

## REACTION CROSS SECTIONS OF Ca ( $4^1S$ , $4^3P$ AND $3^1D$ STATES) WITH HALOGENATED COMPOUNDS AND WATER<sup>§</sup>

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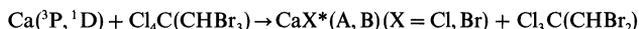
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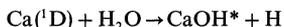
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By using two independent and different methods, absolute values of the reaction cross-sections have been determined for the following chemiluminescent reactions



and



Both chemiluminescence and laser-induced fluorescence spectra are reported. A comparison with related types of reactions is also presented.

### INTRODUCTION

The reactivity of calcium atom with halogenated compounds has been studied by many authors.<sup>1–15</sup> These works include ground state Ca( $^1S$ ) and metastable states Ca\* ( $^3P$  and  $^1D$ ) with pure halogens and organic compounds, in cell and beam conditions, by monitoring Chemiluminescence and Laser Induced Fluorescence (L.I.F.). Recently oxidation reactions involving excited alkaline-earth atoms with organic compounds, such as alcohols, ketones, etc., have opened the possibility of studying chemiluminescent processes associated to the monohydroxide and monoalkoxide products.<sup>1,9,15</sup> On the other hand, Parson *et al.*,<sup>8,9</sup> have studied the reaction dynamics of Ca( $^1S_0$ ,  $^3P_1$ ) with some peroxide type molecules under single collision

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conditions. They found different reaction products depending upon the electronic state of the Ca atom. A good example of this different dynamical behavior is that of the  $\text{Ca}^* + \text{H}_2\text{O}_2$  reaction,<sup>8</sup> in which it was found that whereas the metastable  $\text{Ca}(^3\text{P})$  reaction produces excited  $\text{CaOH}$ , the ground state Ca reaction yields predominantly  $\text{CaO}$  emission. Quantitative data on these excited reactions are not only important, but also necessary to test modern theoretical treatments on reactive collisions so we report here measurements made by above mentioned two techniques, on cross sections and branching ratios for the different exit channels leading to the formation of the  $\text{CaX}$  product (respectively  $\text{CaCl}$ ,  $\text{CaBr}$ , and  $\text{CaI}$ ) in ground and first electronically excited states. Reaction cross-section data of the  $\text{Ca}(^1\text{D}_2) + \text{H}_2\text{O}$  system is also reported.

## EXPERIMENTAL

The experimental apparatus is a Broida oven already described in details.<sup>16</sup> The Calcium vapor formed in a furnace is entrained with helium by a fast pumping toward the reaction zone Z. By setting a D.C. discharge in the furnace, it can be excited and the fast pumping allows atoms in metastable states  $^3\text{P}$  and  $^1\text{D}$  to be present in Z. The absolute concentration of these species have been measured by a procedure which is shortly described below and their relative concentration could be varied by changing parameters (pression, temperature, discharge current) whose influence is described in ref.<sup>17</sup> The chemiluminescence spectra are taken with a monochromator Bausch & Lomb (0.6 m focal length). The L.I.F. is obtained with a home-made dye laser, pumped by a B.M.Industrie YAG laser (30 Hz, 200mJ at 532 nm, 10 ns pulse duration), and observed through the Bausch & Lomb monochromator with large slits used as a filter. Standard microcomputer equipment is used to record and data analysis.

The results obtained on both chemiluminescence and laser induced fluorescence are comparable to those obtained in single collision conditions. Indeed, a comparison made on the  $\text{Mg} + \text{Cl}_2$  system between beam-gas and bulk conditions has shown that the effect of the carrier gas (at a few torr) in a Broida oven is to thermalise the rotational population, with no detectable effect on vibrational and electronic energy distribution of the  $\text{A}^2\Pi\text{-X}^2\Sigma^+$ -transition.<sup>18</sup> A lifetime measurement of the 0-0 band of this transition in  $\text{CaCl}$  showed no He pressure dependence in the range of pressure used, and gave 30ns, which is in very good agreement to the already published values.<sup>19</sup> As the concentration of reactive species are the same order of magnitude in both experiments, and as the radiative lifetime are short (see comments of the Fig. 3 below), this is not surprising.

The absolute concentration of reactant ( $\text{Ca}^3\text{P}$ ),  $\text{Ca}(^1\text{D})$  and product ( $\text{CaX}$ ,  $\text{CaOH}$ ) were measured, by comparing their fluorescence desexcitation with the emission of a quartz tungsten halogen lamp (Oriol n°6332), whose calibration was made from the NIST traceable calibrated quartz tungsten halogen lamp (type .6315 FEL 1000). By measuring the efficiency of our light detection system-solid angle of the collected light through the focusing lens-, we were able to determine, in addition, an absolute value of the cross section involved in the reaction forming  $\text{CaOH}$ . Another method based on the variation of the fluorescence intensity with the organic reactant concentration was also used to determine the absolute cross section of  $\text{CaBr}$  formation.

**Table 1** Experimental conditions.

Heating ( $w$ )		300–350
Discharge current (mA)		0–120
Partial pressure (torr)	Helium	2–10
	Ca( $4^1S$ )	$\approx 3.10^{-4}$
	Ca( $4^3P$ )	$\approx 5.8.10^{-8}$
	Ca( $4^1D$ )	$\approx 5.8.10^{-10}$
	H <sub>2</sub> O	$\approx 5.1.10^{-8}$
	CCl <sub>4</sub>	$\approx 2.6.10^{-7}$
	CHBr <sub>3</sub>	$\approx 3.10^{-7}$

Table 1 lists the most relevant experimental conditions and parameters of the present experiments.

