

## REACTION DYNAMICS OF TRANSLATIONAL AND ELECTRONIC EXCITATION IN $\text{Ca} + \text{SF}_6$ COLLISIONS†

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Relative values of the total chemiluminescence cross-section for the crossed molecular beam  $\text{Ca}^* + \text{SF}_6 \rightarrow \text{CaF}(A^2\Pi) + \text{SF}_6$  reaction have been measured as a function of collision energy. Both metastable calcium atom states  $^3P$ ,  $^1D$  were produced by low voltage dc-discharge while translational excitation of the  $\text{SF}_6$  beam was achieved via the seeding technique. Whereas chemiluminescence yield from the  $\text{CaF}(A^2\Pi)$  was observed from both of the metastable atom reactions, no chemiluminescence signal was detected from the ground atom reaction even though enough translational excitation was used to produce that excited product. By changing the discharge conditions different metastable concentrations were produced to measure the state-to-state cross-section for both  $^3P$  and  $^1D$  reactions, as a function of collision energy, up to 0.6 eV. Laser induced fluorescence of the atomic  $4s5s\ ^3S_1 \leftarrow 4s4p\ ^3P_J$  ( $J = 0,1,2$ ) lines have been measured to account for the metastable population in the  $J = 1$  level.

### INTRODUCTION

The reaction of alkaline-earth with dihalogens and other molecules has been widely studied.<sup>1-9</sup> Recently the reaction of Ca atoms with group VI hexafluorides  $\text{RF}_6$  where  $R = S, Te, W$  have attracted considerable attention.<sup>1,8-9</sup> In particular, chemiluminescence studies from  $\text{Ca}^* + \text{SF}_6$  have been reported including reactivity of selected fine (spin-orbit) structure states<sup>8</sup> and photon yield recently measured.<sup>9</sup> The  $\text{Ca}^* + \text{SF}_6 \rightarrow \text{CaF}(X) + \text{SF}_5$  reaction has recently been studied by the laser induced fluorescence technique.<sup>9b</sup> In this study a considerable vibrational but low rotational excitation for the  $\text{CaF}$  products was found as well as the absence of ground state products from the ground state reactants.

In the present work we present state-to-state cross-sections as a function of both translational and electronic excitation of the reactants. We find that ground state reaction does not produce chemiluminescence photon yields, i.e.  $\text{Ca}(^1S) + \text{SF}_6 \rightarrow \text{CaF}(A^2\Pi) + \text{SF}_5$  even though we put enough translational excitation to overcome

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the thermodynamic barrier. On the other hand both metastable atom reactions do produce CaF in its *A* state with similar cross-section at low collision energy. As the collision energy is increased beyond 0.4 eV, the electronic branching  $\sigma_{3P}/\sigma_{1D}$  ratio rises due to an enhancement of the Ca  $^3P$  reaction cross-section.

