

# Some Investigations of the Chemiluminescence Spectra from the Reactions of Ca and Sr with SF<sub>6</sub>

W. Berneike, H. J. Löffler, and H. Neuert

I. Institut für Experimentalphysik der Universität Hamburg

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The appearance of the chemiluminescence spectra from the reactions of the alkaline earth metals  $M = \text{Ca}$  and  $\text{Sr}$  with  $\text{SF}_6$  is only understood by the participation of excited metal atoms in the reactions. This has been ascertained by measuring the dependence of the intensities of the metastable Ca-line 657.3 nm and of a representative CaF band on the  $\text{SF}_6$  gas pressure in the reaction chamber. By a detailed analysis of the well resolved  $A-X$ - and  $B-X$ -systems of both of the reactions some earlier values of  $D_0(\text{F}-\text{SF}_5)$  given in the literature can be excluded, while the recently found value (Kiang et al.) of  $3.9 \pm 0.14$  eV is well confirmed.

## Introduction

The chemiluminescence from the reactions of the alkaline earth metals  $M = \text{Ca}$ ,  $\text{Sr}$  and  $\text{Ba}$  with  $\text{SF}_6$  has been investigated by several authors [1–4]. It has been shown that it is brought about by molecular bands in the visible region of the MF-molecules which are electronically excited in the  $A$ -,  $B$ - or  $C$ -systems. Additionally several atomic lines appear, markedly those from the metastable states of the alkaline earth atoms. The former experiments were aimed to find the molecular constants of the MF-species and to compare them with the results from further reactions yielding MF-molecules (such as from  $M + \text{F}_2$ ).

In some recent investigations of reactions with  $\text{SF}_6$  using metastable M-atoms Zare et al. [1] ascertained another and evidently more accurate value of the dissociation energy  $D_0(\text{F}-\text{SF}_5) \leq 3.95 \pm 0.14$  eV. Using this value, which is strikingly higher than the earlier values given in the literature [5–9], it is evident that starting with Ca- or Sr-atoms in their ground state no emission from electronically excited states of the MF-molecules can be expected, contrary to the experimental results. Accepting a lower value for  $D_0(\text{F}-\text{SF}_5)$  like the value of 3.39 eV according to [6–8] an excitation of the  $A$ -systems in the lower  $v'$ -states might be reached. In earlier publications on the reactions of Ca and Sr with  $\text{SF}_6$  the energy balance and the reaction mechanism were not considered in detail.

Reprint requests to Prof. Dr. H. Neuert, I. Institut für Experimentalphysik, Universität Hamburg, Jungiusstraße 9, D-2000 Hamburg 36.

Because of the importance of an accurate value of  $D_0(\text{F}-\text{SF}_5)$  for the appearance and the structure of the chemiluminescence from these reactions as well as for a discussion of further properties of the  $\text{SF}_6$  molecule, like the electron affinities of  $\text{SF}_6$  and  $\text{SF}_5$  and the dissociation into  $\text{F}^- + \text{SF}_5$  or  $\text{SF}_5^- + \text{F}$  by thermal electron attachment [6–8, 10], some completing investigations using an ordinary Ca or Sr atomic beam are described and discussed in the following.

## Apparatus

The experiments were performed using a one-chamber device which has been described in [11]. The atomic beam from a stainless steel oven entered the reaction chamber into which the gas was introduced by a capillary in front of the orifice of the oven. The gas pressure in the chamber could be varied from  $1-20 \times 10^{-1}$  Pa. The spectrometer and the registration device have been described as well. It is important to consider that in a one-chamber apparatus secondary reactions can participate in the chemiluminescence in a more profound way as in a two-chamber device which is more suitable to study the single impact processes.

## Results

An overview spectrum of the reaction  $\text{Ca} + \text{SF}_6$  in the visible region showed the CaF-bands of the  $A-X$ - and  $B-X$ -systems, as well as some lines of Ca, particularly those from the metastable state  $4^3\text{P}$ .