## RESULTS AND DISCUSSION

The observed chemiluminescences are due to the transitions  $A^2\Pi-X^2\Sigma^+$  and  $B^2\Sigma^+-X^2\Sigma^+$  of the CaX radical, and of the A-X transition of CaOH. For the three halogenated compounds, energy conservation precludes ground state Ca  $4^1S$  to give chemiluminescence : we have determined the cross section and the branching ratio of the formation of the A and B states, from the two metastable states  $^3P$  and  $^1D$ . For H<sub>2</sub>O, only the  $^1D$  state is involved.

### CaOH

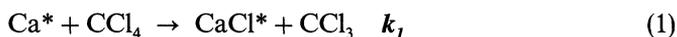
We have used results obtained on CaCl chemiluminescence already published<sup>10</sup> and summed up here; namely:

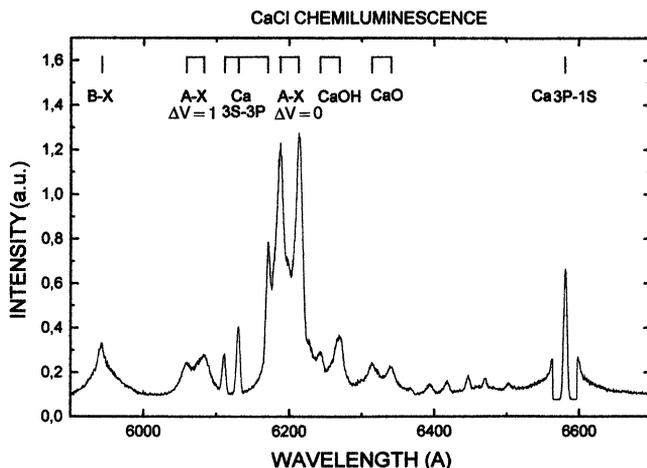
- (a) the cross sections of the A and B formation in the reactive collision  $Ca^* + CCl_4 \rightarrow CaCl(A,B)$  where  $Ca^*$  represents Ca( $^3P$ ) or Ca( $^1D$ ), have the following values and

$$\sigma(^3P) = 0.25 \text{ \AA}^2 \text{ and } \sigma(^1D) = 1.77 \text{ \AA}^2.$$

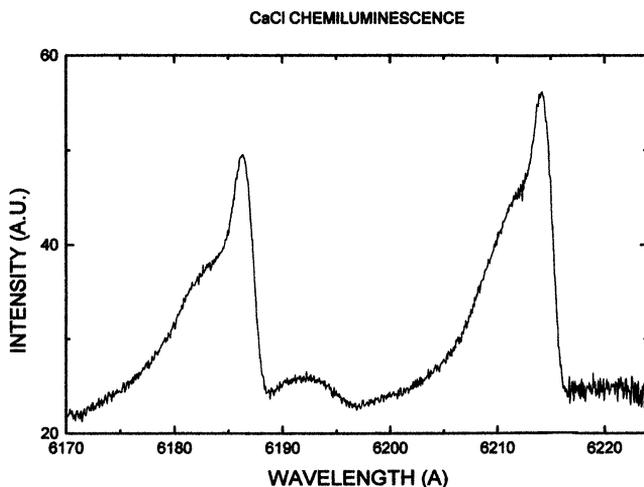
- (b) the branching ratio of the A/B CaCl states formation follows the  $^3P/^1D$  concentration, indicating that the B state is preferentially formed by the  $^1D$  state, in agreement with the energy scale and with adiabatic correlation rules.

Figure 1 shows the chemiluminescence of CaCl obtained with CCl<sub>4</sub> and H<sub>2</sub>O as reactants, where one can see the CaCl(A-X and B-X transitions), and CaOH(A-X transition) bands. L.I.F. experiments show that actually CaCl is formed even in the presence of water, but mainly in the ground state (see below). So, essentially the following processes are taking place:





**Figure 1a** Low resolution chemiluminescence spectrum of CaCl and CaOH obtained by  $\text{Ca}^* + \text{CCl}_4$ ,  $\text{H}_2\text{O}$  reactions. The  $^3\text{P}-^1\text{S}$  transition at 653 nm has been attenuated.  $\text{A}^2\Pi-\text{X}^2\Sigma^+$  and  $\text{B}^2\Sigma^+-\text{X}^2\Sigma^+$  of CaCl, and  $\text{A}^2\Pi-\text{X}^2\Sigma^+$  transitions of CaOH are observed, together with some bands of CaO, and triplet transitions of Ca at 610–616 nm.



**Figure 1b** The  $\text{A}^2\Pi-\text{X}^2\Sigma \Delta v=0$  transition of CaCl is shown at higher resolution, by using an OMA (1.15 m focal length).