## EXPERIMENTAL

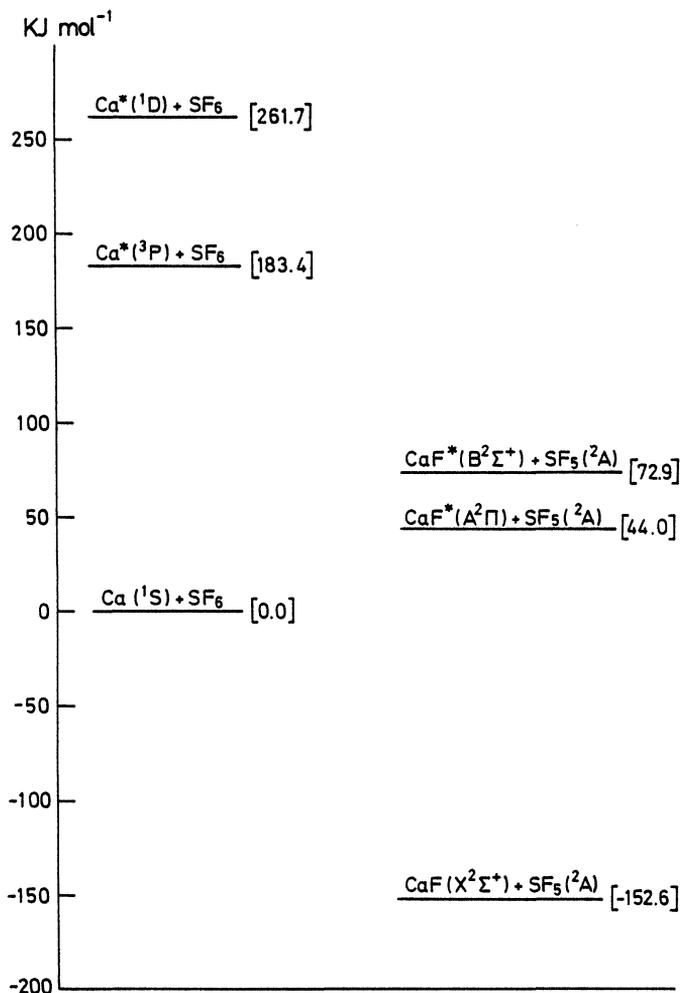
The experimental technique consisted in one of our crossed molecular beam apparatus described elsewhere<sup>1</sup> which was adapted for molecular beam chemiluminescence work. Therefore only a brief description is given here. An effusive Ca beam ( $T = 1370$  K) and a supersonic SF<sub>6</sub> beam, seeded in He at different mole fractions, were used in the present experiments. The metastable Ca\* source consisted of a stainless steel heated oven where ground state Ca atoms are excited to metastable  $^3P$  and  $^1D$  by a low-voltage dc discharge. The atomic beam crosses a modulated SF<sub>6</sub> beam which density and velocity distributions were measured by using a quadrupole mass filter and time-of-flight technique. Both the metastable and product emission intensities were measured, at the cross-beam volume, via a field lens telescope coupled to a RCA C31034 photomultiplier tube connected to a preamplifier and, then to a (phase sensitive) lock-in detector. The volume observed by the telescope used for the chemiluminescence detection was of the order of 3 mm<sup>3</sup> always less than the collision volume which was about 6–8 mm<sup>3</sup> depending upon the collision angle. Care was taken with the beams and the telescope alignment to guarantee that the observation volume was independent of the collision angle. Nevertheless by changing the nozzle stagnation pressure two experiments at 90 and 150 degrees were carried out at the same collision energy. As it is mentioned below a similar chemiluminescence yield was obtained. These results were used to normalize the data used in the excitation function determination. Under typical conditions our experiments consisted in measuring both the total and differential chemiluminescence cross-section for different (electronically excited) product channels as a function of the electronic and/or translational excitation of the reactants. To this end, in addition to the seeding technique, we have also changed the collision angle between the two beams in order to vary the translational energy of the reactants. Following the same procedure described elsewhere<sup>1</sup> the spectral response of our system was properly calibrated and several (narrow band) interference filters used to isolate the particular emission band under study. *Table 1* lists the most relevant experimental conditions for the present experiments.

## ENERGETICS

Figure 1 shows the energy levels of the product and reactant in the title reaction. Note that both chemiluminescent channels, i.e. the *A* and *B* states of the CaF are exoergic if metastable atoms are used, but endoergic for the electronic ground state. In principle, chemiluminescence can be expected by electronic excitation of the atom or by translational excitation of the reagents.

