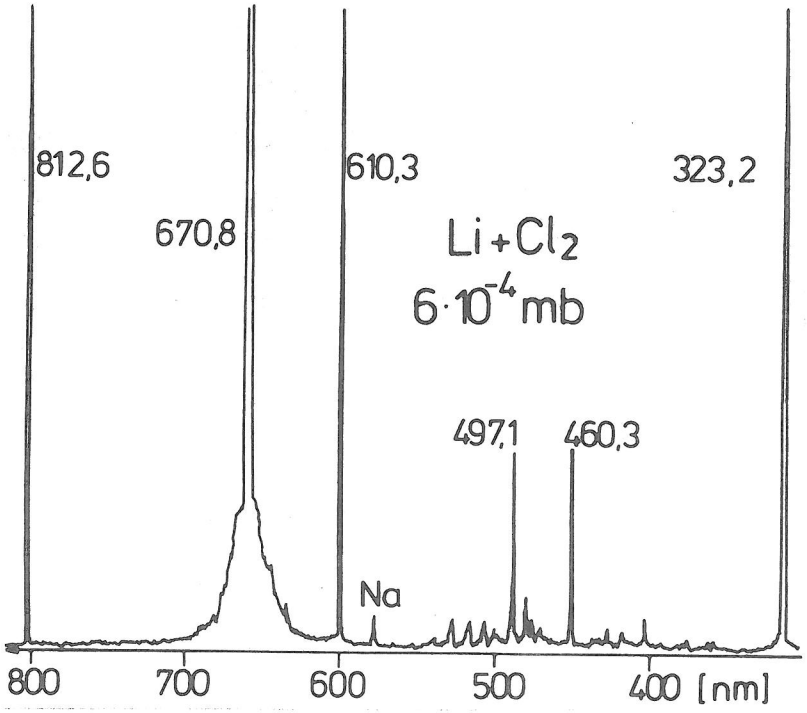

Fig. 1. Li atomic excitation in the $Li+Cl_2$ chemiluminescence reactions and molecular bands in the 470-560 nm region.

The excitation of Li_{*2}^{*} can arise from a process like $LiCl^{*}+Li_2 \longrightarrow LiCl+Li_2^{*}$. Besides, a recombination radiation of $Li^{*}+Li \rightarrow Li_2^{*}$ can be considered, but seems to be negligible.

In all cases of the chemiluminescence of the alkali elements with halogen gases no excitation of halogen molecules has been reported nor could it be unambiguously observed in our experiments with Li. (More recent measurements with I_2 have still to be analysed.) Whether some unresolved continuum spectra, as shown in fig. 2, can be traced back to an excitation of SF_6 is still uncertain.

In the experiments with K, Cs, Rb band structures of electronically excited alkali halides MX^{*} have been observed (4). We easily were able to reproduce those spectra for the K-halides for comparison. Molecular emission is mainly associated to M_2+X_2-reactions. In the case of Li no band spectra could

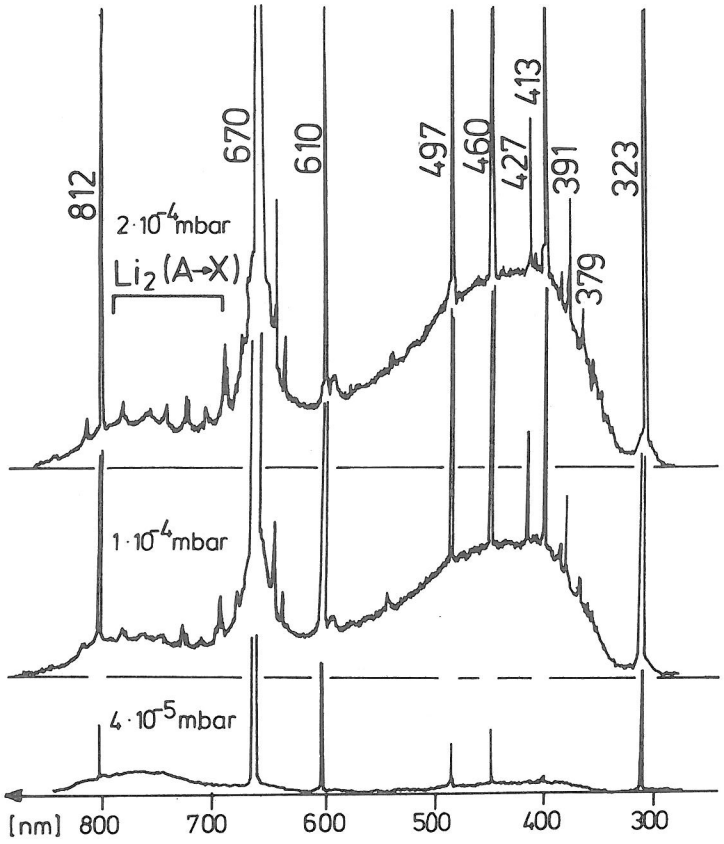

Fig. 2. $Li+SF_6$; pressure dependence of Li atomic excitation and $Li_2^-(A \rightarrow X)$ bands.

unambiguously be observed from the Li-halides. This could be understood as a consequence of the existence of several competing exit channels from the electronically excited states (13) of the Li-halides. In more recent experiments we definitely have observed chemiluminescence spectra from electronically excited states of NaCl, NaBr, and NaJ, but the results still have to be analysed. They will be published elsewhere.