Both reaction are exoergic, as the bond energy of CaCl is  $4.2 \text{ eV}^{20}$ , and the bond energy of  $\text{H}_2\text{O}$  is  $5.1 \text{ eV}^{21}$ . To get the value of the reactive cross section for the formation of CaOH (A), we write the following equations:

$$I(\text{CaCl}) = K \cdot v_r \cdot n(\text{CCl}_4) \cdot [n_D \cdot \sigma_D(\text{CaCl}) + n_p \cdot \sigma_p(\text{CaCl})]$$

$$I(\text{CaOH}) = K \cdot v_r \cdot n(\text{H}_2\text{O}) \cdot [n_D \cdot \sigma_D(\text{CaOH})]$$

where  $I(\text{CaCl})$  represents the total intensity recorded for the A-X and B-X emissions  
 $v_r$  represents the average relative velocity of the two reactants  
 $n(\text{CCl}_4)$  represents the concentration of  $\text{CCl}_4$   
 $n_D$  and  $n_P$  are the concentrations of  $^1D$  and  $^3P$  states of Ca respectively  
 $\sigma_D$  and  $\sigma_P$  are the cross sections of the two states to form  $\text{CaCl}(\text{A}, \text{B})$  respectively

$K$  is a constant, including all the geometrical and detector sensitivity factors, that has been measured. We use equivalent definitions for CaOH A-X emission.

We now take

$$v_r(\text{Ca} + \text{CCl})/v_r(\text{Ca} + \text{H}_2\text{O}) = .625 \text{ (from the experimental conditions).}$$

$$n(\text{CCl}_4)/n(\text{H}_2\text{O}) = 5 \text{ (from vapor pressure values at room temperature)}$$

$$n_P/n_D = 99 \text{ under these experimental conditions}^{17}$$

a) We form the ratio  $(1)/(2) = I(\text{CaCl})/I(\text{CaOH})$ , which is measured (by taking the integrated intensities, averaged over some spectra) to be equal to 20.9, from where we get

$$\sigma_D(\text{CaOH}) = 0.048 * 0.625 * 5 * [1.77 + 0.25 * 99] \cdot 10^{-20}, \text{ e.g.}$$

$$\sigma_D(\text{CaOH}) = 3.96 \text{ \AA}^2$$

b) We use the expression (2), by setting

$v_r = 825 \text{ m/s}$ ,  $n(\text{H}_2\text{O}) = 1.79 * 10^{15} / \text{m}^3$  (measured), and  $n_P = 2.05 * 10^{15} / \text{m}^3$  (measured), and  $I(\text{CaOH}) = 1.2 * 10^{12} \text{ hv/s}$  (measured), from where we get

$$\sigma^1D(\text{CaOH}) = 3.96 \text{ \AA}^2$$

The excellent agreement between the two values, which are obtained by independent methods, makes us confident to give the results with an uncertainty of  $\pm 5\%$

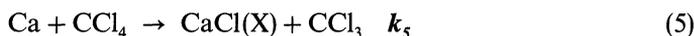
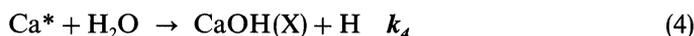
$$\sigma_D(\text{CaOH}) = 3.96 \pm .2 \text{ \AA}^2$$

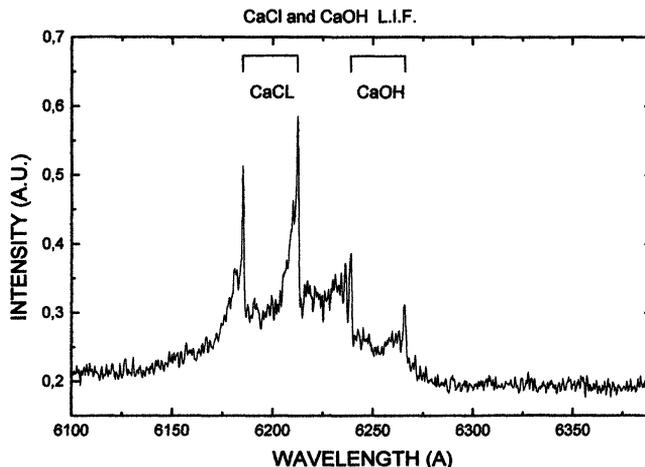
This value can be compared to that of  $6.5 \text{ \AA}^2$ , obtained by Oberlander *et al.*,<sup>8</sup> for the reaction of Ca( $^1D$ ) with  $\text{H}_2\text{O}_2$  to form CaOH(A). The difference between the two values could be explained by considering the exoergicities of the two reactions. It is likely that the more exoergic reaction shows a greater reaction cross-section.

## CaCl

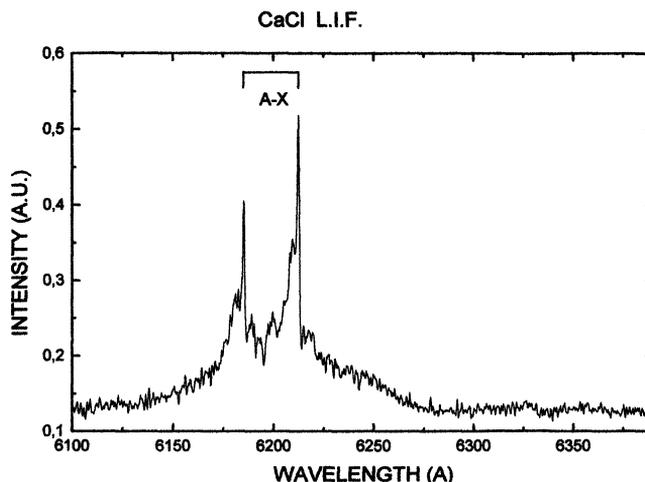
Figure 2 displays two excitation spectra obtained with the same reactant as in Figure 1. In the upper one, where Ca is excited by the discharge (which means that  $\text{Ca}4^1S$ ,  $\text{Ca}4^3P$ , and  $\text{Ca}3^1D$  are present). Both CaCl and CaOH bands are seen. In the lower one, where only Ca ground state is reacting, only CaCl bands are seen.

