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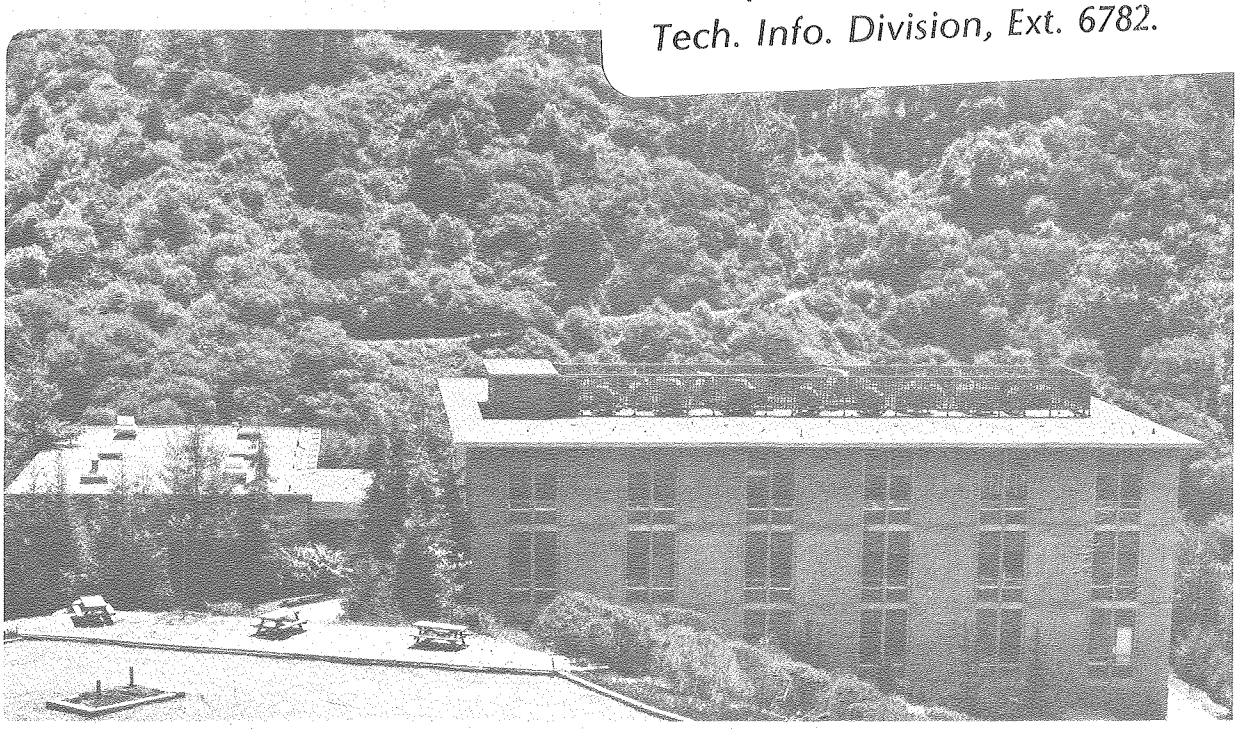

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CROSSED MOLECULAR BEAM STUDIES OF CHEMILUMINESCENT REACTIONS: $F_2 + I_2$, Br_2 and ICl

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ABSTRACT

The chemiluminescent bimolecular halogen-halogen reactions, $F_2 + I_2$, Br_2 and ICl, have been studied by the crossed molecular beam technique. Undispersed chemiluminescence was measured as a function of collision energy and, for $I_2 + F_2$, as a function of the two beam pressures. Although no spectra were obtained to positively identify the emitters as IF*, ClF* and BrF*, arguments are given to support this identification. The observed reaction thresholds of 4.2 and 5.9 kcal/mole for $I_2 + F_2$ and ICl + F_2, respectively, are the same as the threshold energies for production of the stable trihalogens I_2F and ClIF. This coincidence of threshold energies, as well as similar high collision energy behavior, implies that the chemiluminescent reaction proceeds via a stable trihalogen intermediate. This mechanism can explain our results and the results of other workers without resorting to a symmetry forbidden four center reaction mechanism. A threshold of 11.3 kcal/mole was found for $Br_2 + F_2$, no threshold for Br_2F has been previously reported. Laser enhancement of the $I_2 + F_2$ reaction was attempted, but no enhancement was seen.

INTRODUCTION

It has been known for a number of years that reaction rates are not determined by energetics alone. Specificity in approach geometry and steric hinderance are two examples of other factors that help determine the reaction cross section.[1] Another factor, which is important only for concerted reactions, is the requirement that orbital symmetry be conserved along the path from reactants to products.[2] A concerted process is symmetry allowed if the occupied molecular orbitals of the reactants continually maintain their symmetry while undergoing transformation into the occupied molecular orbitals of the products. If the orbital symmetry cannot be maintained, then the reaction is symmetry forbidden and a high reaction barrier is predicted. The symmetry conservation requirement holds only for concerted reactions though, reactions proceeding via a two- or multi-step process are not subject to these rules.

The halogen-halogen reactions have been studied as possible exceptions to the rule.[3-6] The molecular orbital diagram for the reaction $I_2 + F_2 \rightarrow 2IF$ is shown in Fig. 9 of reference 6. Two of the occupied molecular orbitals of the reactants correlate with excited product molecular orbitals, implying that four reactant electrons would have to be excited to give ground state products and therefore this reaction should have a high barrier. While this diagram assumes a C_{2v} transition state, the other transition symmetries consistent with a concerted mechanism are likewise forbidden. A crossed molecular beam study of the reaction of $Br_2 + Cl_2$ showed no evidence of BrCl production up to 30 kcal/mole

collision energy, in support of the forbidden four center reaction theory.[3]

