Alkali-Halide Chemiluminescence: Studies on the Fluctuation Bands from some Alkali (Li, Na, K)-Halogen (Cl, Br, I)-Reactions

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Molecular chemiluminescence spectra from selected alkali-halogen reactions are presented using a beam-gas arrangement operating with pressures between 10^{-1} mtorr (single collision conditions) up to 10 mtorr in the reaction zone. Spectra are presented for the chemiluminescent reactions $M_2 + X_2 \rightarrow MX^* + MX$, where $M_2 = K_2$, Na_2 and $X_2 = Cl_2$, Br_2, I_2. The MX^* emitter is identified by comparison with previous absorption and emission studies of these molecules. The sodium reaction with I_2 as well as all lithium reactions with different halogens (Cl_2, Br_2, I_2) do not yield appreciable molecular emission. The differences in molecular chemiluminescence intensities among this type of reactions can be understood in terms of the Landau-Zener formalism for an electron jump and turn out to be consistent with the results from measurements on absorption, emission and dissociation.

Introduction

The power of the beam-gas chemiluminescence technique has been clearly demonstrated in alkali-halogen reaction studies discussed in the literature [1 – 5]. An excellent review is given in [1]. In general, the technique provides a wealth of kinetic and spectroscopic information which is so vast that the amount we learn from a particular study seems only limited by our ingenuity to extract results from the web of data. However, most of the experimental set-ups used in different laboratories are restricted in their applicability to the study of reactions of the heavier alkali-halogen reaction systems because of the oven temperature limitations (and/or oven gasket problems) inherent in their design.

In order to extend the alkali-halogen chemiluminescence technique, we have constructed a beam-gas arrangement to allow for sustained high temperature operation at up to 1400 K to study *all* alkali-halogen reactions including lithium systems.

From even a cursory investigation of previous alkali-halogen chemiluminescent and molecular dynamic studies, it can be generalized that these reactions yield product molecules in highly excited rotational and unknown vibrational levels. This implies that the observed spectra are not easy to analyse. The spectra of all MX^* molecules generated by reaction $M_2 + X_2$ show poorly defined "bandheads", since the heads tend to form at low rotational

levels. Also, the strongest observed transitions involve high vibrational quantum numbers in the lower (ground-) state, which are difficult to identify since vibrational constants derived from low levels cannot always be accurately extrapolated.

Investigations on chemiluminenscent alkali-halogen reactions have a long tradition with respect to atomic excitation [2]. Whereas, since the thesis of Levi [6] molecular investigations have only been reported for some of these reactions [3, 4], where typical fluctuation bands of the alkalihalides (MX) have been registered under single-collision conditions.

This paper deals with molecular chemiluminescence and gives additional results on the spectra mentioned above. Beyond this, it gives a plausible explanation for the striking differences concerning the intensities of the MX^*-emissions from the alkali-halogen-reactions, which we have studied.

Experimental

All spectra shown were obtained with a differentially pumped two-chamber apparatus, very similar in design to the set up used by Oldenborg et al. [3]. In this way investigations of the chemiluminescence from single collision conditions up to gas pressures of 10^{-1} mtorr [5] can be performed.

The light emitted by the reaction was focused on the slit of a McPherson-1 m-scanning-monochromator. A cooled EMI 9558 QB PM with a S 20 cathode was attached to the exit slit. The registered spectra given here were not corrected for spectral response.
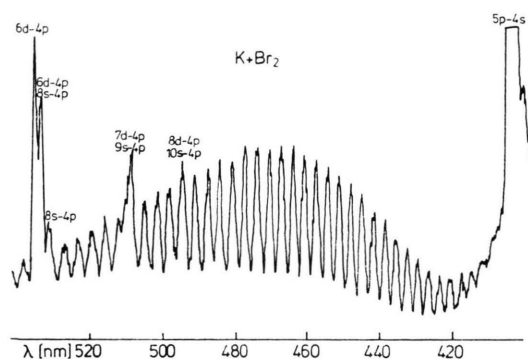
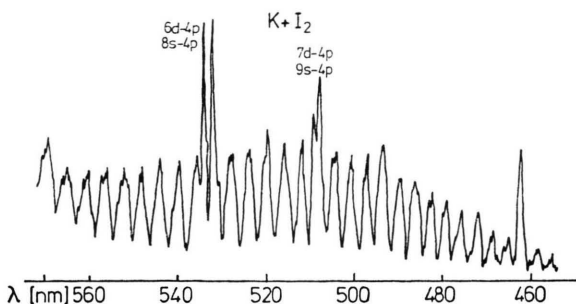Fig. 2. Chemiluminescent spectrum of KBr, consisting of 53 bands.