The reactions involved are now:





**Figure 2a** Laser Induced Fluorescence of CaCl and CaOH  $A^2\Pi^2-X^2\Sigma^+$   $\Delta v=0$  transitions, obtained by  $Ca^* + CCl_4, H_2O$  reactions.



**Figure 2b** Laser Induced Fluorescence of CaCl  $A^2\Pi-X^2\Sigma^+$   $\Delta v=0$  transition obtained from  $Ca(4^1S) + CCl_4$  reaction.

The comparison of the two spectra, which show similar intensities for CaCl signal in both cases, indicates that the CaCl X state formation is not affected by the presence of  $H_2O$ . It must be mentioned that both CaCl(X) and CaOH(X) are also formed by cascading from A and B states formed by reactions 1 and 2. The measured ratio of the intensities (obtained by the measurements of the surfaces, averaged over some spectra) of the two CaCl induced fluorescence gives

$$r = I_{CaCl}(\text{reaction } 1 + 3 + 5) / I_{CaCl}(\text{reaction } 5) = 1.08$$

We have included reaction (1) which, by cascading populates CaCl ground state. We then write

$$r = [(k_1 + k_3) * Ca^* + k_5 * (Ca - Ca^*)] / (k_5 * Ca) \quad (6)$$

As  $Ca^*$ , which represents here  $Ca(3P)$  only, is measured to be  $2.10^{-4}$  of  $Ca$ , one can make the approximation  $Ca - Ca^* \sim Ca$ , which gives

$$k_5 = (.02/8) * (k_1 + k_3) \quad (7)$$

If we estimate the cross section of the reaction (3) to be between 1 and  $10 \text{ \AA}^2$ , that implies that *the cross section of the reaction (5) is between .003 and .03 \AA}^2*.

The cross sections of the formation of A and B states are calculated by the following way:

The ratio of the intensities of the B-X to A-X has been measured.<sup>10</sup>

$$I(B-X)/I(A-X) = .15 = \sigma(^1D)\{B-X\} / [\sigma_D(A-X) + \sigma_p(A-X)] \quad (8)$$

We know that  $\sigma^3P(A-X) = .25 \text{ \AA}^2$  and

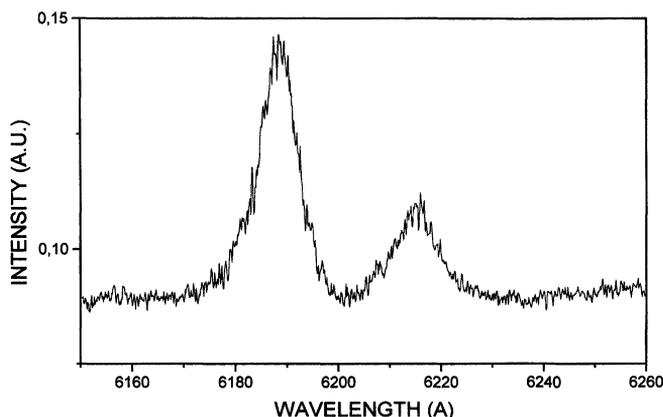
$$\sigma_D(A-X) + \sigma_D(B-X) = 1.77 \text{ \AA}^2 \quad (9)$$

It is easy to deduce from these three equations that

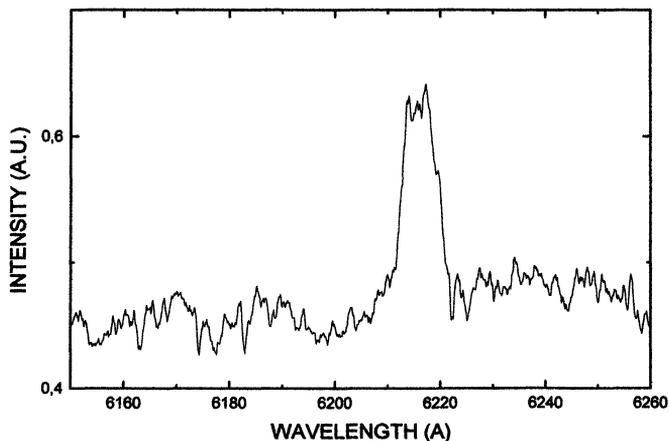
$$\sigma_D(A-X) = 1.50 \text{ \AA}^2$$

$$\sigma_D(B-X) = .27 \text{ \AA}^2$$

In Figure 3 are shown results obtained when the fluorescence induced by laser is dispersed by the monochromator: on the upper spectrum the laser wavelength was set at the maximum of the  $A^2\Pi_{3/2} - X^2\Sigma^+$  at 6185.4 \AA; on the lower spectrum, the laser wavelength was set on the maximum of the  $A^2\Pi_{1/2} - X^2\Sigma^+$  at 6212.7 \AA. One can see in the first one the two components of the A state, the first being pumped by the laser, and the second being excited by energy transfer or by intramolecular relaxation. In

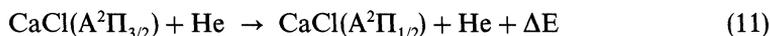


**Figure 3a** Signal observed by the monochromator when only the  $A^2\Pi_{3/2} - X^2\Sigma^+ \Delta v = 0$  transition is excited by the laser.