Another study, by Birks, Gabelnick and Johnston,[4] involved the reaction of $I_2 + F_2$ at low pressure and room temperature in a flow apparatus. The chemiluminescence, in the 450-750 mm range, from the reaction was identified as $IF(B^3\Pi_0^+ \rightarrow X^1\Sigma_0^+)$ and $IF(A^3\Pi_1 \rightarrow X^1\Sigma_0^+)$ and was found to be linear in I_2 pressure. A thorough investigation of the F_2 dependence was not done although it was found that the chemiluminescence increased with increasing F_2. Birks et al. offered two mechanisms as possible explanations for their results; an atom recombination or a four center reaction. Both mechanisms would be sufficiently exoergic to allow one electronically excited IF to be formed, but the four center mechanism was favored as being in better agreement with the pressure dependence results. Figure 1 shows a molecular orbital diagram for the case of excited IF production, in either the $B^3\Pi_0^+$ or $A^3\Pi_1$ state, by a four center reaction mechanism. Again, excitation of reactant electrons would be required for this reaction to be allowed. While the reaction of $I_2 + F_2$ is 60 kcal/mole exoergic, this is just enough to excite $IF(B^3\Pi_0^+)$ and is not sufficient to make a four center mechanism symmetry allowed. Engelke, Whitehead and Zare tested the effect of I_2 electronic excitation on IF* production in a crossed beam experiment.[6] I_2 was excited to the $B^3\Pi_{0u}^+$ state ($\pi^* \rightarrow \sigma^*$) using an Ar^+ laser, and IF* production enhancement was found to correlate with I_2^* excitation. The reaction was attributed to a four center reaction mechanism. This is surprising because excitation of a reactant electron from a π^* to a σ^*

orbital would not result in a symmetry allowed four center mechanism. Engelke et al. later began to doubt their results because they could not observe any IF* emission in a repeat of the experiment.[6b]

Another crossed beam study, done by Valentini, Coggiola and Lee[5] of the reaction of F_2 with I_2, ICl and HI again provided evidence against a four center reaction mechanism. In the reaction of I_2 and F_2 a stable trihalogen, I_2F, was observed above a threshold collision energy of 4.0 kcal/mole with IF appearing above a collision energy of 6.1 kcal/mole. The IF product angular distribution did not have the backward-forward symmetry that would be expected if it were produced via a four center reaction mechanism. Similar results were obtained for F_2 + ICl, with a threshold of 6.0 kcal/mole for ClIF and 20.1 kcal/mole for IF production. In the case of F_2 + HI, a threshold of 11 kcal/mole for HIF production was observed but the collision energies used were not high enough to see IF from this reaction. The conclusion reached by Valentini et al. was that there was no four center reaction occuring but that a stable trihalogen was formed and the light observed by Birks et al. was due to subsequent reaction of the trihalogen with a fluorine atom. The IF produced in the crossed beam reactions was attributed to unimolecular decomposition of the highly excited trihalogen intermediates.

In an effort to further understand the mechanism of chemiluminescence production in the halogen-halogen reactions, we have studied the reactions of F_2 with I_2, ICl and Br_2 using the crossed molecular beam method coupled with photon detection. Our results provide a connection between those

of Valentini et al. and Birks et al. and suggest an explanation of the chemiluminescence at low activation energies.

EXPERIMENTAL METHOD

The reactions were studied using a new photon detection crossed molecular beam machine. Schematics of the main chamber are shown in Fig. 2, with the various parts labeled A-Q. The chamber consists of a 0.125 inch wall, 11 inch O.D. stainless steel 304 tube that is 31.5 inches long and divided into two separately pumped (J,J') chambers by a stainless steel foil cone (F). The cone acts as a beam catcher for the supersonic beam source (A-E). A quasi-effusive source (G) crosses the supersonic beam at 90° and the light from the reaction zone (either due to chemiluminescence or laser induced fluorescence) is collected and focussed (L-N) onto a photomultiplier (RCA C31034) or onto the slits of a spectrometer (Jobin Yvon HRP 0.6 M). Laser baffle arms may be attached to flanges I and I'. The pressure is monitored by ion gages (K).

The entire reaction chamber and all other surfaces in the reaction chamber (e.g., the foil cone, source reducer) were painted with 3M 101-C10 Nextel Velvet Black Paint with the exception of a few surfaces that could not be painted (e.g., beam chopper (D), nozzle faces). This paint was chosen because it produces an extremely flat black finish and does not have the usual requirement of a high temperature bakeout.

After a couple coats of paint, the main chamber was heated with heating tapes and pumped for two weeks. The ultimate reaction chamber pressure obtained was 2.2×10^{-7} torr.

The supersonic source used for the F_2 beam has been described in detail elsewhere.[7] Briefly, the source consists of a resistance heated nickle nozzle with a 0.003 inch diameter hole. The nozzle temperatures used in this experiment were between 300 and 700°K, well below the temperature at which the dissociation of fluorine molecules becomes significant. The temperature was monitored using a chromel:alumel thermocouple spot welded to the tip of the nozzle. The collision energy of the F_2-X_2 pairs was varied by changing the seeding ratio of the F_2 in the rare gas carrier (1% F_2/He, 10% F_2/Ar and 7% F_2/He+Ar were used) and the source temperature. The pressure behind the nozzle (approximately 600 torr) was measured using a capacitance manometer. The nozzle (A) was directed at a 0.030 inch diameter skimmer (B), 0.229 inches away and a tuning fork (D) was mounted in front of the skimmer to chop the F_2 beam. The distance from the nozzle to the collision zone was 2.69 inches.

The quasi-effusive source (G) was used for the I_2, ICl and Br_2 beams and is also shown in Fig. 2. The nozzle consists of a 0.25 inch stainless steel tube that has been copper plated and then machined to 0.5 inch diameter. The nozzle can be maintained at a temperature between -140 and +130°C by heat conduction through the copper plating from a liquid N_2 feed tube (M) and resistance heating wires (N) in the copper block/clamp. The clamp and alignment screws (P) held the nozzle

at the proper height and in alignment. A radiation shield (Q) was necessary to prevent photons from the resistance heating wire from reaching the photomultiplier. The temperature is monitored by a copper:constantan thermocouple attached to the nozzle tip. The nozzle hole diameter is 0.015 inch and was directed at a 0.070 inch diameter skimmer (not shown) 0.200 inch from the nozzle. The distance from the nozzle to the collision zone was 0.56 inch.