**Table 1** Typical experimental conditions

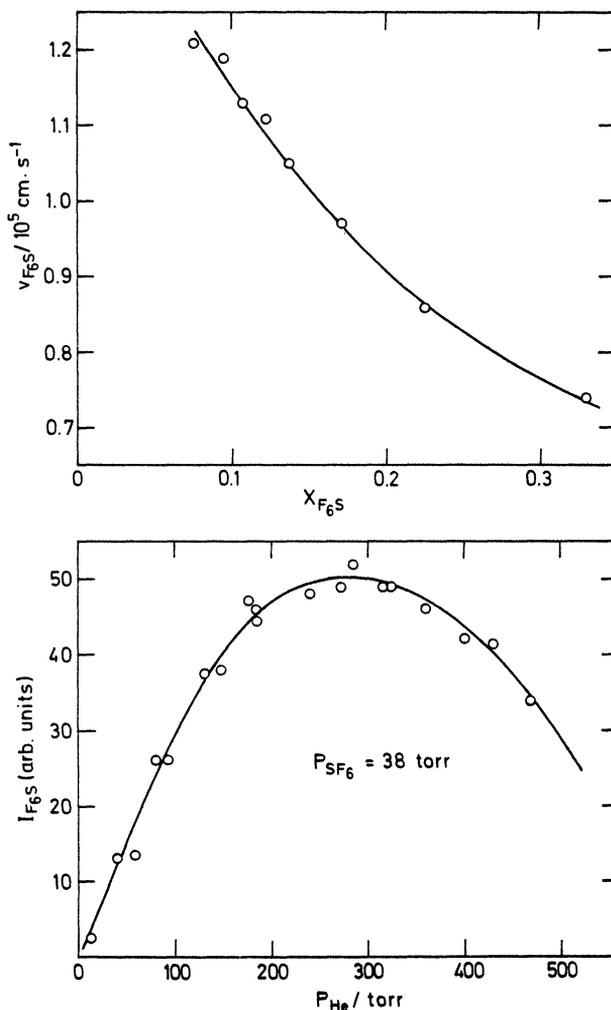
Oven temp/K	1,373
Discharge voltage/V	30
Discharge current/A	1.5
Nozzle temp/K	373

**Figure 1** Energy levels for the  $\text{Ca} + \text{SF}_6 \rightarrow \text{CaF} + \text{SF}_5$  reaction. Energy units in  $\text{KJ} \cdot \text{mol}^{-1}$ . Numbers in parenthesis are the energy of each state in the same units.

## RESULTS

A. SF<sub>6</sub> Beam Densities and Most Probable Velocities

As mentioned above we have prepared distinct SF<sub>6</sub> beams by diluting them in different ratios with He as carrier. Figure 2 (bottom) shows the SF<sub>6</sub> He seeded beam intensities, as a function of the carrier gas pressure, estimated via quadrupole mass analysis. Figure 2 (top) represents the most probable SF<sub>6</sub> beam velocities determined by the time-of-flight (TOF) technique, as a function of the SF<sub>6</sub> mole fraction. Under the experimental conditions of the present study the velocity spread of the SF<sub>6</sub> beam



**Figure 2** (Top): Most probable SF<sub>6</sub> beam velocity ( $v_{\text{mp}}$ ) versus SF<sub>6</sub>/He mole fraction in the nozzle oven. (Bottom): Experimental SF<sub>6</sub> beam densities as a function of the carrier (He) nozzle pressure. The solid lines are smooth lines drawn through the points.

$\Delta v/v$  was ca. 8%. Therefore the main source of the spread in the translational energy arises from the broad velocity distribution of the Ca\* beam. At the higher collision energy ( $E_T = 0.6$  eV) the FWHM of the relative translational distribution of the reactant turns out to be around 35%. No cluster formation of the SF<sub>6</sub> molecules was detected in the quadrupole mass spectrometer (even though we worked at low enough electron energy to preserve significantly their concentration). In addition, different runs were carried out at the same collision energy (for example 0.36 eV, 0.58 eV in Table 2) but varying the seeding mixture as well as the collision angle. No significant change was observed in the chemiluminescence yield providing that the collision energy was the same.