**Figure 3b** CaCl  $A^2\Pi_{1/2}-X^2\Sigma^+ \Delta v=0$  transition observed by the monochromator when only the  $A^2\Pi_{1/2}-X^2\Sigma^+ \Delta v=0$  transition is excited by the laser (see text).

the second there is only the  $A_{1/2}$  component, as predicted by energy considerations. If one takes the radiative lifetime of the A state  $\tau = 33$  ns,<sup>19</sup> the probability of energy transfer cannot be very large as the two following processes must be considered:

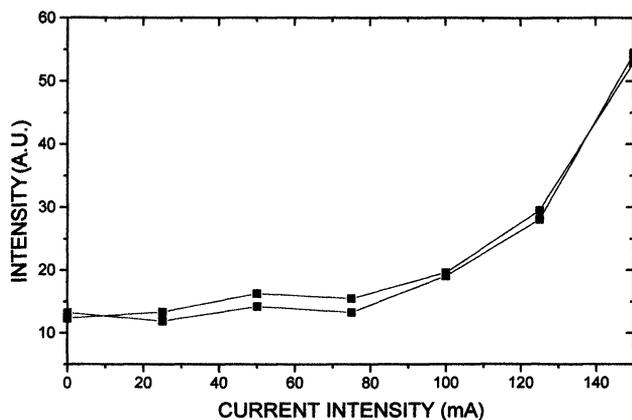


For the first process, where M represents any atomic (Ca, Ca\*) or molecular (CCl<sub>4</sub>, CaCl) species, the M concentration is of the order of 10<sup>16</sup>/m<sup>3</sup>, and the cross section would be unrealistically large. For the second process, as He pressure is of the order of 1 torr, the calculated cross section would be ca. 160 Å<sup>2</sup>, which seems too large. In that case the energy balance involves only  $\Delta E = 70$  cm<sup>-1</sup> for similar rovibrational levels, and in any case this observation implies that the intensity of the  $A^2\Pi_{1/2} - X^2\Sigma^+$  transition is always increased by transfer from the  $A^2\Pi_{3/2}$  component. One can conclude that there is certainly an intramolecular conversion from the  $A^2\Pi_{3/2}$  to the  $A^2\Pi_{1/2}$  component.

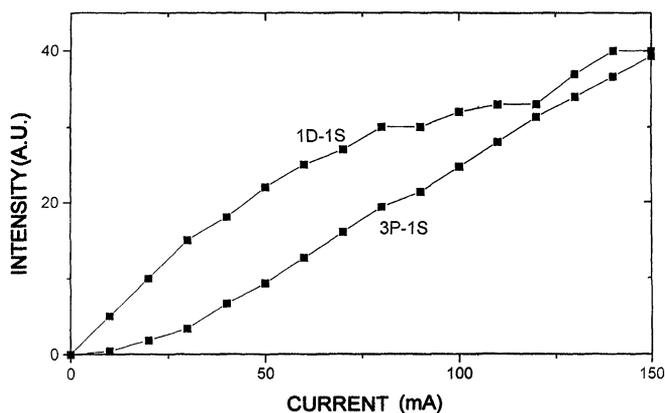
Figure 4 displays the variation of the  $A^2\Pi_{3/2}-X$  and  $A^2\Pi_{1/2}-X$  intensities, excited by the laser light, with the discharge current  $i$ . The sharp increase of both intensities when  $i$  reaches 75 mA is indicative of an increasing of the *direct formation of the X state*, as the chemiluminescence, which reflects the direct formation of the excited states, does not show this variation at all. The increase can be attributed to the opening of the channel:



whose cross section has been estimated to be about 300 times higher than the channel (5) (see above), as the concentration of the <sup>3</sup>P state increases with the current in these experimental conditions (see Fig. 5).



**Figure 4** Intensity dependence (arbitrary units) of the CaCl  $A^2\Pi_{1/2}-X^2\Sigma^+$  and  $A^2\Pi_{3/2}-X^2\Sigma^+$   $\Delta v = 0$  transitions with the current of the discharge which produces the metastable states of Ca.

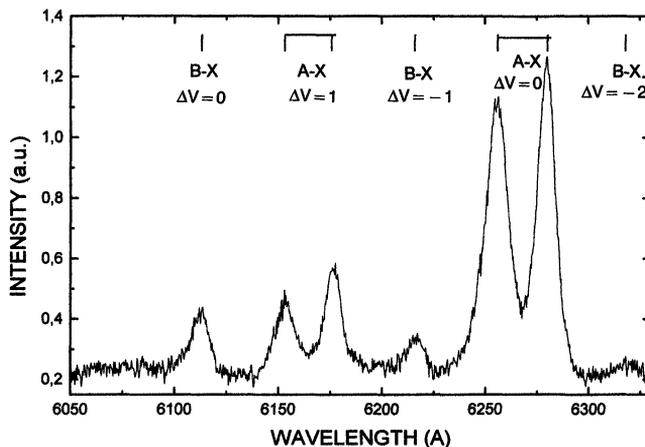


**Figure 5** Intensity dependence (arbitrary units) of Ca transitions  $3P-1S$  at 653nm and  $1D-1S$  at 457 nm, with the discharge current. The intensity of the atomic transitions have been set on the same scale for convenience.