The I_2, ICl and Br_2 beams were produced as quasi-effusive beams with Mach numbers of 3-4. The beams were run at approximately 1 torr pressure and were not seeded. The I_2 (Mallinckrodt Analytical Reagent, resublimed crystals, 99.9 percent pure) reservoir was kept at approximately 80°C in an oil bath. The stainless steel gas lines were heated, using heating tapes, to 120°C and the nozzle to 125°C to prevent I_2 condensation. The nozzle temperature was not varied. The same conditions were used for Br_2 (Baker Analyzed Reagent, 99.9 percent pure) except that the bromine reservoir was kept at 0°C in an ice bath and a needle valve was used for pressure control. The ICl (Research Organic/Inorganic Chemicals, 99.5 percent pure) reservoir was kept at 0°C in an ice bath and the gas lines and nozzle were left at room temperature The velocity distribution for all the beams, at different temperature and seeding ratios for F_2, were measured using the time-of-flight technique.[8]

The collection optics consists of four lenses and an iris.[9] Basically, the light from the reaction center is collected by the first lens and sent as a parallel beam to the second lens which focusses the

light onto an iris for spatial filtering (light coming from sources other than the collision zone is rejected). The next two lenses focus the light from the iris onto the photocathode or spectrometer slits. All the lenses are synthetic fused silica. The acceptance angle for the collection optics is 0.32 steradians which gives an overall efficiency 1.7 percent at 5000 Å with respect to the total light emitted into 4π radians. The photomultiplier was cooled to dry ice temperatures and had a dark count of 25 cps with a 1700V bias. The output from the photomultiplier went first into an amplifier-discriminater (Pacific Precision Model AD4) then into a gating circuit (Ortec Model 9320) triggered by the F_2 beam chopper. The gating circuit directed the signal into a dual channel scalar (Ortec Model 9315) for automatic background (beam-off) subtraction. Each experiment consisted of seven 200 second counting periods, at seven to ten temperatures for each gas pair. For each run, the room temperature data point was used as a normalization point and was measured first and last in the run. In no case were the two room temperature points in disagreement, within experimental error.

The light from the reactions was measured as a function of collision energy; the $I_2 + F_2$ chemiluminescence was also measured as a function of F_2 pressure and I_2 pressure, the latter being adjusted by changing the heater setting of the reservoir. The $ICl + F_2$ data was checked for interference by any I_2 impurity in the ICl by measuring the chemiluminescence signal with the I_2 reservoir at 0°C. No signal was seen at this low I_2 pressure, so the light observed in the $ICl + F_2$ reaction was just

due to ICl, not I_2. Chemiluminescence from a $Cl_2 + F_2$ reaction would not be allowed energetically in these expeirments. All threshold determinations are the result of two separate experiments.

An attempt was made to obtain a spectrum of the weak chemiluminescence observed. The spectrometer was aligned with the machine[9] and three methods were attempted in recording the spectrum of $I_2 + F_2$, 1 percent in He, at high collision energies, the strongest of the three reactions. First, the photomultiplier was attached to the photographic exit of the spectrometer and the spectral range of 6040Å - 9180Å was scanned having the photomultiplier output recorded by an electrometer connected to a chart recorder. Detecting no spectrum in this way, photon counting using the photomultiplier was tried, again without success. Finally, a camera was attached to the photographic exit and, using Polaroid Land film type 57 high speed, the film was exposed for one hour at 5500Å and 6500Å. No spectrum was observed due to insufficient chemiluminescent yield, although both the $A \rightarrow X$ and $B \rightarrow X$ transitions should have been detected.[4] Since the $I_2 + F_2$ is the strongest reaction, no attempt was made to record the spectrum of the other two reactions.

RESULTS AND ANALYSIS

In each of the three reactions studied, $F_2 + I_2$, ICl and Br_2 chemiluminescence was observed, although the intensity was too low to obtain a spectrum. Without a spectrum, positive identification of the emitting species cannot be made although the possibilities are limited;

only excited diatomics or triatomics can be formed. The photomultiplier used (RCA C31034), can detect light only in the 200-900 nm range, so we cannot detect single quantum vibrational transitions for the diatomic[10] or triatomic[11,12] halogens. There is insufficient collision energy to enable electronic excitation of the reactant diatomic halogens.[9] Because both beams must be running to see signal, emission from hot F_2 can also be excluded. Using the value for the threshold of I_2F (F_2I was not seen) and ClIF measured by Valentini et al., the formation of an electronically or highly vibrationally excited trihalogen is likewise energetically inaccessible. We are, therefore, limited to considering the formation of a highly vibrationally excited or electronically excited diatomic in the reaction. The multiple quantum vibrational transition required to produce light in the 200-900 nm range would not only be very improbable, but would also have such a long lifetime that we would be unable to see it in our experimental arrangement. Therefore, the light must be coming from an electronically excited diatomic reaction product like IF^*, ClF^* or BrF^*.

The chemiluminescence of the $I_2 + F_2$ reaction was measured as a function of I_2 pressure (Fig. 3) and F_2 pressure (Fig. 4). The signal was linear with respect to I_2 pressure, with the counts going to zero as the I_2 pressure goes to zero. The signal was likewise linear in F_2 pressure although the line does not go through zero as the F_2 pressure goes to zero. The reason for the non-zero intercept is that the F_2 source is a supersonic source and as the pressure behind the nozzle is reduced, the source eventually undergoes a transition from supersonic

flow to effusive flow.[13] In this transition region, the beam intensity in the collision zone is no longer proportional to nozzle pressure.

The linearity of the signal with respect to both I_2 and F_2 pressure, coupled with the fact that the signal is correlated with the chopped F_2 beam, means that the reaction is the result of a single bimolecular collision between I_2 and the F_2 beam. This excludes several possibilities, specifically:

1) Any mechanism that would require background F_2 or F atoms. Because the signal is correlated with the chopped F_2 beam, we know that the chemiluminescence is the result of a reaction of the beam F_2 molecules. If a secondary reaction of products with background F or F_2 was also required, the chemiluminescence would have a quadratic dependence on F_2 pressure.
2) Any mechanism requiring more than one collision in the interaction region. This would give a higher than linear dependence on either I_2 or F_2 pressure.
3) Any mechanism involving I atoms. A reaction of F_2 with I atoms is not sufficiently exoergic to produce electronically excited IF, the exclusion of possibilities (1) and (2) above removes any atom recombination mechanism.
4) Any mechanism involving I_2 or F_2 dimers. This would give a quadratic pressure dependence on I_2 or F_2 pressure.