### B. Product Chemiluminescence and Electronic versus Translational Excitation

Different crossed beam experiments (at a fixed collision energy) were carried out for which the  $n(^1D)/n(^3P)$  ratio was modified by varying the discharge conditions. Essentially two factors were changed (a) the voltage of the discharge and (b) the oven temperature which was slightly raised over the experimental run. Keeping the oven temperature fixed around 1400 K the (voltage/V)/(current/A) of the discharge was varied from 10/0.4 to 35/1.5. In these conditions we found that the  $n(^1D)/n(^3P)$  ratio changed from 0.1 to 0.6. The product chemiluminescence was monitored as a function of both metastable emission intensities. Under our experimental conditions the two metastable contributions to the product chemiluminescence have to be considered and therefore we can write for any CaF emission intensity,  $I_{\text{CaF}}$ , the following relation

$$I_{\text{CaF}} = n_{\text{SF}_6} \bar{V}_R \left\{ \frac{I_{3p}}{A_{3p} F_{J=1}} \sigma_{3p} + \frac{I_{1D}}{A_{1D}} \sigma_{1D} \right\} \quad (1)$$

where  $I_i$ ,  $\sigma_i$ ,  $A_i$  are the particular ( $i = ^3P, ^1D$ ) metastable emission intensity, relative cross-section and atomic transition probability, respectively and  $n_{\text{SF}_6}$  and  $\bar{V}_R$  stand for the number density of the SF<sub>6</sub> and relative velocity of the reactants.  $F_{J=1}$  is the fraction of  $^3P$  in the  $J = 1$  level. Equation 1 can be rearranged as follows

$$\frac{I_{\text{CaF}}}{I_{3p}} = n_{\text{SF}_6} \bar{V}_R \left\{ \frac{\sigma_{3p}}{A_{3p} F_{J=1}} + \frac{I_{1D}}{I_{3p}} \frac{\sigma_{1D}}{A_{1D}} \right\} \quad (2)$$

Therefore a plot of  $I_{\text{CaF}}/I_{3p}$  versus  $I_{1D}/I_{3p}$  should give a straight line with a slope and intercept ratio given by

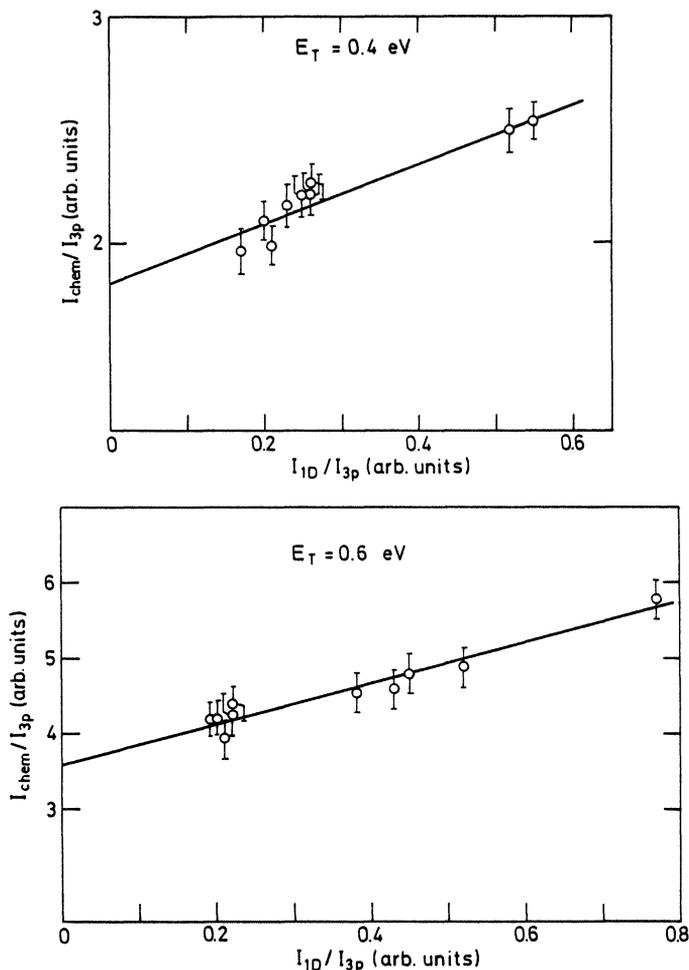
$$\text{slope/intercept} = \frac{\sigma_{1D}/A_{1D}}{\sigma_{3p}/A_{3p} \cdot F_{J=1}}$$

