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D. KHALIL, N. BILLY, G. GOUEDARD and J. VIGUE

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CHESTER J. DYMEK, Lt Col, USAF
Chief, Chemistry

RONALD J. LISOWSKI, Lt Col, USAF
Chief Scientist

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CROSSED BEAM STUDIES
OF SOME CHEMILUMINESCENT REACTIONS PRODUCING IF

By D. KHALIL, N. BILLY, G. GOUEDARD and J. VIGUE

Laboratoire de Spectroscopie Hertzienne de l'ENS (*)
24, rue LHOMOND, 75231 PARIS CEDEX 05

(*) Associated with CNRS and University P. et M. CURIE

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ABSTRACT

We have studied the following series of chemiluminescent reactions: F_2 + HI, CH_3I, CF_3I, CH_2I_2, CHI_3 and CI_4. All these reactions can produce IF in the B state. With respect to the previous studies which were made under flow conditions, we have used a crossed beam experiment. In these conditions, the chemiluminescence signal is very small for the reactions of the iodomethanes (if we except the particular case of CI_4 which gives a large signal due to iodine impurity), but this signal is considerably larger for HI. In this case only, the spectrum of the chemiluminescence was recorded, which shows that the emitter is indeed IF in its B state.

We have tried to understand the mechanism of excitation of this chemiluminescence by a generalization of the mechanism introduced by Kahler and Lee for the F_2 + I_2 reaction. This mechanism involves in a first step the formation of the HIF radical and a quasi-free F atom. The fluorine atom in the HIF radical migrates to form HF and leaves the I and F atoms free to recombine in any electronic state. Fluorine migration seems forbidden by steric arguments in the case of the CH_3IF radical (or similar radicals), explaining the very low chemiluminescence branching ratio in these reactions.

1) INTRODUCTION

The study of chemiluminescent reactions is a fascinating subject. The interest in such studies comes from very different reasons: from applied physics - a search for chemical lasers - to theoretical considerations - understanding how nonadiabatic reactions can occur. The reactions of fluorine molecules with various Iodides (organic or mineral) are sufficiently exoergic to produce electronically excited IF molecules, following equation (1):

$$F_2 + RI \longrightarrow IF(A,B) + RF \qquad (1)$$
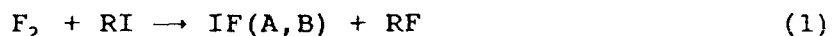
These chemiluminescent reactions have been the subject of numerous works (1-24). However, most of these works were done in flow experiments, with typical pressures around 1 mbar. In such conditions, the chemiluminescence may be due to a chain of two reactions implying an intermediate radical RIF:

$$F_2 + RI \longrightarrow RIF + F \qquad (2)$$

$$F + RIF \longrightarrow RF + IF(A,B) \qquad (3)$$
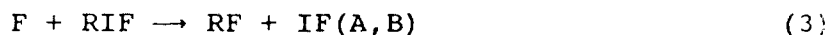
This two-collision mechanism appears to be dominant even in the crossed-beam experiments of J. Wanner and coworkers (10-12), where a Fluorine atomic beam reacts with an Iodide beam. In a recent study (13), this group has shown the importance of wall reactions in the formation of the I_2F radical.

After C.C. KAHLER and Y.T. LEE (7), we have made a detailed study of the $F_2 + I_2$ chemiluminescent reactive collision, under crossed-beam conditions (24). We have used here the same techniques to study the series of reactions with the following iodides: HI, CF_3I , CH_3I , CH_2I_2 , CHI_3 , CI_4 . After some general informations on these reactions (section 2), we describe the experimental set-up in section 3, the experimental results in sections 4 and 5, and we discuss these results in section 6.

2) GENERAL INFORMATION ON THE STUDIED REACTIONS

2a) Previous studies

Only few studies treat of the chemiluminescence branch of these reactions. The reactions $F_2 + HI$, CH_3I , CH_2I_2, CF_3I have been studied by Estler, Lubman and Zare (3) under flow conditions, and their report is a very brief contribution to the General discussion of a Faraday Discussion. Many flow experiments have
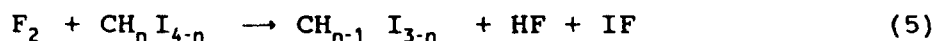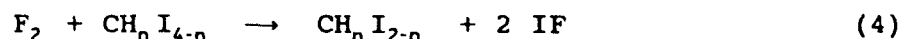
been done (17-22) by the group of C. Whitehead, but the fluorine reactant was introduced in the atomic form, with only a small amount of fluorine molecules. This was also the case in a 1972 study by Schatz and Kaufman (8), and more recently in a work of Cha and Setser (23). Other Fluorine donors, like O_2F, have also been used by Coombe and Horne (9). Obviously, these numerous works are not directly relevant to the present work. They are useful in establishing the importance of the two-collision mechanism (reactions 2 and 3) in the excitation of the chemiluminescence under multiple collision conditions.

Y.T. Lee and his coworkers (4,5,6) have proved the existence of the radicals I_2F, HIF, CH_3IF and they measured their stabilities. These results were established by direct detection of these products in a crossed-beam study of the $F_2 + I_2$, HI, CH_3I reactions. This work is particularly interesting as it also gives some insight in the shape of the I_2F, HIF, CH_3IF radicals, with the Fluorine atom outside. The CF_3IF radical has been observed in matrix isolation, and its infrared spectra studied (25).

In the case of the $F_2 + I_2$ reactions, the threshold of formation of I_2F (5,6) and the threshold of the chemiluminescence (as measured in a crossed-beam experiment (7)) appear to be very close, strongly suggesting that the mechanism of the chemiluminescence is a two-step mechanism in a single collision, these two steps being described by reactions (2) and (3). It is interesting to extend these studies to other reactions to see if this explanation of the mechanism is general.

2b) Energetics of these reactions

We can evaluate easily the energetics of reaction (1) using the values of the bond strengths (26-36). Table 1 presents these evaluations for the reactions with HI, CH_3I and CF_3I. The C-I and C-F bond energies do not depend very much on the other atoms bonded to the carbon atom, so that the energetics for the other Iodomethanes are expected to be very similar to the one of the CH_3I reaction. The available energy for products is large enough to populate the IF in the B state up to its dissociation limit. However, it is interesting to remark that most of the exoergicity comes from the formation of the HF or CF bond, and the way this energy can be channeled into IF electronic excitation is not trivial. In the case of the Iodomethanes reactions, IF can be formed by other reactions than reaction 1:

$$F_2 + CH_nI_{4-n} \longrightarrow CH_nI_{2-n} + 2\ IF \qquad (4)$$

$$F_2 + CH_nI_{4-n} \longrightarrow CH_{n-1}I_{3-n} + HF + IF \qquad (5)$$

Because three bonds are broken and only two new bonds are formed,

these reactions are endoergic or weakly exoergic and cannot produce electronically excited IF, even at the highest collision energy available in our experiment (around 110 kJ/mole).