Fig. 3. Chemiluminescent spectrum of KI, consisting of 40 bands.

Results

The Figs. 1 – 3 show the so-called fluctuation bands emerging from the reactions of potassium with the halogenes Cl_2, Br_2 and I_2 [7]. The following results may be noted:

— The band systems show different maxima of intensity. For KCl at 500 nm, for KBr at 470 nm and for KI at 520 nm.

— The reactions yield greater intensity and hence more fluctuation bands with decreasing molecular weight (KCl: 63, KBr: 53, KI: 43).

— For KCl and KBr the short-wavelength-cutoff is screened by the atomic emission $5^2 P \rightarrow 4^2 S$ of potassium whereas for KI the most energetic band can be identified at about 450 nm.

As other authors have shown [3, 8, 9], these fluctuation bands represent the transitions from a loosely bound, covalent upper state to the vibrational levels of the deep potential well of the ionic ground-state (see Figure 5). That means, the most energetic band corresponds to its lowest vibrational state, where the fluctuating intensities are governed by the Franck-Condon-factors. But here the narrow spacing of the flat covalent potential makes the transitions unresolvable.

Using the vibrational numbering of the corresponding groundstate of Levi [6] for KCl and KBr and of Kaufmann et al. [9] for KI the evaluation of the Birge-Sponer-plot yields vibrational constants ω_e, which are about $10 - 20$ cm^{-1} smaller than those of Brumer and Karplus [10]. It also roughly reflects the anharmonicity constant $\omega_e x_e$, and for high vibrational quanta it gives evidence for the influence of a positive $\omega_e y_e$, which is typical of ionic molecules.

A very similar but much weaker chemiluminescence of fluctuation bands could be registered for NaCl; NaBr was even less intense [5] and NaI was undetectable. The spectrum of the chlorine reaction is shown in Figure 4. As for KCl and KBr, the short-wave-length-cutoff is screened by an atomic line (here the NaD-line), which in addition herewith probably conceals an intensity maximum. Atomic emission dominates the spectrum for all the sodium reactions.

A Birge-Sponer-plot for NaCl and NaBr [5] reveals an approximately linear decrease of the spacings with increasing vibrational numbering and
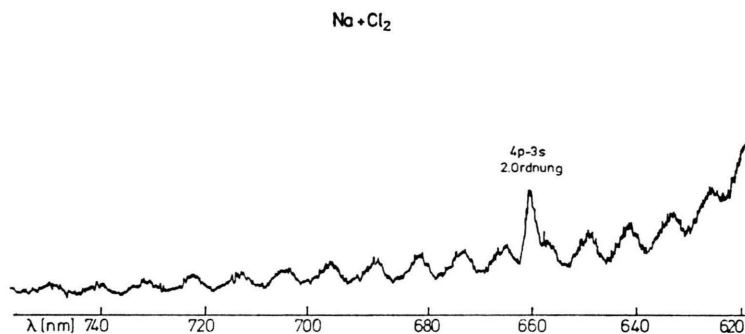
Na + Cl₂

thereby reflects the well known ratio of the $\omega_e x_e$ of NaCl and NaBr.

For the sodium reactions, the fluctuation bands cannot be associated with definite vibrational levels. This is because there is no overlap with the band systems reported by Levi [6]. The spectral range, where she has measured the band positions (for NaBr in absorption and emission, for NaCl only in absorption) lies much further to the shortwave side of the spectrum. This discrepancy will be explained in the next chapter.