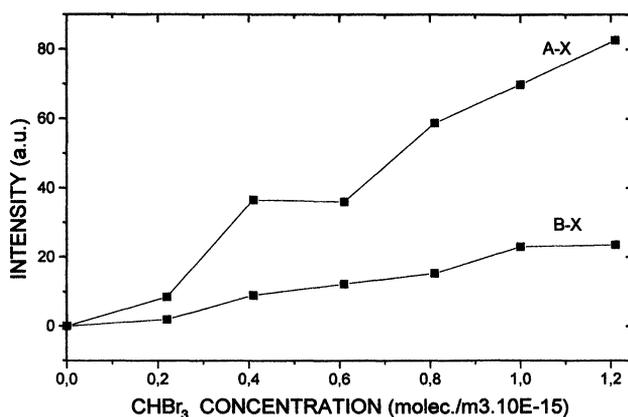
## CaBr

### DETERMINATION OF CROSS SECTIONS

As for CaCl, we have determined the cross sections and the branching ratio of the formation of the A and B states of CaBr. Figure 6 displays a typical spectrum of CaBr chemiluminescence obtained by reaction of  $Ca^*$  with  $CHBr_3$ . One can see the  $A_{3/2}-X$  and the  $A_{1/2}-X$   $\Delta v = 0$  and  $\Delta v = 1$  transitions, and the B-X  $\Delta v = 0, -1, -2$  transitions.



**Figure 6** Chemiluminescence spectra of the CaBr obtained with the  $\text{Ca}^* + \text{CHBr}_3$  reaction. The  $\text{A}^2\Pi - \text{X}^2\Sigma^+ \Delta v = 0, +1$  transitions are observed, together with the  $\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+ \Delta v = 0, -1, -2$  transitions.



**Figure 7** Variation of CaBr  $\text{A}^2\Pi - \text{X}^2\Sigma^+ \Delta v = 0$  and  $\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+ \Delta v = 0$  chemiluminescence intensities (a.u.) with  $\text{CHBr}_3$  concentration.

Figure 7 shows the variation of the intensities of these transitions ( $\Delta v = 0$ ) with the organic reactant concentration. The plot is linear, and the intensity of A-X emission is 3.2 times that of the B-X emission. This result is used in the following calculation:

Let  $I(\text{AX})$  be the intensity of the total A-X transition

$$I(\text{AX}) = K \cdot n(\text{RX}) \cdot v_r \cdot [n_D \cdot \sigma_D + n_P \cdot \sigma_P] \quad (12)$$

The slope of the variation

$$I(\text{AX})/n(\text{RX}) = a = K \cdot v_r \cdot [n_D \cdot \sigma_D + n_P \cdot \sigma_P] \quad (13)$$

depends of the products. Thus, for CaBr one can write:

$$a(\text{CaBr}) = K \cdot v_r \cdot [n_D \cdot \sigma_D(\text{CaBr}) + n_P \cdot \sigma_P(\text{CaBr})] \quad (14)$$

$$a(\text{CaBr})/n^1\text{D} = K \cdot v_r \cdot [\sigma_D(\text{CaBr}) + (n_P/n_D) \cdot \sigma_P(\text{CaBr})] \quad (15)$$

$$a(\text{CaCl})/n^1\text{D} = K \cdot v_r \cdot [\sigma_D(\text{CaCl}) + (n_P/n_D) \cdot \sigma_P(\text{CaCl})] \quad (16)$$

$$a(\text{CaBr})/a(\text{CaCl}) = v_r \cdot (\text{Ca} + \text{CHBr}_3)/v_r(\text{CaCCl}_4) \cdot [\sigma_D(\text{CaBr}) + (n_P/n_D) \cdot \sigma_P(\text{CaBr})] / [\sigma_D(\text{CaCl}) + (n_P/n_D) \cdot \sigma_P(\text{CaCl})] \quad (17)$$

As we have  $v_r'/v_r = 1.09$ , from the values of  $\sigma_D(\text{CaCl}) = 1.77 \text{ \AA}^2$  and  $\sigma_P(\text{CaCl}) = .25 \text{ \AA}^2$ , we can deduce from the measured slopes ( $7.2 \cdot 10^{-15}$  and  $7.5 \cdot 10^{-15}$  respectively) the relation

$$\sigma_D(\text{A-X}) + 100 \cdot \sigma_P(\text{A-X}) = 23.58 \text{ \AA}^2$$

for the formation of CaBr A state. This result implies that these two cross sections are similar to those obtained for CaCl, with  $\sigma_P(\text{CaBr})$  slightly lower than  $\sigma_P(\text{CaCl})$ , as its maximum value is  $.236 \text{ \AA}^2$ .

We can then write similar equations as for CaCl:

Let now  $I'(\text{B-X})$  be the intensity of the total B-X transition of CaBr.

$$I(\text{B-X}) = n(\text{CHBr}_3) \cdot v_r \cdot (n_D \cdot \sigma_D(\text{B-X})) \cdot K \quad (18)$$

if we assume that the B state is preferentially formed by the <sup>1</sup>D state, and

$$I(\text{B-X})/n(\text{RBr}) = v_r \cdot [n_D \cdot \sigma_D(\text{CaBr})] \cdot K \quad (19)$$

and we have a similar relation for  $I(\text{B-X})$  of CaCl. We form the ratio of the slopes measured for the two emissions, which is equal to 2.27, and we get in a similar manner as above