2c) Nature of the chemiluminescent emissions

Most of the chemiluminescent signals involving IF are due to the B state emission towards the ground X state, and some experiments have reported emission of the A state. The B state of IF has a radiative decay rate $\Gamma = 1.2 \times 10^5$ s^{-1} (27) and the observation time t_{obs} (defined as the average time spent by a molecule in a region where its emission can be detected) is of the order of 5 μs. In the absence of predissociation and quenching processes, the fluorescence yield Y is given by:

$$Y = 1 - \exp(-\Gamma t_{obs}) \approx \Gamma t_{obs} \qquad (6)$$

for small values of the time t_{obs}. This yield is comparable to 1 for the B state. The A state radiative decay rate is not known for IF, but, by comparison with ICl (37), it can be estimated to be considerably smaller than the one of the B state, of the order of 10^3 s^{-1}. Accordingly, the A state fluorescence yield is surely very small (around 1%) in our experiment.

In the F_2 + HI reaction, the HF product can be formed in highly vibrationally excited states of the ground electronic state X. These states can emit visible radiation by overtone emission with $\Delta v \geqslant 4$ (38), and thus HF can contribute to the chemiluminescence. The Einstein A coefficients for these emissions are very small, in the 10^{-2} -1 s^{-1} range (depending on v and Δv). The corresponding fluorescence yield is extremely small, typically below 10^{-6}. We have no evidence of the contribution of these HF emissions in our experiments, although the F_2 + HI reaction can produce large amounts of vibrationally excited HF molecules.

3) THE EXPERIMENT

A detailed description of our beam machine has been given in references (24,39,40). We recall here the main features and describe the modifications:
- the two beams cross at right angle.
- the fluorine beam is unchanged, with a nozzle diameter of 200 μm, a temperature up to 700 °C. Fluorine is seeded in Helium (10:90), and the source pressure is varied in the 0-1300 mbar range.
- several types of Iodide beams were used. In some experiments with HI, CF_3I, CH_3I, the beam source is differentially pumped. It is produced by a supersonic expansion of pure HI

through a 100 μm glass nozzle and is collimated by a 1mm wide slit (as the I_2 beam in reference 40). However, this arrangement leads to small signals and we have also runned these beams without the collimating slit, enhancing the chemiluminescence by a large factor ($\approx$ 20). For the more condensable Iodides CH_2I_2, CHI_3, CI_4, the nozzle was replaced by 10 mm long glass capillary of internal diameter 1mm. The gas line was made of glass and teflon pipes, to minimize corrosion.

- HI was obtained from Air Liquide, and CF_3I from Fluorochem Limited. The source pressure was controlled by a regulator, in the 100-400 mbar range, and the pressure was measured by a Barocell gauge. In order to minimize the I_2 beam content, the HI bottle was cooled to 0°C. The various Iodomethanes were obtained from Janssen Chimica (CH_3I, CH_2I_2, CHI_3) and Fluka (CI_4) and used without further purification (this point will be discussed below). Their vapor pressure was controlled by varying the temperature of the oven (using a thermostat Lauda RCS6), kept always smaller by at least 10-20°C below the one of the nozzle. As we had no way of heating the pressure gauge, we have no measurement of the source pressure in these cases (except CH_3I for which the vapor presssure at ordinary temperature is large).

- the total chemiluminescence signal is detected by an Hamamatsu R 464 photomultiplier with a bialkali photocathode, in some experiments, a filter (Schott BG 39, 3 mm thick) was used to reduce the stray light emitted by the hot fluorine beam oven. The optics collects roughly 3% of the total chemiluminescence.

The monochromator (Jobin-Yvon THR 1500) receives the light through the same three-lens system used already in our previous chemiluminescence experiment (24). The photomultiplier we use now is Burle C31034A, with a GaAs photocathode, cooled to -50°C by a thermoelectric chamber (Products for Research TE210 RF), giving a dark count rate around 1-2 counts per second.

We use fast photon counting electronics. When the signals are measured as a function of source pressures and temperatures, we just manually record the readings of the scalers. For the chemiluminescence spectrum, the rather complex procedure we described in reference (24) was also used here.

4) THE UNDISPERSED CHEMILUMINESCENCE SIGNALS

The total chemiluminescence signals as collected by the photomultiplier inside the scattering chamber can be studied as a function of the conditions of the beam sources: pressure and temperature. When possible, we have studied the chemiluminescent signals as a function of the F_2 beam source pressure and temperature, and as a function of the iodide beam source pressure. The variations with the beam source pressure give information on

the molecularity of the reaction, and the variation with the F_2 beam temperature gives access to the variation of the chemiluminescence cross-section with the collision kinetic energy

4a) The F_2 + HI reaction.

The variation with the F_2 beam source pressure is plotted on figure 2. The shape of this variation is very similar to what we observed in the F_2 + I_2 study, and can be explained as previously. For low source pressure p_0 , the intensity of a supersonic beam is proportionnal p_0 $M^2 \approx p_0^2$ (where M is the Mach number proportionnal to p_0^α with α close to 1/2). For intermediate values of p_0 , the beam intensity should be linear in p_0 . Then, for large p_0 , some saturation appears, probably due to imperfect skimming, or to diffusion by the backgroud gas in the source chamber. Although not obvious at first sight, we think that these observations are perfectly compatible with the reaction as implying only one molecule from the F_2 beam. This molecule must be F_2 and not F for the two following reasons:
- no chemiluminescence reaction is possible only with one Fluorine atom
- the F content of the beam is extremely small when the source temperature is below 500°C.