The chemiliminescent reaction is indeed the result of a collision between one I_2 and one F_2 molecule. A four center reaction cannot, therefore,

be excluded. A pressure dependence study of the other two reactions was not made.

The chemiluminescence signal was measured as a function of collison energy for all three reactions. The velocity distribution of the three quasi-effusive beams (I_2, Br_2 and ICl) and of the supersonic fluorine beams (1 percent/He, 10 percent/Ar, 7 percent/Ar and He, each at the three nozzle temperatures) were converted to relative velocity distributions using a computer program described elsewhere.[9] This program takes the angular spread (and therefore the collision angle distribution) into account, as well, in calculating the relative velocity distribution. The distribution for the nozzle temperature at which data were recorded was interpolated from the distributions measured at three temperatures. A second program[9] uses a functional form of the reaction cross section to calculate the chemiluminescence signal from the relative velocity distribution. The cross section function is then varied until the calculated signal fits the experimental signal, within experimental error. A cross section weighted mean of the collision energy distribution can then be calculated.

In fitting the threshold data for $I_2 + F_2$, a cross section of the form $\sigma = C(1 - (E_T/E))^{.5}$ was used where E_T is the threshold energy, E is the collision energy and C is a normalization constant. The result is shown in Fig. 5 where the collision energy axis represents the cross section weighted mean collision energy. E_T is 3.4 kcal/mole and is the threshold collision energy; this does not include internal energy. The amount of energy in the internal degrees of freedom can

be calculated assuming thermal equilibrium. In both the supersonic and quasi-effusive molecular beams there is a certain amount of cooling in the internal degrees of freedom as well as in the translational degree of freedom. Because vibrational spacings are generally large with respect to kT over our temperature range (300-700°K), little vibration to translation energy transfer occurs and the vibrational temperature should remain at nozzle temperature. Rotational spacings are generally small and energy transfer is efficient so the rotational temperature and translational temperature are close to equal. The translational temperature T_o, can be calculated from

$$T_o/T_n = (1 + (RM^2/2C_V))^{-1}$$

where M is the Mach number and T_n is the nozzle temperature.[14] Table I lists the temperatures and internal energy associated with vibration and rotation, along with the Mach numbers, for the beams used in this experiment. For the threshold in the $I_2 + F_2$ reaction, the internal energy was 0.8 kcal/mole so the total threshold energy was 4.2 kcal/mole.

We can make no distinction, in this experiment, between the effects of translational and internal energy. We are assuming that the three forms of energy available are equally effective in promoting the reaction, although this assumption is not necessarily true in general.[15,16] The thresholds all occurred near the room temperature end of the collision energy ranges for the various fluorine mixtures,

so there should be little contribution from the internal energy of F_2 molecules in the supersonic beam. Most of the internal energy comes from the quasi-effusive source and, again, may or may not contribute equally with translational energy.

The higher energy data for $I_2 + F_2$ was fit using a cross section fo the form $\sigma = C((E/E_T) - 1)^A$. While the threshold cross section function is derived from scattering theory,[17] this higher energy form has no physical significance and was only used to derive a cross section weighted mean collision energy. The $I_2 + F_2$ data for the entire collision energy range studied is shown in Fig. 6. The parameters used in fitting the data were $E_T = 1.0$, $A = 4.95$.

The threshold cross section function was used again in the analysis of the $ICl + F_2$ data, shown in Fig. 7. The threshold collision energy, E_T, is. 5.1 kcal/mole, the internal energy at the temperature corresponding to that point is 0.8 kcal/mole bringing the threshold energy for the reaction 5.9 kcal/mole. The $ICl + F_2$ reaction was not studied at higher energies.

The data for the $Br_2 + F_2$ reaction, shown in Fig. 8, presented special problems in analysis. Looking at the $I_2 + F_2$ data in Fig. 6, as the collision energy increases past approximately 5 kcal/mole the chemiluminescence starts to level off. The same phenomenon was observed by Valentini et al.[5] for I_2F. In the case of $Br_2 + F_2$, the leveling-off and decrease in chemiluminescence with increasing collision energy occurs very shortly after the reaction threshold. The experimental points may be fit to a cross section function, as before, but the cross

weighted mean collision energy calculated from such a fit does not provide a linear translational energy scale for a graph. On the low energy side of the chemiluminescence curve, the high energy tail of the collision energy distribution is given more weight while the opposite is true of the high energy part of the chemiluminescence curve. For this reason, the translational energy scale for the Br_2 + F_2 data was determined in two steps. The threshold, low energy part of the curve was placed, as for the other curves, on a cross section weighted mean collision energy axis. The cross section function used was a quadratic equation with no physical signficance. The threshold collision energy is 10.7 kcal/mole, the internal energy is 0.6 kcal/mole for a total threshold energy of 11.3 kcal/mole for Br_2 + F_2. The rest of the collision energy axis was taken from the high energy I_2 + F_2 results because collisions of I_2 with 1% F_2/He have a collision energy distribution almost identical to that of Br_2 with 1% F_2/He, which was the mixture used to obtain this data. Therefore, while the energies near the threshold of the reactions represent cross section weighted mean collision energies for the reaction of Br_2 with F_2, the rest of the energy axis does not have the true mean energy for this reaction, although the difference is not large.

To summarize the results, light was seen in each of the three reactions and is attributed to the formation of electronically excited diatomic products, IF^*, ClF^* and BrF^*. The thresholds for the chemiluminescent reactions are 4.2 kcal/mole for I_2 + F_2, 5.9 kcal/mole for ICl + F_2 and 11.3 kcal/mole for Br_2 + F_2. In the case of I_2 + F_2

and $Br_2 + F_2$, a leveling off or actual decrease in chemiluminescence with increasing collision energy was observed.

DISCUSSION

While our data on the pressure dependence of the chemiluminescence is consistent with a bimolecular reaction, the energy dependence of the light production follows closely with that of the production of trihalogen molecules indicating that another mechanism, other than a four center reaction, may be responsible. The energetics for the three reactions are shown in Fig. 9, included are the energy levels for the stable trihalogens observed by Valentini et al. In the case of $I_2 + F_2$, our chemiluminescence threshold of 4.2 kcal/mole agrees very well with Valentini's threshold of 4.0 kcal/mole for I_2F formation. Another similarity between our chemiluminescence results and Valentini's trihalogen results is the leveling off of the chemiluminescence after approximately 6 kcal/mole collision energy, which Valentini attributed to the unimolecular decomposition of I_2F.