The branching ratio  $\sigma_{1D}/\sigma_{3p}$  could be obtained if  $A_{1D}$ ,  $A_{3p}$  and  $F_{J=1}$  are known. Figure 3 shows this type of linear plot for the chemiluminescence of the CaF(A) at two different collision energies. These results indicate that this two-state model analysis seems to be satisfactory to account for the observed chemiluminescence. From the analysis of these linear plots the collision energy dependence of the

**Table 2** Carrier gas (He) pressures of the SF<sub>6</sub> beams and collision energies including chemiluminescence intensities and cross-sections for both metastable reactions (see text and equation)

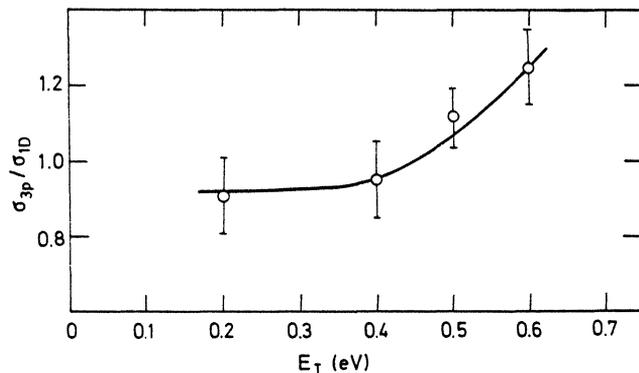
$P_{\text{He}}/\text{torr}$	$E_T/\text{eV}$	$I_{\text{chem}}/\text{a.u.}$	$I_{3p} \times 10^{-2}/\text{a.u.}$	$I_{1p}/\text{a.u.}$	$\sigma_{3p}/\text{a.u.}$	$\sigma_{1p}/\text{a.u.}$	$n_{\text{SF}_6}/\text{a.u.}$	Collision angle/degrees
282	0.58	2.78	22.57	17.40	0.98	0.82	51	
249	0.55	2.28	19.90	14.32	0.93	0.80	51	
224	0.54	2.21	19.69	14.17	0.94	0.85	50	
190	0.50	1.86	19.16	14.01	0.89	0.83	47	
165	0.48	1.59	19.32	14.40	0.84	0.81	43	
140	0.45	1.42	19.16	14.94	0.87	0.86	38	
104	0.41	0.92	18.69	14.32	0.77	0.81	30	150
86	0.39	0.73	19.16	12.63	0.72	0.77	25	
58	0.36	0.47	19.32	13.63	0.71	0.76	17	
310	0.58	3.22	22.99	23.49	1.00*	0.82	53	
274	0.57	2.28	19.06	10.78	0.98	0.82	51	
332	0.60	2.38	19.00	12.17	1.00	0.80	51	
434	0.36	0.59	7.40	17.40	0.75	0.80	40	
331	0.34	0.66	7.56	18.10	0.71	0.76	47	
251	0.31	0.53	6.56	10.40	0.72	0.78	51	
216	0.29	0.61	8.08	11.47	0.73	0.79	50	
142	0.25	0.54	8.40	11.86	0.87	0.94	39	
117	0.23	0.52	9.29	13.40	0.89	0.97	34	90
84	0.21	0.38	8.66	11.24	1.00	1.10	25	
183	0.27	0.62	8.03	10.63	0.85	0.92	46	
384	0.35	0.56	7.88	9.16	0.74	0.79	45	
425	0.36	0.59	8.40	9.78	0.77	0.82	42	
55	0.20	0.23	8.45	10.16	1.01	1.10	17	

\* All data were normalized to this value.