The variations of the chemiluminescence signal with the HI beam source pressure are shown in figure 3. It is close to linear at high collision energies, but it is strongly nonlinear at low collision energies. We explain these observations as follows. The HI beam contains a small, but noticeable fraction of dimers $(HI)_2$. This fraction increases very rapidly with HI source pressure, as usual for the formations of small clusters in supersonic expansion (41-45). The reaction of these dimers with F_2 is also chemiluminescent and moreover, we must assume that this reaction has a lower threshold than the reaction of the monomer. The dimer reaction should proceed along equation (7):

$$F_2 + (HI)_2 \longrightarrow IF + HF + HI \qquad (7)$$
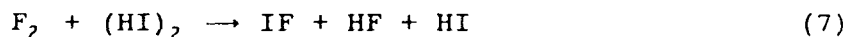
At low collision energy, the dimer reaction dominates the signal while at large collision energy the monomer reaction dominates in particular because it is more abundant (this question is further discussed in part 6).
We have fitted the curves of figure 3 by the equation (8):

$$S = b \times p_0 + c \times p_0^\beta \qquad (8)$$

where p_0 is the HI source pressure. The background signal (stray

light, dark counts) has been substracted from the plotted data; the b and c terms represent the signals respectively due to the monomer and dimer reactions. The fits are good with β values close to 3. The semi-empirical equations giving the dimer density of rare gas beams predicts a dependence in $p_0^{7/3}$, and they have also been successfully applied to HF beams.(43)

The variation of the signal with the temperature of the Fluorine beam source has been plotted on figure 4. The temperature has been converted to a mean kinetic energy scale, assuming that the supersonic beams have the theoretical velocities corresponding to large Mach numbers (this has been verified for the Fluorine beam, whose velocity gives the dominant contribution to the relative velocity). In the region of low-collision energy, where most of the signal comes from the dimer reaction we have plotted the total signal and the signal corrected by substraction of the dimer and background signals (as given by the above analysis). Although we have not made a very precise analysis of the beam velocity distributions, we can deduce the chemiluminescent reaction threshold. This value appears in table 2, which recalls also the value obtained by Valentini et al (5,6) for the appearance of HIF in the same collision. This result will be discussed in part 6.

4b) The F_2 + iodomethanes reactions.

We have tried to reproduce this study with the four Iodomethanes and with CF_3I. If we except the case of CI_4, the maximum chemilumin ...... signal was extremely small, of the order of 1000 counts per s cond in the best case. The dependence of this signal with Iodide beam source pressure is represented in figure 5, in the case of CH_3I and CF_3I. This dependence is linear with a good approximation, proving that the dimer contribution to the signal is weak, although dimerization of CH_3I is easy (46).In the case of CH_2I_2 and CHI_3, we have not found any table of the vapor pressure as a function of the temperature, but only their boiling temperature (47). Using analogies with the other halomethanes which are better known (48), one can easily derive an approximate formula for the pressure as a function of the temperature (49). The chemiluminescence signal appears to be a linear function of the source pressure in these two cases, but it remains very small. On the contrary, with CI_4 , a very large signal (up to 8×10^6 counts/s) was observed. This signal increased regularly with the CI_4 oven temperature. We think that it is due to the molecular Iodine impurity present in CI_4. We have recorded the dependence of the chemiluminescence signal with the Fluorine beam temperature for the CI_4 beam and for an I_2 beam under the same conditions. These two experiments give very similar results, as shown in figure 6. It appears almost impossible to reduce the Iodine

content of CI_4 so as to really observe the F_2 + CI_4 reaction, and we will not discuss this reaction anymore. For the other Iodomethanes we have also observed that impurity contributes to the chemiluminescence signal. A clear manifestation was the observation of a signal which increases when lowering the Iodide pressure. This problem was almost completely solved by putting a w gas line, in replacement of the one which served with HI, and whose Teflon tubes had become violet, saturated by Iodine. We think that the signals reported here are truly due to the reaction of Fluorine molecule with the Iodide in the beam source. However, with such a low signal level, the contribution of a very minor impurity cannot be excluded. Because of the weakness of the signals, we have collected only very limited data as a function of the fluorine beam source pressure.

The signals as a function of the Fluorine oven temperature are plotted in figure 7. They increase rapidly with the collision energy. We can deduce from these curves approximate thresholds for the chemiluminescent reactions. These results are summarized in table 2.

5) THE SPECTRUM CF THE F_2 + HI CHEMILUMINESCENCE AND ITS ANALYSIS

5a) The experiment

This experiment is completely similar to what was done in our F_2 + I_2 study (24). We used the same recording procedure, so that each data point corresponds to an integration of 59 seconds. During this experiment, the typical value of the undispersed fluorescence signal is about 2×10^6 counts/s. The monochromator was used with 2.5 mm wide slits, giving a typical bandpass of 0.48 nm. The peak signal given by the photomultiplier on the monochromator was 80 counts/s. This gives a maximum signal to noise ratio of about 50. The spectrum covers the range from 450 nm up to 727 nm, by 0.24nm steps; its recording lasted 34 hours, during which the undispersed chemiluminescence was stable to 16%. The spectrum is plotted on figure 8 after background substraction and normalization by the total chemiluminescence signal.

As in our previous work (24), we have calibrated the spectral sensitivity of the detection system with a tungsten ribbon lamp. The slitwidth were only 5 μm, so as not to saturate the photomultiplier. Two measurements made with different temperatures of the lamp (2300 and 2600 K) have given sensitivities in good agreement (within 1%). The spectrum shown in figure 8 has not been corrected for the spectral sensitivity dependence.

5b) Analysis of the spectrum.

We have used the previously developed linear fit procedure to extract from this spectrum the rovibrational population of IF in the B state. This procedure is fully described in our previous paper to which we refer the reader. Briefly, we use the fact that the intensity at a given wavelength is a linear function of the rovibrational population $P(v,J)$, and we express this relation without any approximation:

- we use the accurate B-X spectroscopy (50) to calculate line positions
- we calculate the Einstein coefficient for each transition from the IF B-X dipole moment function obtained by Trautmann et al (51), and vibrational wavefunctions in the B and X state by numerical integration of the Schrödinger equation.
- for each step of the monochromator we estimate the contribution of each line to the signal using its triangular apparatus function, corresponding to the slitwidth.

From the observed spectrum, the population $P(v,J)$ could be deduced by inverting this system of linear equations. We assume that the micropopulation $\pi(v,J) = P(v,J)/(2J+1)$ is a smooth function of $x=J(J+1)$. Then we reduce the dimension of the system by fitting only a limited set of $\pi_i = \pi(v,J_i)$, where the J_i values are rather arbitrarily chosen and π is given by linear interpolation (in x) between two J_i values.

This work is presently in progress.