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The MF-band structures were comparable to those observed by Menzinger [12] from the reaction  $\text{Ca} + \text{F}_2$ . It is known that the potential curves of the MF-molecules have nearly the same position of the minima in the ground and in the electronically excited states [13], so that sequences with  $\Delta v = \text{const}$  appear, where  $\Delta v = 0, \pm 1$  are predominant. As for doublet states a spin separation of the  ${}^2\Pi - X^2\Sigma$ -transitions becomes visible depending on the angular momentum projection (1/2 or 3/2). Since mainly the energetically lower lying transitions of the  $A - X$ -systems are important for the energy discussion, they have been registered for  $\Delta v = 0$  with good resolution (Figure 1). The doublet structures and the different rotational branches (see Herzberg [14]) expected, as well as the appearance of the 'head of heads' [13] can be recognised. Evidently the  $A$ -system is excited to higher  $v'$ -values. However, the spectrum seems not to be well suited for a more precise determination of the  $(\text{F}-\text{SF}_5)$  dissociation energy.

The structure of the  $B - X$ -system is in accordance with the chemiluminescence spectrum given by Kiang et al. [1] from the reaction of  $\text{Ca}_m^* + \text{SF}_6$ . According to Fig. 2 an excitation of at least up to  $v' = 18$  can be established.

The spectrum from the reaction  $\text{Sr} + \text{SF}_6$  involves the  $A^2\Pi - X^2\Sigma$ -system in the visible region (Figure 3). Up to 642 nm it is in agreement with the results from Steimle et al. [2]. In so far as this part of the spectrum has been studied from  $\text{Sr} + \text{F}_2$  (Engelke [15] and Menzinger [12]) the structures presented here are of the same kind. In the 625–645 nm region the  $\Delta v = 1$ -transitions appear. The

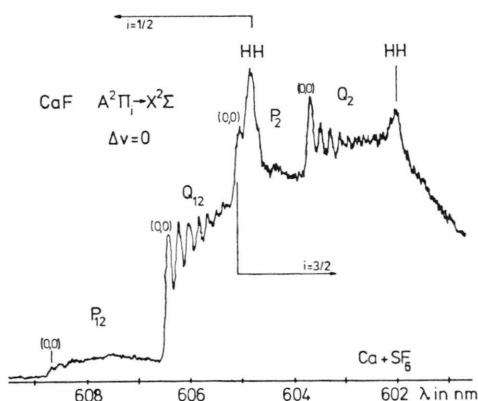


Fig. 1.  $\text{CaF} - A^2\Pi_1 - X^2\Sigma$ -band system ( $\Delta v = 0$ ) from  $\text{Ca} + \text{SF}_6$ .

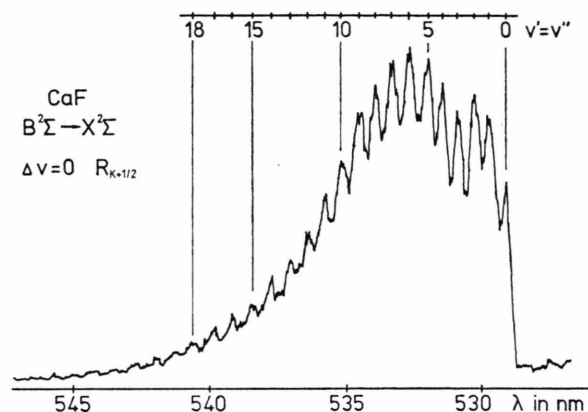


Fig. 2.  $\text{CaF} - B^2\Sigma - X^2\Sigma$ -band system ( $\Delta v = 0$ ) from  $\text{Ca} + \text{SF}_6$ .

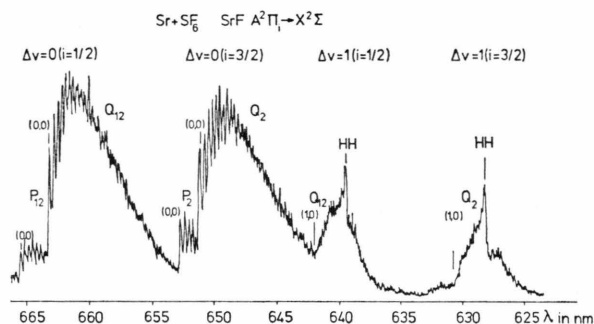


Fig. 3.  $\text{SrF} - A^2\Pi_1 - X^2\Sigma$ -band systems ( $\Delta v = 0.1$ ) from  $\text{Sr} + \text{SF}_6$ .

maxima at about 639.5 nm and 628.5 nm may be attributed to the head of heads of this sequence. But the shorter wave length parts could not be ascertained unambiguously. It is true that the intensity maximum of the  $\Delta v = 0$  ( $\Omega = 1/2$ )-bands from the  $\text{Sr} + \text{F}_2$ -reaction has been found at  $v' \approx 20$  while from the  $\text{Sr} + \text{SF}_6$ -reaction it appears at  $v' \approx 5$ , which is either a consequence of the different exothermicities of these reactions or of a different distribution of the energy on the reaction products. Finally, the analysis of the spectrum shows the excitation of the  $A$ -system up to  $v' = 30$ .