The agreement between our results and Valentini's suggests that the mechanism shown in Fig. 10 involving the formation of the trihalogen, I_2F, and subsequent reaction of the end iodine with the departing fluorine atom may be responsible for the light we see. The pressure dependence studies restrict the chemiluminescent reaction to a single collision mechanism, so we propose that the two step reaction of

$I_2 + F_2 \rightarrow I_2F + F$, $I_2F + F \rightarrow IF^* + IF$ may occur in a "single collision" between F_2 and I_2. In the vast majority of collisions occurring above threshold in the collision zone, the I_2 and F_2 would react to form I_2F and F, the products would separate and be detected in the experiment by Valentini et al. but not in this experiment. In a few of the collisions, the I_2 and F_2 react to form I_2F but the F atom does not escape before a secondary encounter occurs giving the second step, $I_2F + F \rightarrow IF^* + IF$ and we detect the light from the IF^*. We have, then, a branched reaction--the major branch gives I_2F and the minor branch results in electronically excited IF. This mechanism brings up several questions: why couldn't Valentini et al. see the minor branch, how does this differ from a four center reaction, does this explain the results obtained by Birks et al.[21] and does the same mechanism hold for the other reactions studied?

Using the following equation:

$$\sigma = S/(v\, N_{I_2}\, N_{F_2})$$

we can calculate, from our data, the cross section for the production of IF^* from $I_2 + F_2$. In the equation, v is the relative velocity of the products and is 1.38×10^5 cm/sec at 15 kcal/mole collision energy. S is the total chemiluminescence signal, which is 1.19×10^7 photons/sec at 15 kcal/mole (corrected for loss due to optics transmission, f number of the collecting optics, photomultiplier efficiency and loss of IF^* due to diffusion out of the collision zone before emission).[18] Using

$N_{I_2} \cong 1.4 \times 10^{10}$ molecules/cc, we calculate a cross section, σ, of $0.002 Å^2$. This cross section is much smaller than the $1\text{-}2 Å^2$ cross section that Valentini estimated for the major reaction branch. About one in one thousand collisions results in the fluorine atom having a secondary encounter with the I_2F and producing IF^*. A $0.002 Å^2$ reaction cross section would have been too small for Valentini et al. to see, especially because there was IF production from unimolecular decomposition of highly excited I_2F as well as from fragmentation of I_2F in the detector ionizer. There are two factors that greatly enhance our detection sensitivity over that of Valentini's; photon background signal in this case is much easier to reduce than particle background signal and we were collecting a sizeable fraction of total chemiluminescence while Valentini was looking at the differential cross section at high resolution. It is not surprising, then, that Valentini did not see the symmetric IF production that would be expected for the minor reaction branch.

The factor that separates the mechanism we are proposing from a four center reaction mechanism is the stability of the trihalogen formed. As pointed out earlier, the symmetry rules that forbid four center reactions require that the reaction be concerted--that the old bonds be broken at the same time as the new bonds are made. In the mechanism we propose, a stable trihalogen is formed first and, in most collisions, it is the final product. In the other minor collision events, the stability of the trihalogen still drives the reaction to begin with, then a second reaction occurs, precluding a separation of

the products of the first reaction. Because we cannot measure angular distributions and the minor reaction path was too small to be seen by Valentini, we can make no estimate of the lifetime of the $I_2F...F$ complex and do not know if it lasts as long as one rotational period, although we expect it to be shorter.

The results presented there provide greater support for the suggestion[5] that most of the chemiluminescence seen by Birks et al. is a result of the reaction of I_2F with F. In our study of the reaction, the light was produced from a single collision and was a low probability event. In the flow system used by Birks, many collisions will take place so the I_2F formed is not restricted to reacting with its "own" fluorine atom. Given the following elementary reactions:

$$I_2 + F_2 \xrightarrow{k_1} I_2F + F \tag{1}$$

$$I_2F + F \xrightarrow{k_2} IF^* + IF \tag{2}$$

$$IF^* \xrightarrow{k_r} IF + h\nu \tag{3}$$

$$IF^* + M \xrightarrow{k_q} IF + M \tag{4}$$

$$I_2 + F \xrightarrow{k_5} IF + I \tag{5}$$

$$I + F_2 \xrightarrow{k_6} IF + F \tag{6}$$

and assuming steady state for I and F atoms we get

$$[IF^*] = k_1[I_2]\ [F_2]/(k_r + k_Q[M]) \tag{7}$$

This is the same expression for the excited IF concentration as is obtained assuming a four center reaction and accurately describes Birk's data.

While it is impossible to make such a clear case for the reactions of ICl and Br_2 with F_2, the data we obtained is consistent with this mechanism. For ICl + F_2, we obtained a threshold of 5.9 kcal/mole while Valentini saw a threshold of 6.0 kcal/mole for ClIF production. The agreement is very good but, looking at Fig. 9, a four center reaction producing IF(A) + ClF would have nearly the same endoergicity. The spectrum of ClF(A→X) has not yet been observed[10] although it is expected to be higher in energy and would not be helpful in distinguishing a four center threshold from a ClIF threshold. While Valentini observed the leveling off of ClIF production with increasing collision energy, our data does not extend to a high enough energy to check for the same effect in the chemiluminescence.

Valentini was unable to see formation of Br_2F, although that may be a detection sensitivity problem rather than an indication that Br_2F is not formed. If the mechanism works for Br_2 + F_2 as well, then the rapid leveling off and decrease of chemiluminescence indicates that Br_2F does not have as high a stability as I_2F and ClIF have. Our

reaction threshold for $Br_2 + F_2$ was 11.3 kcal/mole. Figure 9 shows the levels for BrF(A) + BrF and BrF(B) + BrF production to be 13.8 and 16.3 kcal/mole, respectively. At first glance it would seem that we are not observing BrF^* emission, that it would be energetically inaccessible. The 13.8 kcal/mole level indicated for BrF(A) was derived from only a few A→X transitions that, most likely, did not even form a complete progression.[9,20] Recent work[21] on the BrF(B→X) transition has provided new information on the dissociation energy for BrF that would be inconsistent with the previous assignments for the BrF(A→X) lines, making the 13.8 kcal/mole level even more suspect. Table II lists the ν_{oo} energies (in kcal/mole) for the B→X and A→X transitions of several dihalogens. The values in parentheses are uncertain. From the trends in the iodine and bromine series, it is certainly possible that the BrF(A) level could be 3 kcal/mole lower than the 13.8 kcal/mole above $Br_2 + F_2$. It would be helpful to have more spectroscopic data about both the BrF(A) and ClF(A) states.