6) DISCUSSION

This discussion will treat first the F_2 + HI reaction as it is the one on which we have collected the most detailed results. We will then try to understand why the reaction with iodomethanes give such a weak chemiluminescence, in crossed beam conditions. Finally, we will briefly discuss the reaction with HI dimers.

6a) The F_2 + HI reaction.

The information that we have collected concern the threshold of the reaction, a rough evaluation of the total chemiluminescence cross-section, and the spectrum of the chemiluminescence.

We may try to guide the discussion by the similarities with the case of the F_2 + I_2 reaction: in particular, in the two cases, the reaction threshold for addition of an F atom on the iodide and the chemiluminescece threshold are very similar (see

table 2). This suggests that the HIF radical is also an intermediate step in the chemiluminescent reactions as I_2F.

However. there are some important differences between the HI case and the I_2 case. The F_2 + HI reaction forms obviously only one IF molecule and theoretical (52,53) and experimental (5,6) arguments prove that in HIF, the Fluorine atom is bonded to the Iodine atom. This means that the IF bond should be formed before the HF bond. In our present understanding of the F_2 + I_2 reaction, the IF bond which forms first in I_2F is left in the ground state, and the second IF molecule which is produced by recombination of the quasi-free I and F atoms is electronically excited. Clearly, it is not possible to apply directly this description to the HI case. A natural way to understand the F_2 + HI reaction is the following.

The collision forms first the HIF radical, with a quasi-free F atom. Following the calculations of Barlett and coworkers (53), the HIF radical is bent with two local minima, with the bond angle (i.e. the H-I-F angle) equal to 137.5° and 82°. The HI bond length is very close (within 0.1 a.u.) to the equilibrium value of the diatomic, while the IF bond length is extended with respect of the diatomic equilibrium value by 0.3 a.u.. These two minima are separated by a small activation barrier of roughly 20 kJ/mole. The absolute minimum, which is not calculated, must obviously look like HF with the Iodine atom weakly bound (possibly to H by an hydrogen bond). To reach this well, there is an activation barrier calculated to be in the range 45-70 kJ/mole. This last barrier is substantial but considerably lower than the available energy especially when the chemiluminescence threshold is reached.

These informations suggest the following mechanism, which is a generalization of the mechanism discussed by Kahler and Lee for F_2 + I_2, by the introduction of migration. Labelling F_a and F_b the two Fluorine atoms, the collision first forms the HIF_a radical with the F_b atom weakly bound to this radical. It seems likely that the F_b atom may be close to the Iodine atom which can bind several fluorine atoms (as clearly attested by the stable IF_5 and IF_7 compounds), but if the IF_b bond is already formed at that time, this will prevent production of excited state of IF. The F_a atom may then migrate over the barrier to form HF, and leave behind the Iodine and the F_b atom able to recombine and form any electronic state of IF.

The existence of a barrier to migration can have consequences on the rate of the process and also on the energy available in the IF_b molecule. It may also explain a higher threshold for chemiluminescence than for HIF formation. The results in table 2 suggest that it may be the case.

It is interesting to remark that this migratory mechanism

may also be active in the $F_2 + I_2$ chemiluminescent reaction, in addition to the direct mechanism introduced by Kahler and Lee. This idea is supported by the trajectory calculations (54,55,56) of the dynamics of $F + I_2$ reactive collision which predict that a large fraction of the collisions are migratory, and also by our experimental results (39) which exhibit a bimodal rovibrational distibution of IF produced by this collision. If two mechanisms (direct and migratory) are active in the $F_2 + I_2$ chemiluminescent reaction, they should most probably lead to different rovibrational distribution of the products. Our results (24) exhibit such a bimodality: the lowest vibrational levels (v = 0-2) have a cold rotational distribution, while the higher vibrational levels (mostly v = 3-7 as for higher v values the rotational distribution is severely truncated by the B state predissociation) have a very hot rotational distribution. We may tentatively assume that this bimodal rovibrational distribution is due to the existence of two mechanisms (direct and migratory) in this reaction.

6b) The F_2 + iodomethane reactions.

The main point that we would like to explain is why the chemiluminescent branch of these reactions is so weak. As already stated, when the substituted methane contains more than one Iodine atom, the chemiluminescent reaction must for energetic reasons produce only one IF molecule. We discuss here the case of CH_3I, as representative of the other cases. The similarity with the reaction with HI is great as the CH_3IF radical is also stable. We must understand why migration of the Fluorine atom F_a is prohibited in the reaction with Iodomethanes.

Two possibilities exist in the substitution of the Iodine atom by an F atom in an Iodomethane molecule: either the Fluorine atom replaces the Iodine atom where it was, or the Fluorine atom comes from the other side, inverting the CH_3 umbrella. These two dynamics seem very unlikely for the Fluorine atom F_a, initially linked to the I atom, because of steric problems (these problems do not exist in the reaction with HI, as H is accessible on all sides):

- in the first case, as Iodine atom is very bulky, the access to the carbon atom of a Fluorine atom is not possible as long as the C-I bond is not considerably extended. This is energetically possible only if a strong IF bond is formed, i.e. a ground state IF molecule. The substitution, if it occurs, will be due to atom F_b.

- in the second case, the Fluorine atom must reach the center of the CH_3 umbrella, on the opposite site of the Iodine atom in order to react. The barrier to this motion is obviously quite high. In this case also this dynamics seems forbidden to the

atom F_a, but may be authorized only to the quasi-free Fluorine atom F_b.

6c) The reaction of F_2 with HI dimers.

We will try here only to show that the density of HI dimers is sufficient in the beam to explain the signal, assuming that the order of magnitude of the cross-section for chemiluminescence is comparable for HI and its dimers (but with a lower threshold for this last species).

To evaluate the dimer density, we will use the semi-empirical equation established by Knuth for rare gases (41), which works very well in this case (42) and applies also to the case of HF dimers (43). This equation relates the dimer fraction in the beam x_d to the source density n_0, the temperature T_0, the nozzle diameter d, and to molecular parameters σ (the zero potential radius) and ϵ (the well depth):

$$\frac{x_d}{(1-x_d)^2} \approx 0.5 \left[n_0 \; \sigma^3 \left(\frac{\epsilon}{kT_0}\right)^{7/5} \; \left(\frac{d}{\sigma}\right)^{2/5} \right]^{5/3} \tag{9}$$

We may estimate σ from the liquid HI density ($\sigma \approx 0.5$ nm), and ϵ from ab initio calculations ($\epsilon = 2.38$ kJ/mole (57)). The comparison with HF dimers is interesting: the well depth is considerably larger, $\epsilon \approx 20\text{-}45$ kJ/mole (58), depending on the estimations. This strong bond is the addition of a strong Hydrogen bond and an important dipole-dipole interaction. In the HI dimer, the bond is only a weak Hydrogen bond.