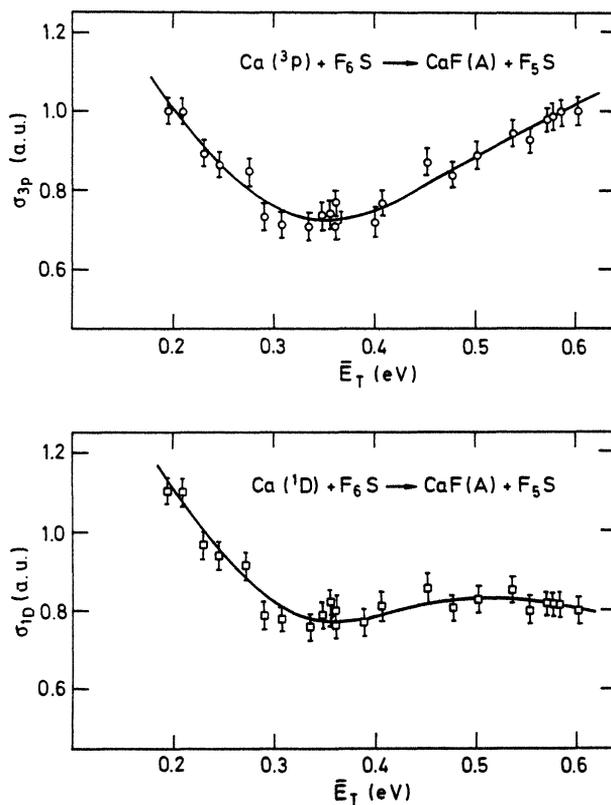


**Figure 3** Product chemiluminescence of the CaF (*A* band) reduced by the <sup>3</sup>*P* metastable emission as a function of the  $I_{1D}/I_{3p}$  ratio for the indicated collision energies.

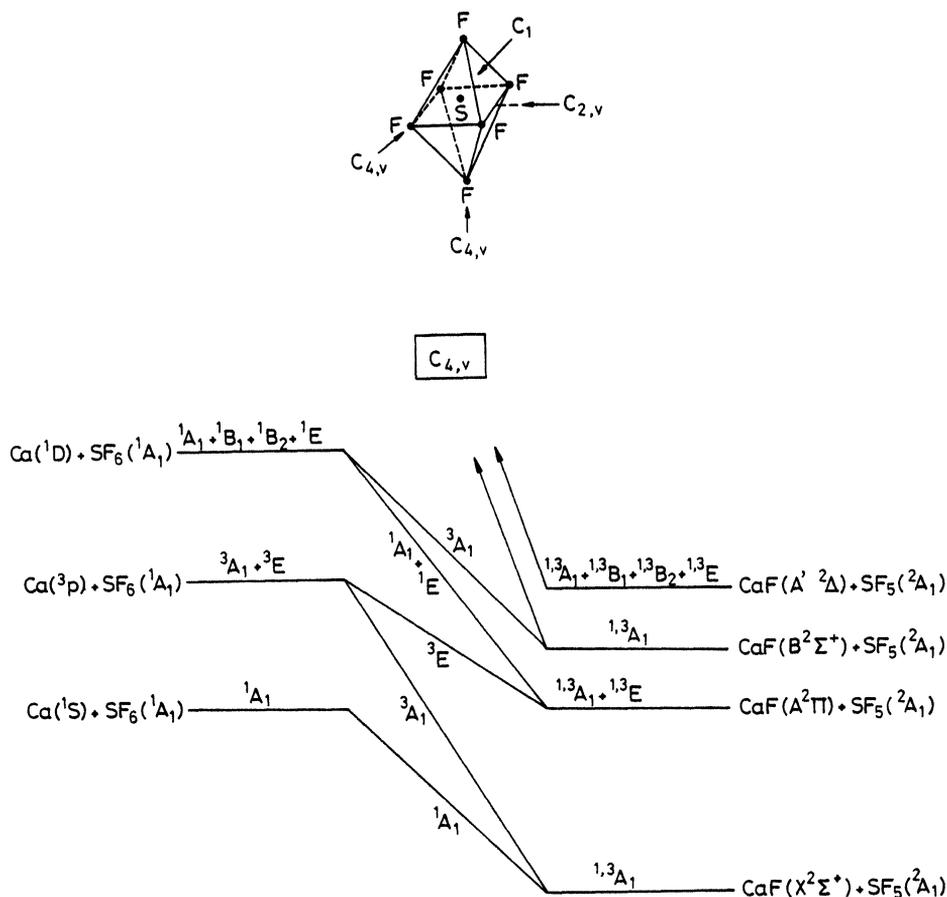
electronic branching was obtained. To this end the lifetimes of the metastable states  $\tau[\text{Ca}^*(^3P - ^1S_0)] = A_{\bar{3}^1}^{-1} = 0.44 \text{ ms}$  and  $\tau[\text{Ca}^*(^1D - ^1S)] = A_{\bar{1}^1}^{-1} = 25 \text{ ms}$  were used. These values were the average from literature values as cited in Ref. 9. In addition we have used  $F_{J=1} = 0.3$  as we have found by comparing the laser fluorescence signals of each  $4s5s^3S_1 \leftarrow 4s4p^3P^{\circ}$  line. This method has been used previously in the literature (Ref. 7) obtaining the same *J*-distribution. The result is shown in Figure 4. The knowledge of the collision energy dependence of the electronic branching ratio leads to estimate the separated (state-to-state) excitation functions for both metastable states to produce the electronically excited CaF in its *A* state. Figure 5 displays both excitation functions obtained via Eq. (1) using the data described in Table 2 as well.