The appearance of a band structure in the same spectral range has already been mentioned by Oldenborg et al. [3] for the reaction of Na with Cl₂ and Br₂. But the weak intensity, which not even allowed Na₂ to be excluded as the emitter, did not allow an identification. Here Na₂ can definitely be excluded, because under special conditions (high Na₂ density because of observation near the alkali oven) its M-X-system could undoubtedly be registered separately, and it showed marked differences from the fluctuation bands.

All reactions with lithium failed to yield comparable emission.

Discussion

Any model applicable to this type of reactions must be able to rationalize the decreasing intensity of the chemiluminescent fluctuation bands in the order of KCl, KBr, KI, NaCl, NaBr and its absence for NaI and all the lithium reactions. This tendency obviously reflects the electron jump probability of the *atomic* reactions in the groundstate, and suggests a corresponding explanation.

The dependence of the emission on reactant pressure proves that the fluctuation bands result from the reaction of one halogen molecule and one alkali dimer [3, 4]. Reactions like M₂ + X yield solely atomic emission [4].

Because of the small ionization potential of the alkali dimers [11] the reaction will be initiated in the same way as the reaction M + X₂, which can typically be described by the electron jump mechanism. For both reactions the probability of an electron jump can be calculated according to the Landau-Zener (LZ) formalism. The probability, P_{ad}, of an adiabatic approach of any two appropriate reactants, i. e. of a reaction initiated by an electronjump, is given by [13, 14]

$$P_{ad} = 1 - e^{-\delta}$$

with

$$\delta = \frac{4 \pi^2}{h} \frac{H_{ik}(R_C)^2}{v_{rad} |\Delta F_{Rc}|}.$$

Here

R_C = crossing radius of covalent and ionic potential surface of the reactants,

v_{rad} = radial relative velocity,

H_{ik} = coupling-matrix element of the ionic and covalent state, which depends exponentially on the nuclear separation,

ΔF_{Rc} = difference of gradients of the two potentials at R_C.

Here a relatively large R_C allows ΔF_{Rc} to be adequately approximated by the assumption of a crossing of a horizontal covalent surface with an ionic one following a R^{-1} dependence.
Then,

$$\delta = \frac{8 \pi^3 \varepsilon_0}{h e^2} \frac{H_{ik}^2 R_C^2}{v_{rad}}.$$

If at least one reactant of an electron jump reaction is a molecule, the possible dependence of H_{ik} on the

relative orientation must additionally be taken into consideration. For $M_2 + X_2$ this means a large reactive cross section for a collinear approach of the center of mass of M_2 and both halogen atoms.

An electron jump, which can be assumed to be vertical, leads to the formation of an M_2^+ ion near its equilibrium distance [15, 16] and of an X_2^- ion. The latter is formed at the repulsive part of its groundstate potential curve, approximately on the same level as the dissociation limit [11, 17 – 19]. This situation predominantly results in

$$M + MX + X.\tag{1}$$

All other reaction channels have a much smaller cross section [4]. Besides chemiionic channels, which normally are forbidden for thermic energies on energetic grounds, the relative importance of the competing reaction channels

$$MX + MX,\tag{2}$$

and

$$MX + MX^*\tag{3}$$

determine the different intensities of the MX* emissions. Here MX* denotes an upper electronic state of the corresponding molecule which correlates with diabatically approaching groundstate-atoms (see Fig. 5 for NaI).

Except for LiCl, the relative intensities of the fluctuation bands correlate remarkably well with the LZ-probability of a second electron jump. That is, systems with large R_C and therefore small H_{ik} [15, 20] (as it is for all potassium-reactions) predominantly follow (3) rather than (2) as a consequence of a vanishing probability of a second electron jump. Correspondingly, all systems involving alkalis with a relatively high ionization potential (e. g. Li) and/ or a relatively small electron affinity (e. g. I) favour products from (2). Thus, in the latter case there are mainly formed vibrationally highly excited groundstate molecules, which do not allow for a detectable chemiluminescence. Here the second electron jump takes place during the approach of the reactants. In contrary, for potassium, rubidium, and cesium for a sufficient part of reactants this second jump occurs by radiating in the visible section of the spectrum

$$MX^* \rightarrow MX + h\nu.$$

For this consideration we may neglect the second excited covalent state (s. NaI** in Fig. 5), cor-

relating diabatically with groundstate alkalis and halogen atoms in their first excited $^2P_{1/2}$-state.