$$I(\text{B-X})_{\text{CaBr}}/I(\text{A-X})_{\text{CaBr}} = .31$$

which gives

$$\sigma_D(\text{A-X}) + \sigma_P(\text{A-X}) = 1.84 \text{ \AA}^2$$

From these relations one gets

$$\sigma_P(\text{A-X}) = .22 \text{ \AA}^2$$

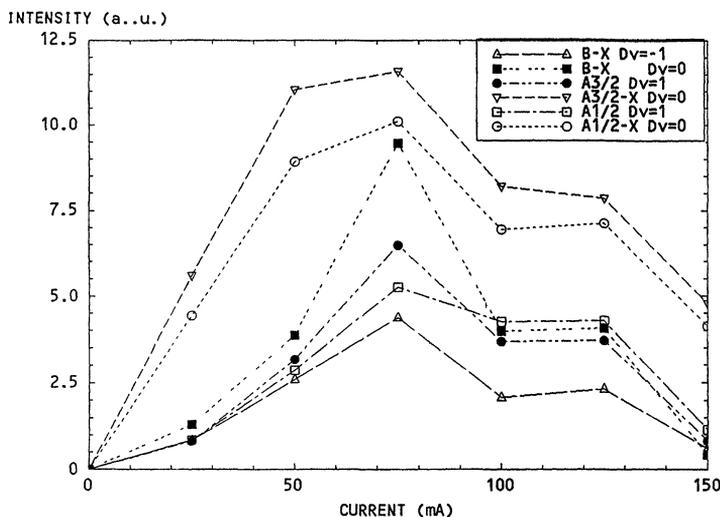
$$\sigma_D(\text{A-X}) = 1.62 \text{ \AA}^2$$

A résumé of the different values of the cross sections is given in Table 2. One can see that CaCl and CaBr have similar values, and that it was not possible to determine the value for the channels leading to ground state products.

The intensity of the A-X and B-X transitions have been recorded with different values of the discharge current which affects the <sup>1</sup>D and <sup>3</sup>P concentrations. The results are shown in Figure 8 where two observations can be made: first—the two metastable states behave in a different manner, as can be observed by comparing

**Table 2** Values of the cross sections of different channels open by the reactions Ca, Ca\* + H<sub>2</sub>O, CCl<sub>4</sub>, CHBr<sub>3</sub>.

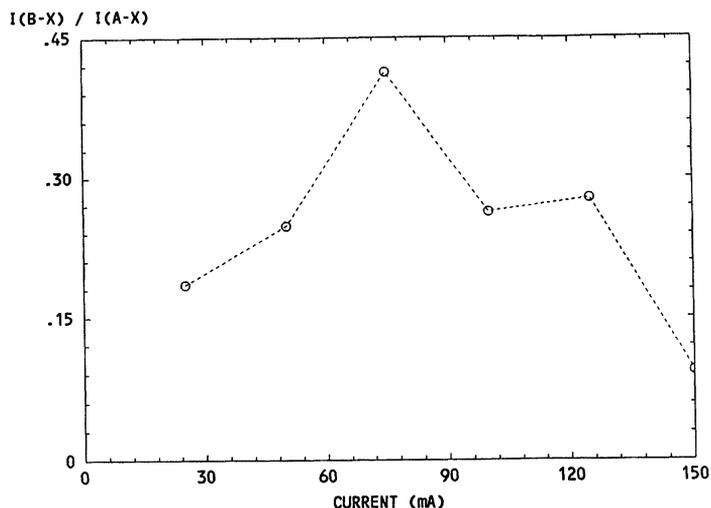
State (M-X)	X <sup>2</sup> Σ <sup>+</sup>	X <sup>2</sup> Σ <sup>+</sup>	X <sup>2</sup> Σ	A <sup>2</sup> Π	A <sup>2</sup> Π	B <sup>2</sup> Σ <sup>+</sup>	B <sup>2</sup> Σ <sup>+</sup>	A + B
State (Ca)	4 <sup>1</sup> S	4 <sup>3</sup> P	4 <sup>1</sup> D	4 <sup>3</sup> P	4 <sup>1</sup> D	4 <sup>3</sup> P	4 <sup>1</sup> D	4 <sup>1</sup> D
σ(CaOH)A <sup>2</sup>					3.96			
σ(CaCl)A <sup>2</sup>	.003 < σ			0.25	1.5		0.27	1.77
	< .03							
σ(CaBr)A <sup>2</sup>				0.22	1.62		0.57	2.19

**Figure 8** Variation of CaBr A<sup>2</sup>Π-X<sup>2</sup>Σ<sup>+</sup> Δv=0 and B<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Σ<sup>+</sup> Δv=0 chemiluminescence intensities (a.u.), and of the <sup>1</sup>D-<sup>1</sup>S at 457 nm intensities (a.u.), with discharge current.

with the Figure 5: this is essentially due to energy pooling, as is studied in details in Ref. 17; second-the A-X and B-X intensity emission reaches a maximum for  $i = 75$  mA, which is almost the same for the <sup>1</sup>D Ca state. As the energy pooling, which corresponds to the reaction



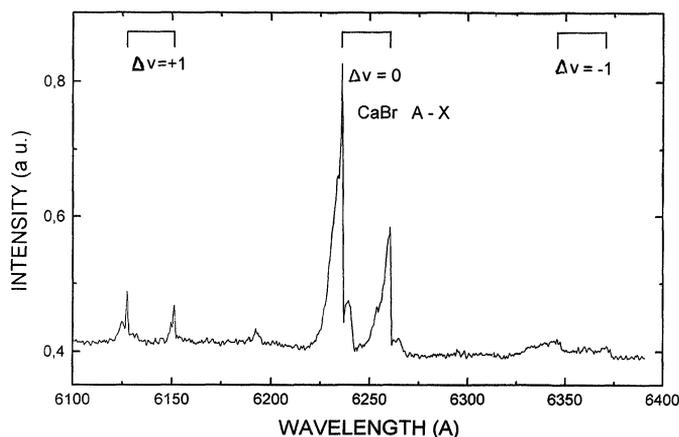
where Ca<sup>\*\*</sup> is mainly Ca(3<sup>1</sup>P) is much more efficient for Ca<sup>1</sup>D than for Ca<sup>3</sup>P<sup>22,17</sup> it is very likely that the above mentioned maximum corresponds to that <sup>3</sup>1P state which can be more reactive than the <sup>1</sup>D or <sup>3</sup>P. Figure 9 shows the variation of the B-X/A-X intensity ratio with the current: the maximum at 75 mA, which corresponds to the maximum of <sup>1</sup>D concentration, confirms the correlation between B state formation and <sup>1</sup>D state concentration already observed for CaCl.