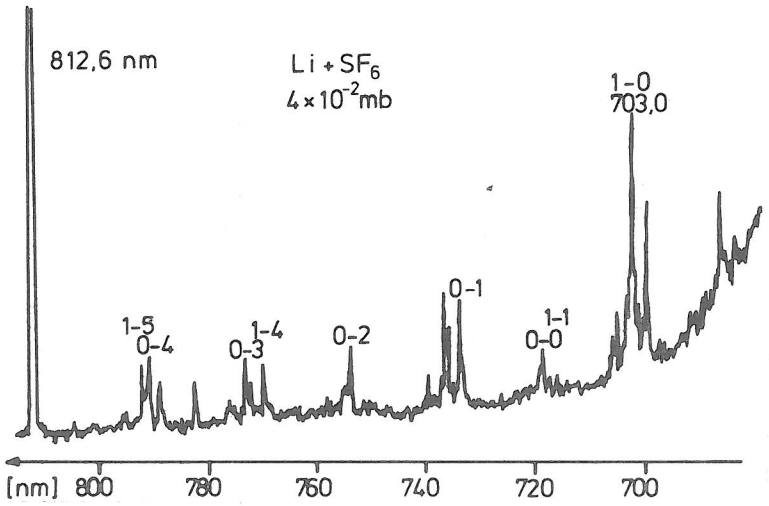

Fig. 3. Li_2(A-X)-luminescence bands in Li+SF_6 reactions observed with higher resolution.

Finally we should like to refer to some curious band structures which have originally been observed by Ham and Chang (14) using Na+Cl_2. They tentatively associated them to $NaCl_2$. In our experiments we have observed these bands reproducibly in all the Li+Cl_2 (and the Cl_2 containing substances) reactions with a remarkable intensity (fig. 4a), too, even using purified Li metal. So we suggest that these structures cannot come from $NaCl_2$ molecules but may be associated to Cl_2. As it is shown in fig. 4b similar band structures have been observed in Li+Br_2 (or Br_2 containing molecules) reactions. In some comparative measurements with Na+Cl_2 these bands appeared much weaker. The transitions responsible for these bands have still to be interpreted.

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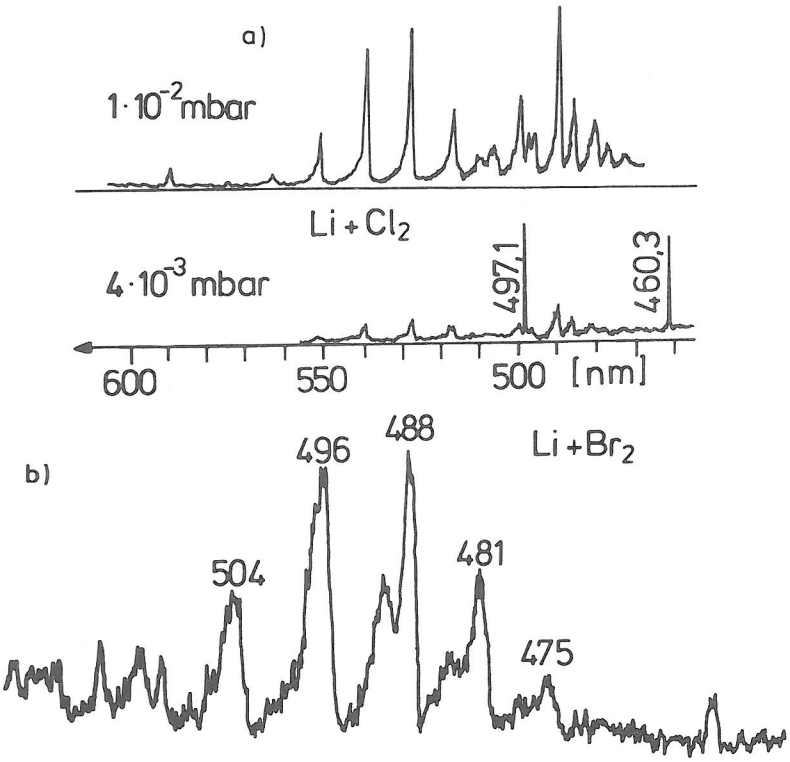

Fig. 4. Band structures in $Li+Cl_2$ (a) and $Li+Br_2$ (b) chemiluminescence reactions.

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