The sensitivity of equation (9) to ϵ and σ is large: $x_d \sim \epsilon^{7/3} \; \sigma^{13/3}$ so that minor errors in these two quantities will induce large errors on x_d. With the present choice of values, we get $x_d \approx 0.02$ for a source pressure of 400 mbar at $T_0 = 300$ K: the dimers remain a minor component of the beam. Then our results suggest that the chemiluminescence signal between F_2 and the dimer has a larger cross section that the same reaction with the monomer.

7) CONCLUSION

The chemiluminescent reactions F_2 + HI and F_2 + iodomethanes have been studied in crossed beam conditions. This allows to investigate the single collision reactive processes. In this way, beam experiments provide informations clearly different from the flow experiments. Moreover, in the case of the reactions between F_2 and iodides, we have shown that the chemiluminescence produced by the single collision process differs strongly from the

one observed in flow experiments, either by its intensity, or by the rovibrational population in the excited state.

The chemiluminescence signal produced by the F_2 + HI reaction is large, and we have recorded its spectrum. The chemiluminescent species is IF(B). Its rovibrationnal distribution is cooler than for the F_2 + I_2 reaction. We have tentatively explained this result by a migration mechanism. This mechanism is a generalization of the one introduced by Kahler and Lee for the F_2 + I_2 reaction. It is a two step mechanism: in the first step, the radical HIF is formed, weakly bound to the other F atom; the second step implies the migration of the fluorine atom in HIF, to form HF, and simultaneously the IF bond is formed with the second F atom.

The chemiluminescences of F_2 + Iodomethanes (CH_3I, CH_2I_2, CHI_3, CF_3I) are much weaker than the F_2 + HI signal. They are also very low with respect to the same chemiluminescences observed in flow conditions. Then in this case of Iodomethanes RI, the F migration in the RIF radical seems to be forbidden by steric arguments.

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Table 1: Energetics of the RI + F_2 systems (in kJ/mole).

R	H	CH_3	CF_3
IF(X) + R + F	182.	116.7	107.6
RIF + F	47.5	49.2	49.2
RF + I + F	0	0	0
RF + IF(B)	-157.5	-108.4	-202.4
RF + IF(A)	-206.9	-157.8	-251.8
RF + IF(X)	-384.3	-335.2	-429.2

Table 2: Thresholds of the chemiluminescent channel and of the RIF radical production in the F_2 + RI reactive systems (in kJ/mole).

F_2 + RI $\longrightarrow$	Chemiluminescence	RIF + F
H	62.2	47.5 (5)
CH_3	75.9	46.0 (4)
$CH_2 I$	82.6	
CHI_2	46.4	

FIGURE CAPTIO..s:

Figure 1: Energetics of the F_2 + HI and F_2 + CH_3 I systems.

Figure 2: Chemiluminescence signal of the F_2 + HI reaction as a function of the fluorine source pressure P_0 . The F_2 source temperature and the HI source pressure were fixed respectively at T_{F_2} = 650 °C and P_{HI} = 400 mbar.

Figure 3: Chemiluminescence signal of the F_2 + HI reaction as a function of the HI source pressure. The experiment conditions are:
a - T_{F_2} = 700 °C ; P_{F_2} = 1070 mbar
b - T_{F_2} = 400 °C ; P_{F_2} = 800 mbar

Figure 4: Chemiluminescence signal of the F_2 + HI reaction as a function of the F_2 source temperature. The beam source pressures have been fixed at P_{F_2} = 520 mbar and P_{HI} = 400 mbar. The F_2 source temperature scale has been converted to a mean kinetic energy scale, as explained in the text.

Figure 5: Chemiluminescence signals of the F_2 + CH_3 I (part A) and F_2 + CF_3 I (part ь), as a function of the iodide source pressure. The F_2 source temperature and pressure have been controled:
   - for F_2 + CH_3 I, curve a: T_{F_2} = 700 °C ; P_{F_2} = 840 mbar
                          curve b: T_{F_2} = 600 °C ; P_{F_2} = 800 mbar
                          curve c: T_{F_2} = 400 °C ; P_{F_2} = 880 mbar
   - for F_2 + CF_3 I, T_{F_2} = 700 °C ; P_{F_2} = 735 mbar

Figure 6: Chemiluminescence signals of the F_2 + CI_4 reaction (curve a) and of the F_2 + I_2 reaction (curve b), as a function of the F_2 source pressure. The experimental conditions are:
   (a) P_{F_2} = 670 mbar ; T_{CI_4} = 50 °C
   (b) P_{F_2} = 670 mbar ; T_{I_2} = 40 °C
To be easily compared with curve a, curve b has been shifted.

Figure 7: Chemiluminescence signals of the F_2 + iodomethane and F_2 + CF_3 I reactions, as a function of the F_2 source temperature.
        Part A: Chemiluminescence of the F_2 + CH_3 I reaction. The experimental conditions are P_{F_2} = 750 mbar ; $T_{CH_3 I}$ = 14 °C ; $P_{CH_3 I}$ = 220 mbar.
        Part B: Chemiluminescence signal of the F_2 + $CH_2 I_2$ reaction. Experimental conditions: P_{F_2} = 800 mbar ; $T_{CH_2 I_2}$ = 15 °C
.
        Part C: Chemiluminescence of the F_2 + CHI_3 reaction. Experimental conditions: P_{F_2} = 870 mbar ; T_{CHI_3} = 85 °C.
        Part D: Chemiluminescence of the F_2 + CF_3 I reaction.

Experimental conditions: P_{F_2} = 735 mbar ; T_{CF_3I} = 25 °C ; P_{CF_3I} = 200 mbar.