**Figure 4** Branching ratio of the  $\text{Ca}(^3P) + \text{SF}_6 \rightarrow \text{CaF} + \text{SF}_5$  versus  $\text{Ca}(^1D) + \text{SF}_6 \rightarrow \text{CaF} + \text{SF}_5$ , as a function of collision energy.



**Figure 5** State-to-state excitation function for the (top)  $\text{Ca}(^3P) + \text{SF}_6 \rightarrow \text{CaF}(A) + \text{SF}_5$ ; (bottom)  $\text{Ca}(^1D) + \text{SF}_6 \rightarrow \text{CaF}(A) + \text{SF}_5$ . The reaction cross-section are in arbitrary units, but the  $\text{Ca}(^1D)$  reaction values are normalized to  $(\text{Ca}^3P) = 1$  at  $E_T = 0.2$  eV.



**Figure 6** Correlation diagram connecting the states of Ca + SF<sub>6</sub> and CaF + SF<sub>5</sub>. C<sub>4,v</sub> symmetry was assumed.

Whereas the Ca <sup>1</sup>D excitation function decreases with collision energy there is a minimum in the <sup>3</sup>P reaction around  $E_T = 0.4$  eV.

## DISCUSSION

### *Electronic Excitation*

The fact that no chemiluminescence was observed with the ground state reaction even though one excites the reactants up to 60 KJ · mol<sup>-1</sup> (i.e. well above the thermodynamic barrier) may indicate a clear example of electronic versus translational selectivity in the reaction dynamics. Figure 6 shows the adiabatic correlations for this reaction assuming C<sub>4,v</sub> symmetry which statistically is less favoured than C<sub>2,v</sub> symmetry. It should be pointed out that the low lying metastable CaF(A'<sup>2</sup>Δ) state has not yet been observed in the context of reaction dynamics, but only in a

spectroscopy study.<sup>10</sup> In fact a recent ligand field calculation<sup>10b</sup> of the electronic states of calcium monohalides predicted that the  $A'^2\Delta$  state should lie slightly above the  $B^2\Sigma^+$  state in CaF. Accordingly the ground state reaction correlates through the  $^1A_1$  surface to the ground state products. With respect to the excited  $^3P$  and  $^1D$  reactions it is interesting to note that the  $A'^2\Delta$  does not correlate adiabatically with both metastable reactions. These may lead adiabatically the excited CaF in the  $A$  state, however the  $^1D$  state may also give the excited  $B$  state as well.