The bands of the  $B - X$ -system registered here are in accordance with the observations of Steimle [2], Menzinger [12] and Kiang [1]. The analysis of the spectrum (Fig. 4) shows the excitation of the  $B$ -system beyond  $v' = 21$ . The  $C - X$ -spectrum which was observed by Kiang [1] and used to determine  $D_0(\text{F}-\text{SF}_5)$  did not appear here.

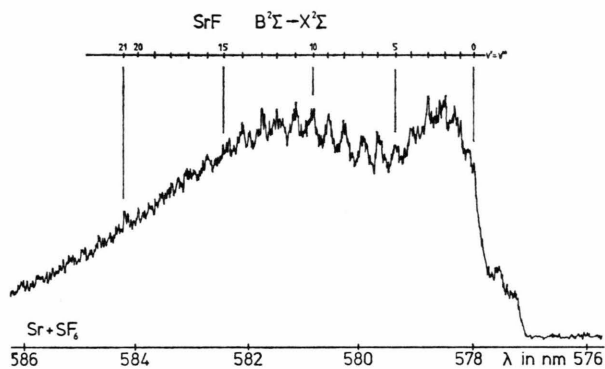
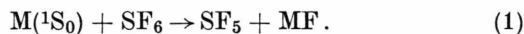


Fig. 4. SrF- $B^2\Sigma-X^2\Sigma$ -band system ( $\Delta v=0$ ) from Sr+SF<sub>6</sub>.

## Discussion

The experiments performed here are to be discussed considering the energy balance of the reactions and the dissociation energy of SF<sub>6</sub>. As pointed out above it will not be sufficient to explain the emission observed in the visible region starting with ground state atoms (<sup>1</sup>S<sub>0</sub>) according to



Neglecting inner and kinetic energy of the reactants and an excitation energy of SF<sub>5</sub> the maximum excitation energy  $E_1$  of the product molecule MF can be ascertained from

$$D_0(F-SF_5) = D(M-F) - E_1(MF), \quad (2)$$

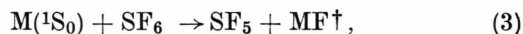
in so far as abundant MF-molecules are produced with the total exothermicity in form of inner excitation energy. The values for  $D(M-F)$  can be taken from Engelke [15]. For the determination of the maximal excitation of the MF-molecules, the  $B-X$ -spectra are best suited while the  $A-X$ -

bands give only an estimate in the Sr+SF<sub>6</sub> case. The  $C-X$ -system appeared only with Ba+SF<sub>6</sub> in the present experiments.

In Table 1, the systems selected, some atomic lines and the highest  $v'$ ,  $v''$ -transitions observed in the  $\Delta v=0$ -bands are given. In Table 2, the upper limits of  $E_1$  and values of  $D_0(F-SF_5)$  derived herefrom are presented.

As can be seen, the values for  $D_0$  differ markedly between each other, and they are not in agreement with the older values given in the literature. Evidently it is not suitable to explain the molecular bands from the reaction (1). It must consequently be suggested that the chemiluminescence is produced by the atoms in their excited states. With regard to the fact that in all the spectra the atomic lines from the metastable atomic states appear with considerable intensity, a decisive participation of the metastable atoms can be expected. The energy balance then has to be completed by the energy of these states. In this way, the experimental situation is that which has been brought about by Kiang *et al.* [1], who started their experiment by at first deliberately producing metastable alkaline earth atoms which subsequently were definitely responsible for the reactions. With this assumption, the energies  $E_1$  derived from the  $v'$ ,  $v''$ -transitions given in Table 1 yield the upper limit of  $D_0(F-SF_5)$  given in the last column of Table 2. Within the limits of the accuracy of the analysis of the presented spectra the value is in good agreement with that originally given by Kiang *et al.*