Figure 8: Spectrum of the chemiluminescence of the F_2 + HI reaction. The operating conditions are T_{F_2} = 600 °C ; P_{F_2} = 770 mbar ; T_{HI} = 25 °C ; P_{HI} = 440 mbar ; and the mean kinetic collision energy is 75.7 kJ/mole.
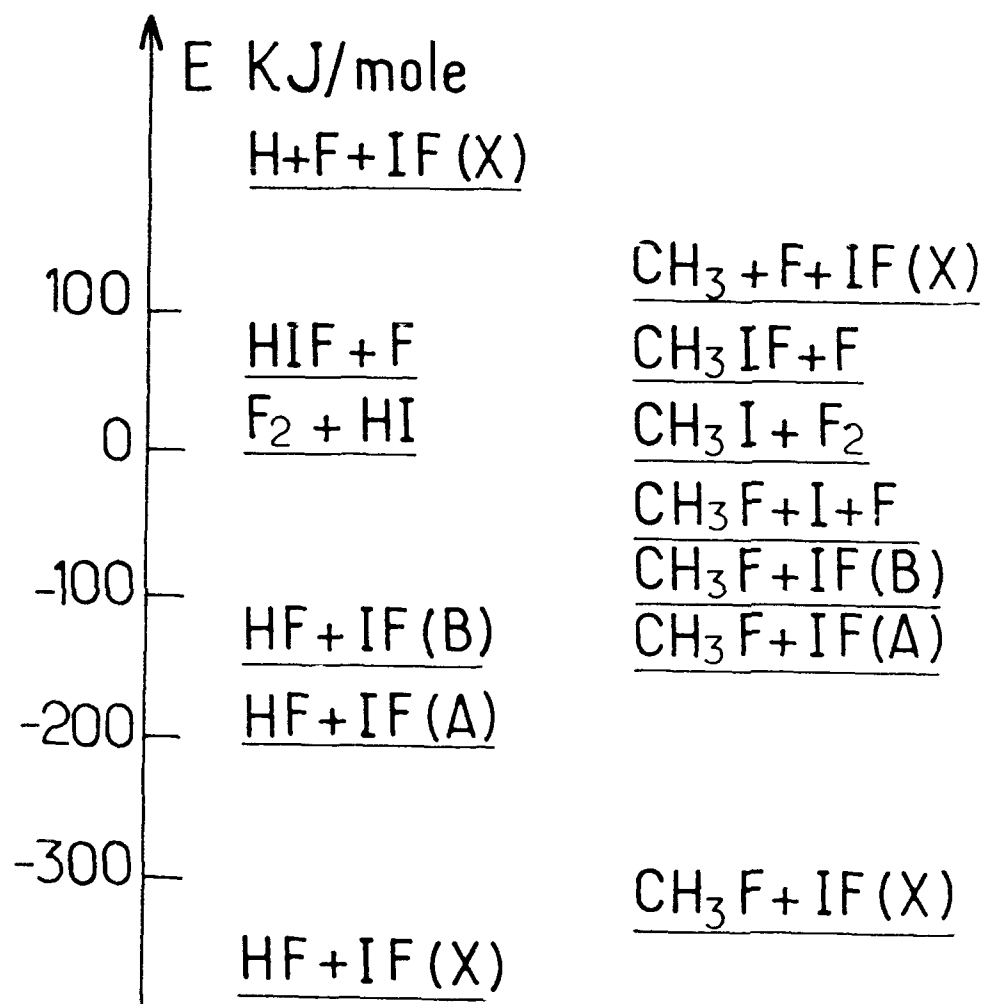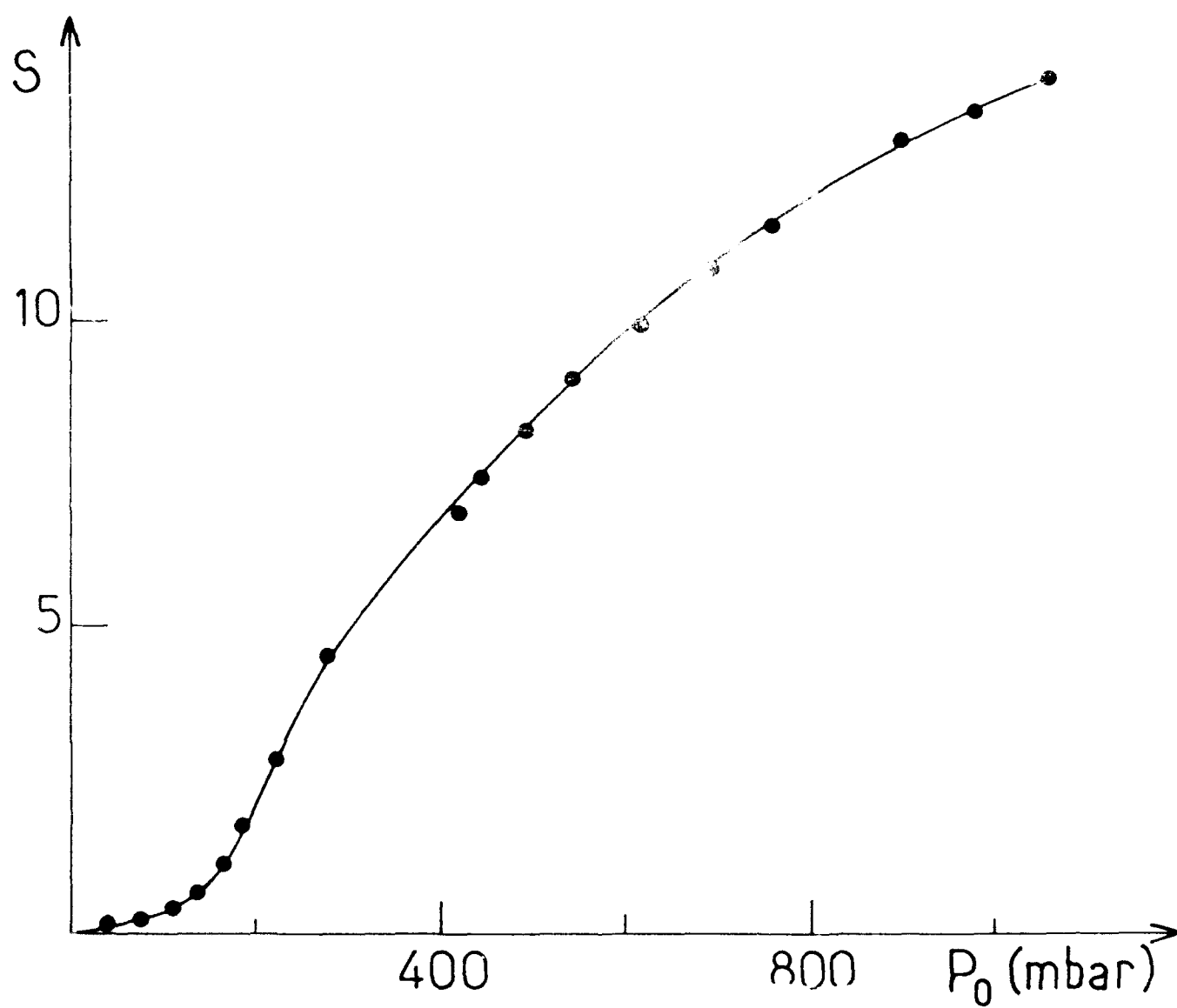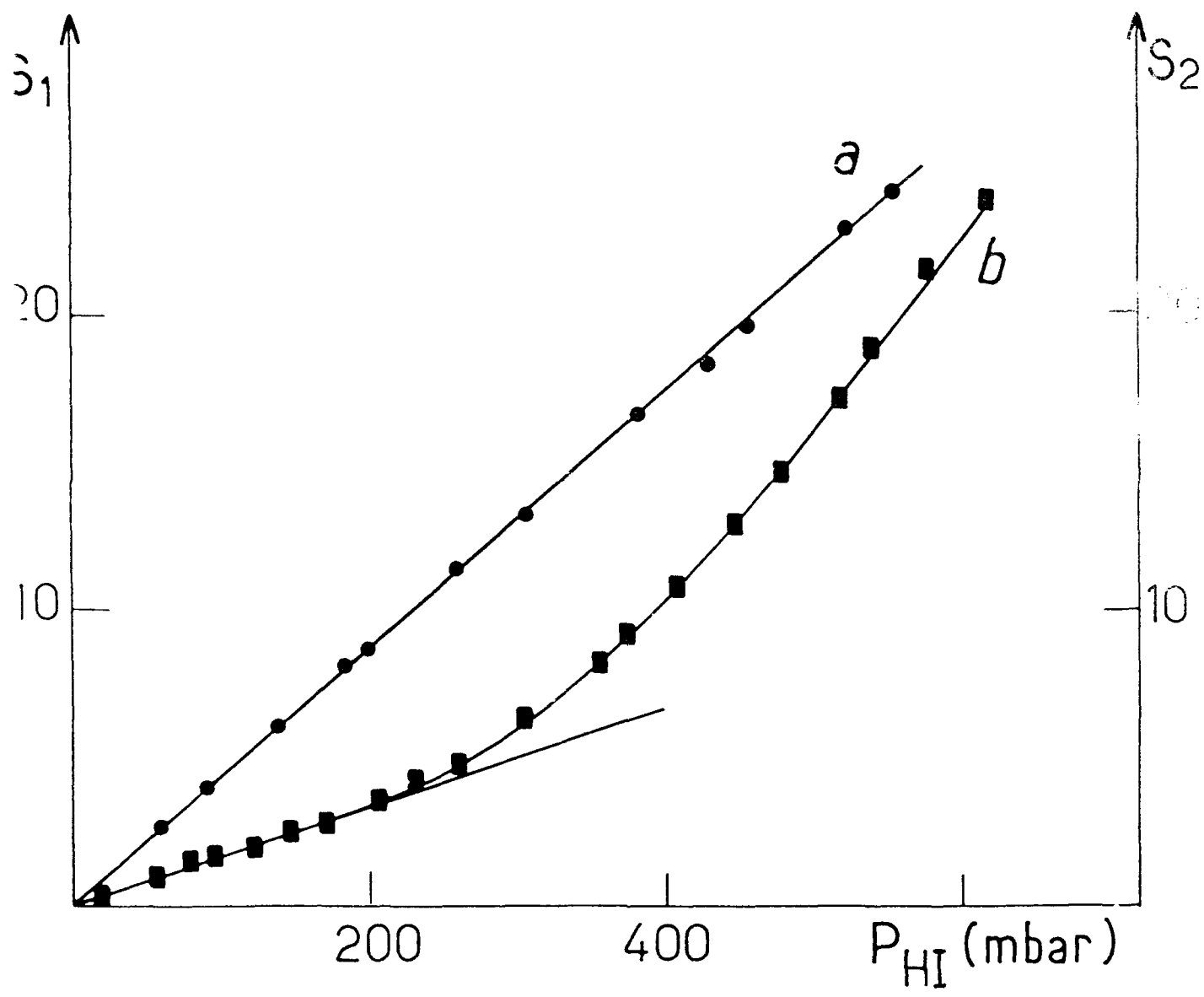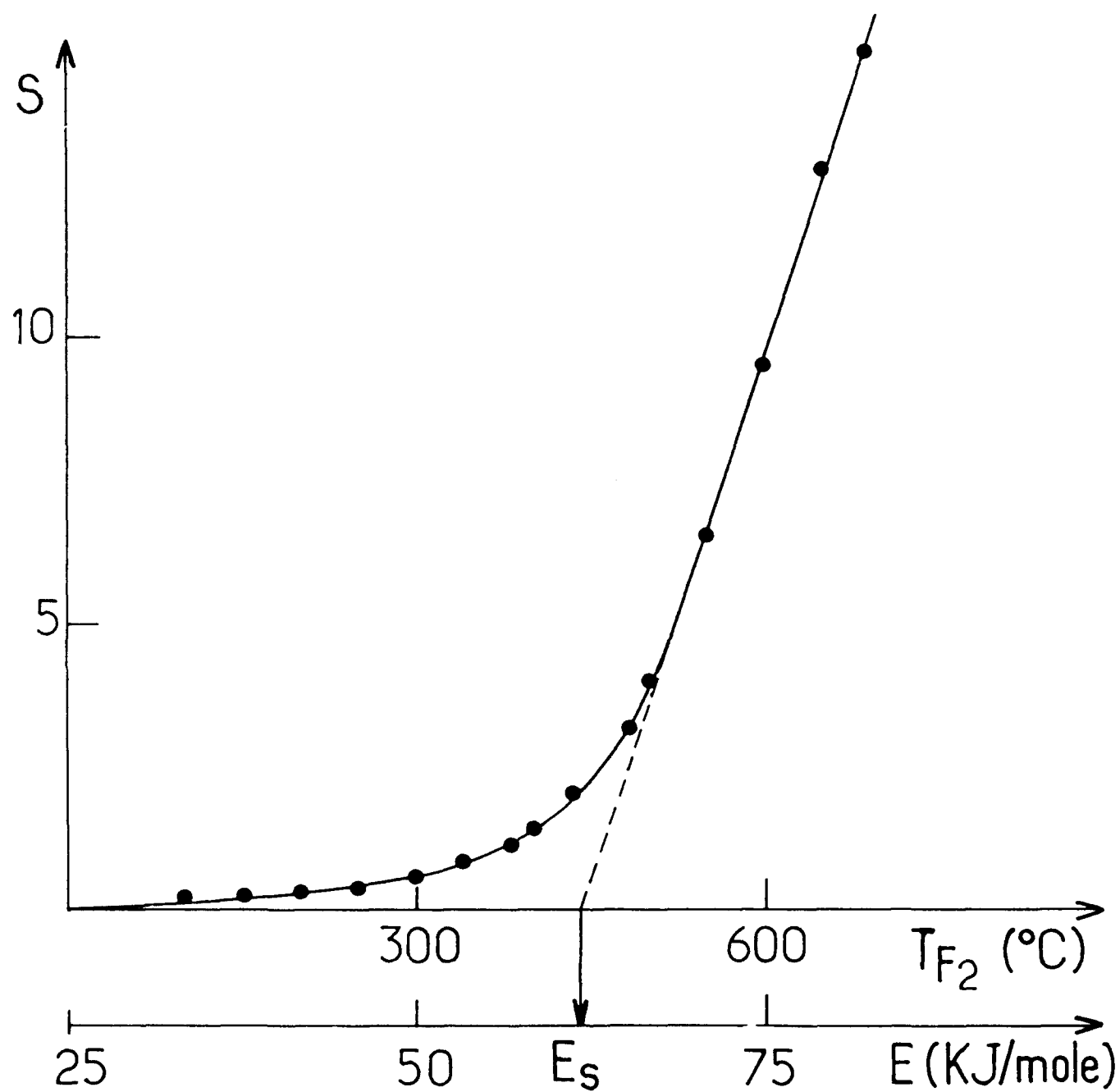
Energy level diagram with vertical axis labeled **E KJ/mole**.