We could also assume the  $C_{2,v}$  group to describe the Ca atom attack through the middle of the central plane of the SF<sub>6</sub> molecule as shown in Figure 6. In this case, as in the previous one, both metastable reactions can lead adiabatically the excited  $A^2\Pi$  state. Finally within the  $C_1$  group of symmetry, the more statistically preferred, only the excited reactants in their  $^1D$  state correlate with the  $A^2\Pi$  state. In summary both types of attack i.e. those described by the  $C_{4,v}$  or the  $C_{2,v}$  group of symmetry are more consistent with the observation of a similar chemiluminescence cross-section for the  $A^2\Pi$  state production than the  $C_1$  group of symmetry description.

It is difficult to rationalize the present results, showing a similar cross-section for both  $^3P$  and  $^1D$  reactions, with those of a previous beam-gas study,<sup>1</sup> at lower collision ( $E_T = 0.12$  eV) energy and probably carried out at different experimental conditions, where a preferred reactivity of the  $^3P$  versus the  $^1D$  state was found. A possible explanation of the different electronic dependence of the chemiluminescence cross-section found in the beam gas study of [1], compared to the beam-beam study here presented could possibly be induced by the cold rovibrational state distribution present in a supersonic SF<sub>6</sub> beam. Unfortunately it is not possible by experimental restrictions to perform measurements with our beam-beam arrangement at such low energy however we believe that the present results are more precise than those of Ref. 1 not only as a result of the better beam-beam experimental conditions, but also because we changed the  $^3P/^1D$  ratio over a significant range.

### Excitation Function

The excitation functions can be classified to belong to the  $-1$  and  $-2$  types, for the  $^3P$  and  $^1D$  reactions, respectively, according to a recent classification scheme.<sup>11</sup> The monotonic decline of the  $^1D$  excitation function may well correspond to a typical harpooning cross-section governing the reaction dynamics. The high harpooning cross-section  $\sigma_h = 108 \text{ \AA}^2$  obtained by the usual crossing radius formulae,  $R_c$

$$\sigma_h = \pi r_c^2; \quad R_c = e^2/[IP(\text{Ca}^*) - EA(\text{SF}_6)]$$

where  $e$ ,  $IP(\text{Ca}^*)$ ,  $EA(\text{SF}_6)$  have the usual meaning<sup>2,12</sup> could originate this long range interaction. It has been shown that in these cases<sup>2b</sup> due to the interaction of the covalent and ionic configuration the interaction is rounded off, rendering the potential quite attractive even beyond the crossing radius. Thus the lower the collision energy,  $E_T$ , the more effectively will this part of the potential pull the reactants in large impact parameter leading to higher cross-sections as  $E_T$  diminishes.

Similar arguments could be invoked to account for the decline in the  $^3P$  Ca excitation function, however the enhancement of the excitation function, beyond

0.4 eV, with respect to the <sup>1</sup>D case cannot be easily explained. The smaller harpooning cross-section ( $\sigma_h = 60 \text{ \AA}^2$ ) leads to speculate about the presence of statistical dynamics, that, in fact, cannot be ruled out when precisely molecular beam studies of the alkali atoms plus SF<sub>6</sub> have shown so.<sup>13,14</sup>

In any case with the information available it seems difficult to address a definitive conclusion about these reaction mechanisms. The lack of information concerning the production of the *X* and *B* states of the CaF makes difficult to interpret the collision dynamics. To this end it would be very interesting to measure the internal state distribution of the CaF by Laser Induced Fluorescence, for example, as a function of collision energy and electronic excitation of the reagents as well. This is in fact what we plan to do next.

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