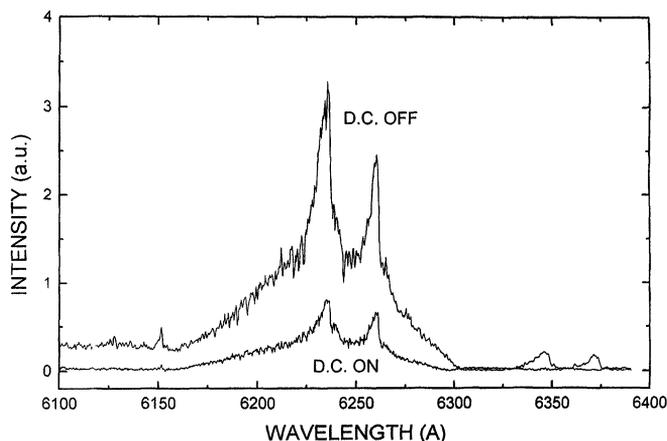
**Figure 9** Variation of the ratio A-X/B-X CaBr chemiluminescence intensities with discharge current.

## LASER INDUCED FLUORESCENCE

A typical L.I.F. spectrum is shown in Figure 10, where one can see the  $\Delta v = 0, +1, -1$  sequences of the  $\text{CaBr } A^2\Pi_{3/2} - X^2\Sigma^+$  and  $A^2\Pi_{1/2} - X^2\Sigma^+$ -transitions. The differences in intensities of the three sequences are due to the band pass of the monochromator, which was set on the  $\Delta v = 0$  region. One striking effect of the Calcium afterglow composition on the reaction products appears in Figure 11: two L.I.F. spectra are shown, the upper one being recorded without discharge (which



**Figure 10** Laser Induced Fluorescence of the  $A^2\Pi - X^2\Sigma^+$  transition of CaBr formed by the  $\text{Ca}^* + \text{CHBr}_3$  reaction.



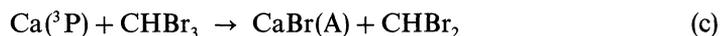
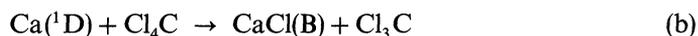
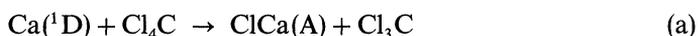
**Figure 11** Laser Induced fluorescence of the  $A^2\Pi-X^2\Sigma^+$   $\Delta v=0$  transition of CaBr, without and with discharge. The discharge decreases the intensity of the induced fluorescence (see text).

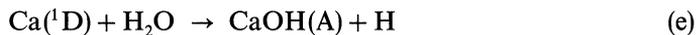
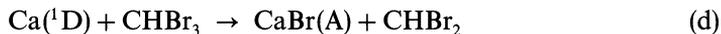
means that only ground states of atomic calcium are reacting), the lower one recorded with discharge “on” (ground and excited states reacting), but the heating was much higher than usual for both (530 W instead of 410 W, which implies a very high vapor pressure of Ca). Two remarks can be made: (i) a continuum appears in both spectra underlying the  $\Delta v=0$  sequence; (ii) a dramatic decrease of the intensity of the second appears.

The observation (i) could be the result of several effects: either a decrease of Ca atoms concentration occurs when the discharge is “on” in these special conditions, or the onset of clusters formation, or another exit channel is open leading to CaBr states which does not cascade toward the ground state, or perhaps calcium atoms in very high concentration severely quench CaBr formation. It is difficult to understand why this special high calcium pressure could open a new channel, and we have no evidence of clusters formation, so that we have no explanation at the moment of this effect, which, however, is reproducible.

## CONCLUDING REMARKS

We have determined the cross sections of the different channels leading to the two first excited states of CaCl and CaBr from the reaction of Ca( $3^1D$ ) and Ca( $4^3P$ ) with  $CCl_4$  and  $CHBr_3$ . The most interesting findings of the present work is the determination of absolute values of the reaction cross-section for several chemiluminescent reactions, namely:





whose results for  $\sigma/\text{\AA}^2$  are: 1.50; 0.27; 0.22; 1.62; 3.96 respectively.

The results are obtained using different and independent methods giving similar values, which make us confident on their validity, within an experimental errors, of the order of 10%. As it could be predicted,  $^1D$  state is more reactive than  $^3P$ , by a factor of 4 to 7. Chemiluminescence is stronger for CaBr than for CaCl, which is confirmed by the higher values of the corresponding cross sections. Laser Induced Fluorescence studies gave some information on the channels leading to the ground states, and on the rotational and vibrational temperatures, but some observations remain to be explained. Further work is now in progress using this technique as well as high-resolution chemiluminescence.

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