When the information on ClF(A→X) transition becomes available it is likely that the reaction of ICl with F_2 could provide information on whether the newly formed ClF or the IF fragment is electronically excited. If the ClF(A→X) and IF(A→X) transition could be separated using a spectrometer, then appearance of light from only one molecule, at a collision energy high enough to allow excitation of either, would answer the question. If IF + ClF(A) lies at least 1 kcal/mole above ClIF + F, then we know that IF(A) is formed, but in the absence of any formation on ClF(A) we can draw no conclusions about which half of the F-X-Y-F is formed in an electronically excited state.

LASER ENHANCEMENT

We attempted to repeat the study done by Engelke et al.[6] in which laser excitation of I_2 enhanced IF^* production. An Ar^+ laser (514 nm) was aligned[9] to excite I_2^* molecules in the collision zone. A pure supersonic F_2 beam was used because argon (in the 10% F_2/Ar mixture) quenched the excited I_2 molecules. The light coming from the reaction zone was dispersed using the spectrometer and recorded using the photomultiplier connected through an electrometer to a chart recorder. A laser power of 3.0 watts was used to record the spectra of I_2^* fluorescence without and then with the F_2 beam on.

Engelke et al. found that 1 in 5 quenched I_2^* molecules formed IF^*, although a value of 1×10^{-3} sec was used as the IF^* lifetime, which is at least 100 times too long. We observed quenching of the I_2 lines ($v' = 43 \rightarrow v''$ progression). We did not observe any emission from IF^* to the blue of 514 nm and conclude that no laser enhancement, at least to the extent reported by Engelke et al., occurs.

If the experimental conditions used by Engelke et al. were not truely single collision conditions, then it is conceivable that their results are due to the same mechanism as Birks et al. That is, I_2F could be formed on one collision then react to form IF^* in a second collision. Exciting the I_2 molecules would increase the number of I atoms through predissociation which would then liberate more F atoms via $I + F_2 \rightarrow IF + F$. Another possibility is that the production of I_2F is enhanced by vibrational excitation of I_2.

The drop in total I_2 fluorescence due to a pure F_2 beam and a pure Ar beam was also measured to determine the quenching cross section

of I_2^* by F_2. A value of 1.8 ± 3.8 $Å^2$ for F_2 was obtained relative to the literature value of 5.11 $Å^2$ for Ar.[22] The uncertainty in the cross section value is largely due to ion gage filament degradation during flux measurements.

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Table I. Internal Energies of the Beam Gases

Beam	Mach Number	Vibration Temperature	Vibration Energy	Rotation Temperature	Rotation Energy
I_2	4.22	397°K	.503	86.9°K	.17
ICl	3.63	397	.358	109.2	.22
Br_2	4.06	397	.410	92.1	.18
10 F_2/Ar, 300°K	15.04	300	.034	6.64	.01
10 F_2/Ar, 700°K	11.78	700	.449	24.5	.05
7 F_2/He+Ar, 300°K	13.09	300	.034	8.46	.02
7 F_2/He+Ar, 692°K	8.64	692	.445	43.6	.08
1 F_2/He, 300°K	18.27	300	.034	4.53	.01
1 F_2/He, 694°K	10.72	694	.449	29.1	.06

Table II. Energy Levels of the v' = 0 Level of the B and A States of Diatomic Halogen Molecules.

	ν_{oo}(kcal/mole)[10]	
	B→X	A→X
I_2	45.0	(33.7)
IBr	46.0	35.1
ICl	49.4	39.0
IF	54.2	44.6
Br_2	45.2	39.5
BrCl	47.8	---
BrF	51.8	(49.3)
Cl_2	50.9	(49.9)
ClF	53.8	---
F_2	Continuum	Continuum

FIGURE CAPTIONS

Fig. 1. Molecular orbital correlation diagram for a C_{2v} transition state four center reaction of $I_2 + F_2 \rightarrow IF^* + IF$.

Fig. 2. (a) Side view assembly cross section of the laser fluorescence - chemiluminescence crossed molecular beam machine. (b) Top view. The labeled parts are (A) supersonic source nozzle; (B) skimmer; (C) beam flag; (D) tuning fork chopper; (E) source differential pumping wall; (F) beam catcher; (G) secondary source; (H) flange for optics; (H) flange for electrical feed-through; (I) flanges for laser baffle arms; (J) diffusion pump ports; (K) ion gage ports: (L) quartz plate sealing the optics system from the machine vacuum; (M) liquid nitrogen feed tube; (N) holes in the copper block/clamp for alumina rods containing nichrome heating wire; (P) 3-point alignment assembly; (Q) black radiation shield.

Fig. 3. I_2 pressure dependence of the chemiluminescence. The intensity scale is in arbitrary units. The pressure scale is the pressure of the chemiluminescence machine main chamber as measured by an ionization gauge.

Fig. 4. F_2 pressure dependence of the chemiluminescence. The intensity scale is in arbitrary units. The pressure, $P(F_2)$, is the pressure, in torr, behind the nozzle.

Fig. 5. Energy dependence near threshold for the reaction $I_2 + F_2$. ● represent the data points, the curve is a fit to the data

given by $\sigma = C(1-(3.4/E))^{.5}$. The intensity scale is in arbitrary units. The collision energy scale is a cross section weighted mean collision energy (see text).

Fig. 6. Energy dependence for the reaction of $I_2 + F_2$. The scales are determined in the same way as for Fig. 5. ● represent the data points.

Fig. 7. Energy dependence near threshold for the reaction $ICl + F_2$. ● represent the data points, the curve is a fit to the data given by $\sigma = C(1-(5.1/E))^{.5}$. The scales are calculated as for Fig. 5.