All these arguments are consistent with other investigations dealing with this type of reaction.

Thus experiments on the dissociation of alkalihalides by shock waves show ionic dissociation products for all molecules containing potassium, whereas LiI and NaI excludingly yield neutral
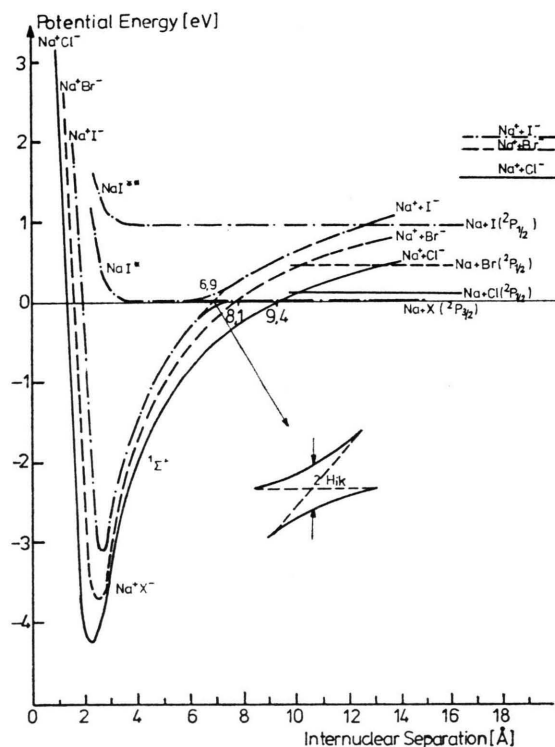

Fig. 5. Approximated potential curves of the sodium halides with the crossing behaviour for NaI. Curves for NaI* and NaI** according to P. Davidovits and D. C. Brodhead, J. Chem. Phys. **46**, 2968 (1967).

products [21]. Absorption measurements dealing with alkalihalides in the gas phase [6, 22 – 24] and in a matrix isolated form [8] provide the same tendency. Only NaI and LiI exhibit a fluctuating bandsystem, where the bands have a resolvable structure, implying an upper potential, which is bound. Its appearance can be understood in terms of Figure 5.

The "avoided crossing" at R_C prevents MX* from dissociating to ground state atoms, thus forming a potential which at least is bound by the spin-orbit-coupling of the corresponding halogen (for $I \approx$

0.94 eV). The resulting curious state has been described by Berry [22].

Thus, the results from absorption- and emission spectroscopy indicate an excited upper state, which can be denoted as $^1\Sigma^+$ for the Hund coupling-case (a) or O^+ for (c). Only for this state the coupling matrix element H_{ik} with the ionic $^1\Sigma^+$-groundstate is sufficiently high to bring about an electron jump.

There is a striking difference for the spectral ranges, where fluctuation bands are registered. Under nearly single collision conditions the emission appears much further to the red side of the spectrum compared with the emission from flames. This distinction can be made plausible by considering the probability of a rotational relaxation before emission [3]. Within the expected short lifetime of MX* with respect to dipole radiation from flames there can be expected a sufficient number of collisions, which result in a rotational excitation of the products in correspondence with the temperature of

the flame [9]. On the contrary for the single-collision-condition a higher rotational excitation must be assumed, which causes an effective potential with a minimum at a longer nuclear separation. Consequently here, according to the Franck-Condon-principle, the transitions to higher vibrational levels of the ground state are favoured and therefore less energetic emission is registered. From this point of view, it can be understood why the fluctuation bands reported by Levi [6] for NaBr do not overlap with ours. The steeper potential of the groundstate of NaX brings about a more drastic influence of the shift of the upper state with respect to the emitted wavelength.

Acknowledgement

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