The mechanism of the reactions starting with an ordinary Ca or Sr atomic beam can be supposed to occur in the following way

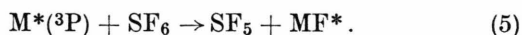
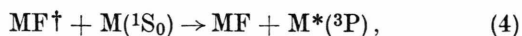


Reaction	MF-systems	$\Delta v = 0$ ( $v'$ , $v''$ ) <sub>max</sub>	Lines observed	$T_e$ cm <sup>-1</sup>
Ca + SF <sub>6</sub>	$A^2\Pi_{1/2} - X^2\Sigma$ ( $\Delta v = 0, \pm 1$ )	—	4 <sup>1</sup> P-4 <sup>1</sup> S	16483.0
	$A^2\Pi_{3/2} - X^2\Sigma$ ( $\Delta v = 0, \pm 1$ )	—	5 <sup>1</sup> P-3 <sup>1</sup> D	16558.0
	$B^2\Sigma - X^2\Sigma$ ( $\Delta v = 0$ )	(18, 18) ± 2	4 <sup>3</sup> P-4 <sup>1</sup> S (metastable; $E(M^*) = 1.9$ eV)	18857.5
Sr + SF <sub>6</sub>	$A^2\Pi_{1/2} - X^2\Sigma$ ( $\Delta v = 0, \pm 1$ )	ca. (30, 30)	5 <sup>1</sup> P-5 <sup>1</sup> S	15071.6
	$A^2\Pi_{3/2} - X^2\Sigma$ ( $\Delta v = 0, \pm 1$ )	ca. (30, 30)	5 <sup>3</sup> P-5 <sup>1</sup> S (metastable; $E(M^*) = 1.8$ eV)	15352.0
	$B^2\Sigma - X^2\Sigma$ ( $\Delta v = 0$ )	ca. (21, 21) ± 2		17303.4

Table 1. Molecular and atomic emission from the reaction of Ca and Sr with SF<sub>6</sub>.

Table 2. Upper limits of  $D_0(\text{F-SF}_5)$ .

	$D(\text{M-F})$ eV [15]	$E_i(\text{MF})$ eV obs. (Tabl. 1)	$D_0(\text{F-SF}_5)$ eV from $\text{M}(^1\text{S})$ - reactions	$D_0(\text{F-SF}_5)$ eV from $\text{M}^*(^3\text{P})$ - reactions
Ca	5.42	3.52	1.9	3.8
Sr	5.49	3.32	2.17	3.97



In the primary reaction (3) the MF-molecules are produced, but the exothermicity is too low to explain the emission observed. Even using the older lower values for  $D_0(\text{F-SF}_5)$  the  $B$ -states cannot be reached at all. The MF-molecules from (3) can eventually only be excited vibrationally in their electronic ground state.

But by the reaction (4) these molecules can in a secondary reaction produce metastable M atoms by  $v-e$ -transfer. These atoms have a comparably long life time ( $\tau \approx 10^{-5}$  s according to [16, 17]) and can therefore be suggested to be responsible for the reaction (5). To confirm this suggestion the inten-

sity of the molecular bands and that of the metastable Ca-line were measured as a function of the SF<sub>6</sub> pressure in the chamber [18]. For this experiment the  $v', v'' = (7.7)$  transition of the CaF-BX-system was selected. The result of the investigation is shown in Figure 5. As is seen, the intensity of the metastable line increases linearly with the SF<sub>6</sub> gas pressure while that of the bands reflects a much stronger increase. This result can be interpreted in favour of the mechanism given above by the reactions (4) and (5).

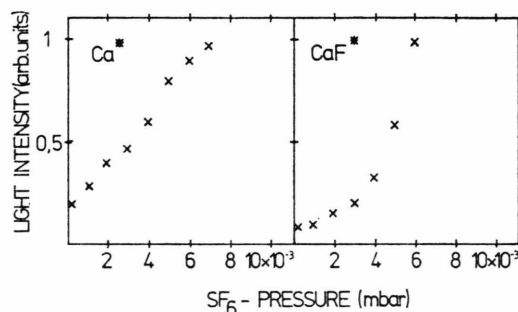


Fig. 5. Dependence of the intensities of the metastable Ca-line 43P and that of the CaF  $v', v'' = 7.7 - B - X$ -transition on SF<sub>6</sub> gas pressure in the reaction chamber.

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