Left column (axis scale from 100 to −300):

- H+F+IF (X) (near +150)
- 100
- HIF + F (~+70)
- F$_2$ + HI (~+30)
- 0
- −100
- HF + IF (B) (~−150)
- HF + IF (A) (~−200)
- −200
- −300
- HF + IF (X) (~−340)

Right column:

- CH$_3$ + F + IF (X) (~+110)
- CH$_3$ IF + F (~+65)
- CH$_3$ I + F$_2$ (~+10)
- CH$_3$ F + I + F (~−80)
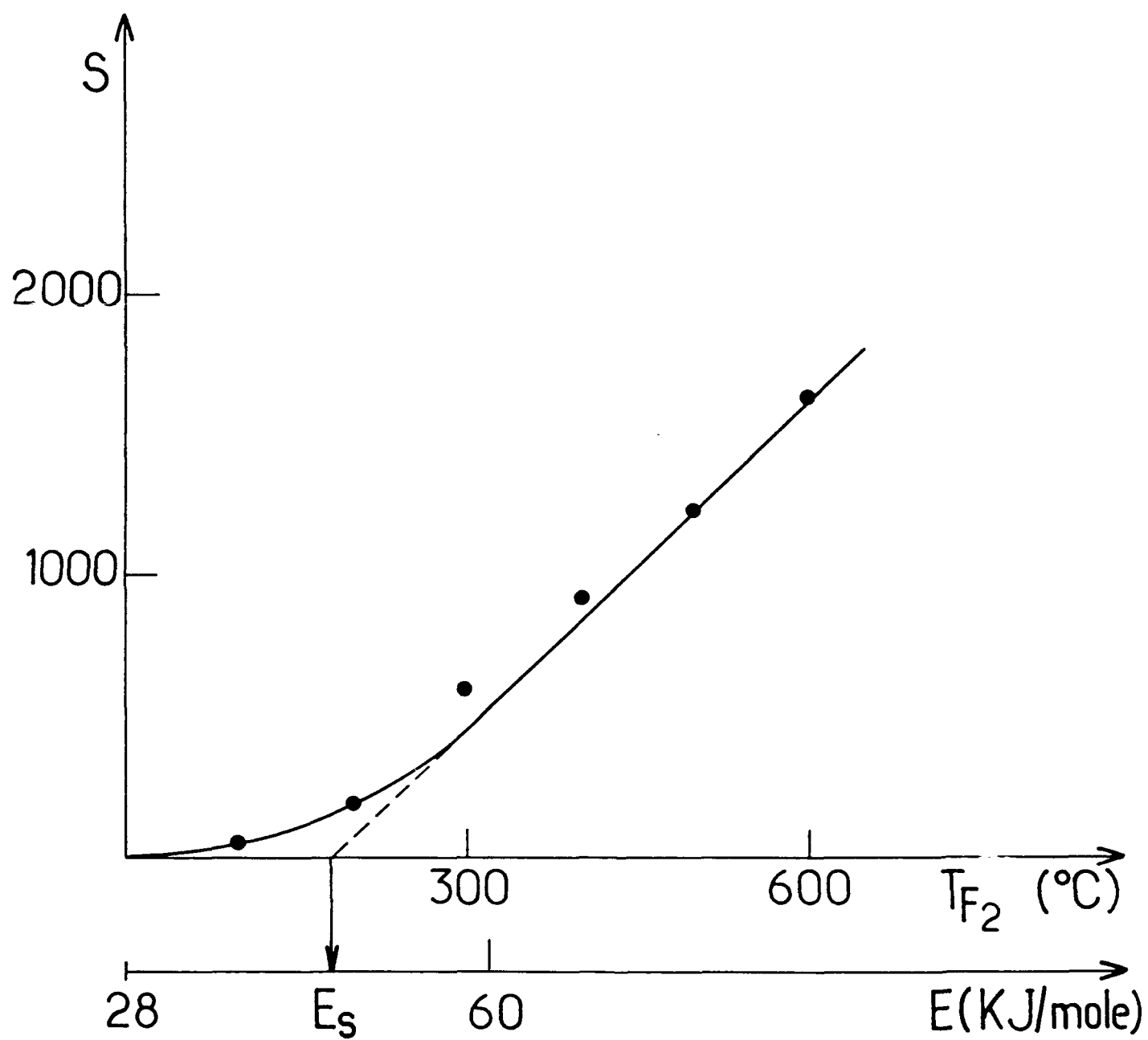- CH$_3$ F + IF (B) (~−110)
- CH$_3$ F + IF (A) (~−130)
- CH$_3$ F + IF (X) (~−290)

Figure 3

Figure 4

Figure 5.A

Figure 5.3

Figure 7 A

Figure 9