Fig. 8. Energy dependence for the reaction of $Br_2 + F_2$. The dots represents the data points, the curve a fit to the data by a quadratic equation (see text). The intensity scale is in arbitrary units, the energy scale is described in the text.

Fig. 9. Schematic energy diagram for the reactions $F_2 + I_2$, ICl, Br_2. The reactants are taken to be at zero energy, the energy scale is in kcal/mole. The energy levels for I_2F and ClIF are taken from reference 5. (B) and (A) refer to the $B(^3\Pi_0^+)$ and $A(^3\Pi_1)$ excited electronic states.

Fig. 10. Schematic of the mechanism proposed to account for the observation of chemiluminescent bimolecular halogen-halogen reactions. The majority of the reactants follow branch 1 wherein a stable trihalogen is formed and an F atom leaves. One out of a thousand collisions follows branch 2 where a

secondary, reactive encounter of the F atoms with the tri-halogen results in the formation of two interhalogens, one being electronically excited.

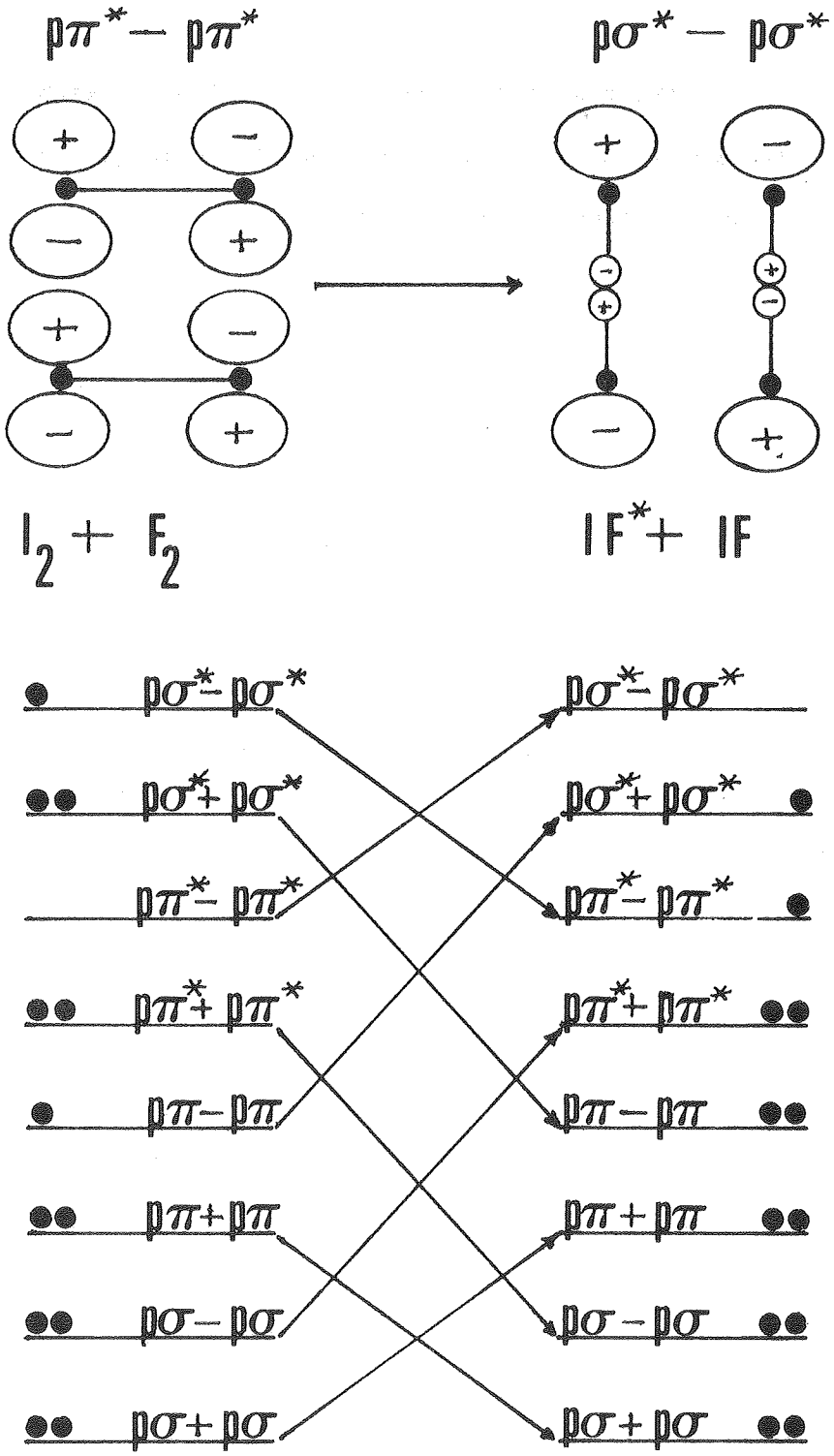

Fig. 1 XBL 805-9623

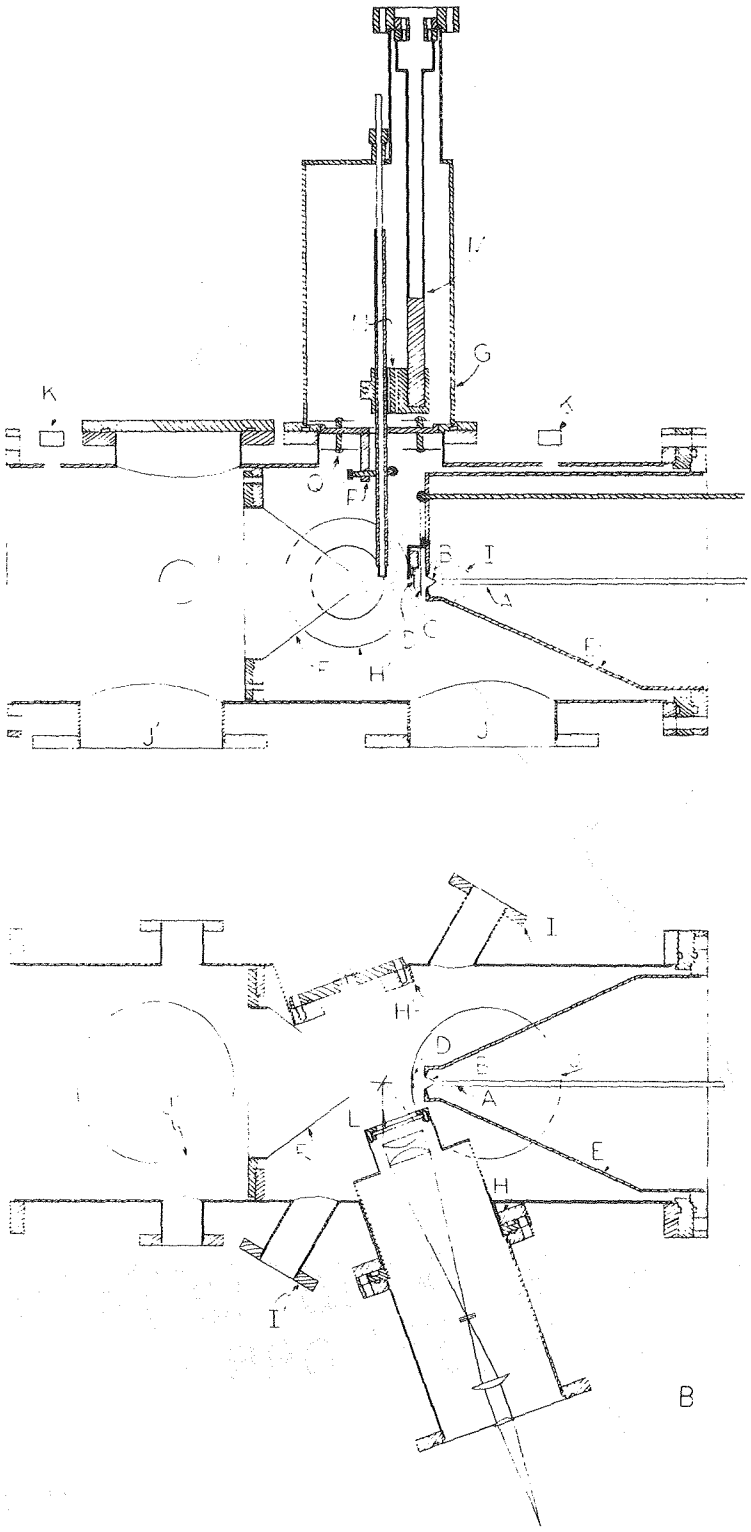

Fig. 2

XBL 805-9620

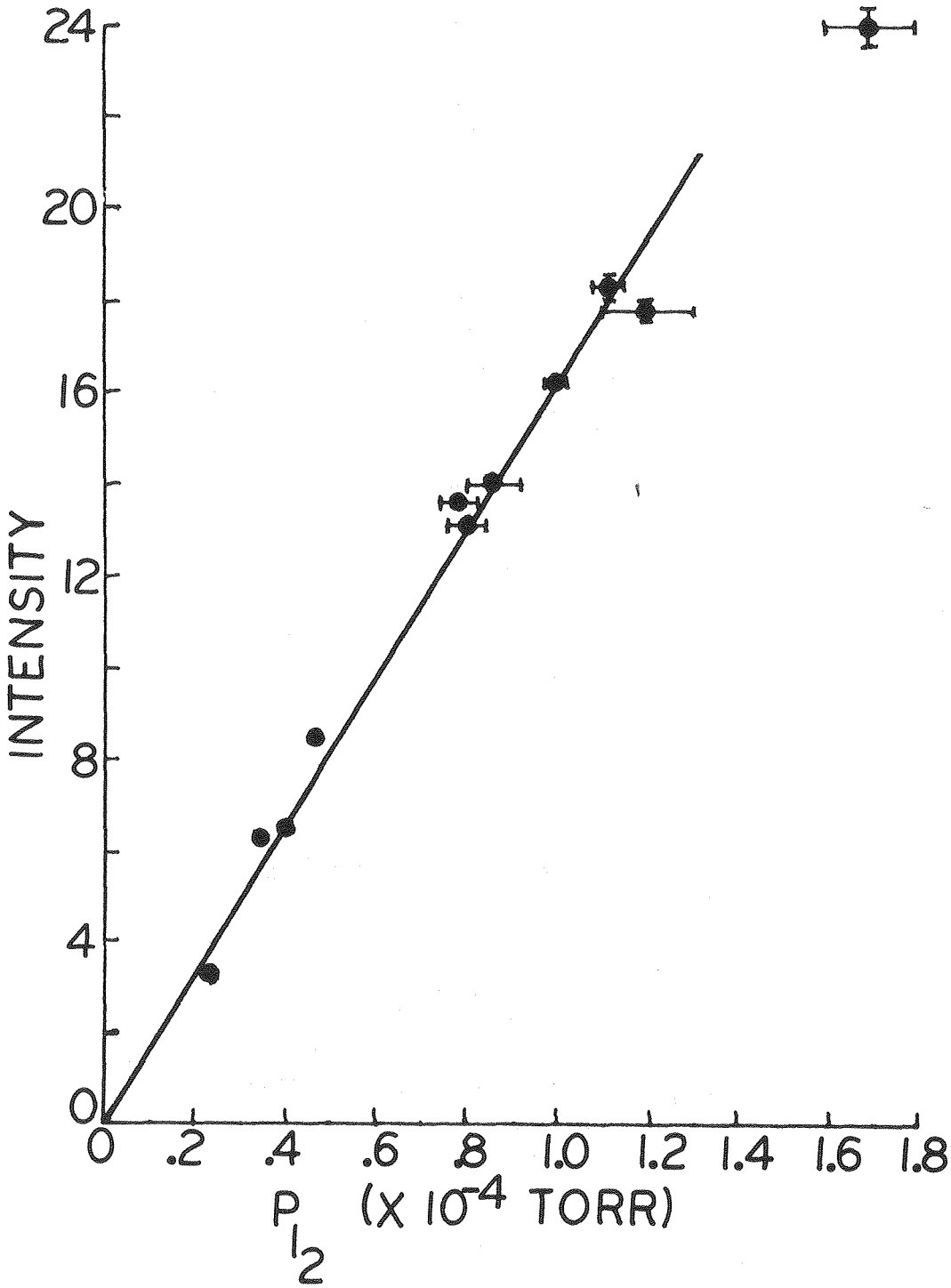

Fig. 3

XBL 805-9624

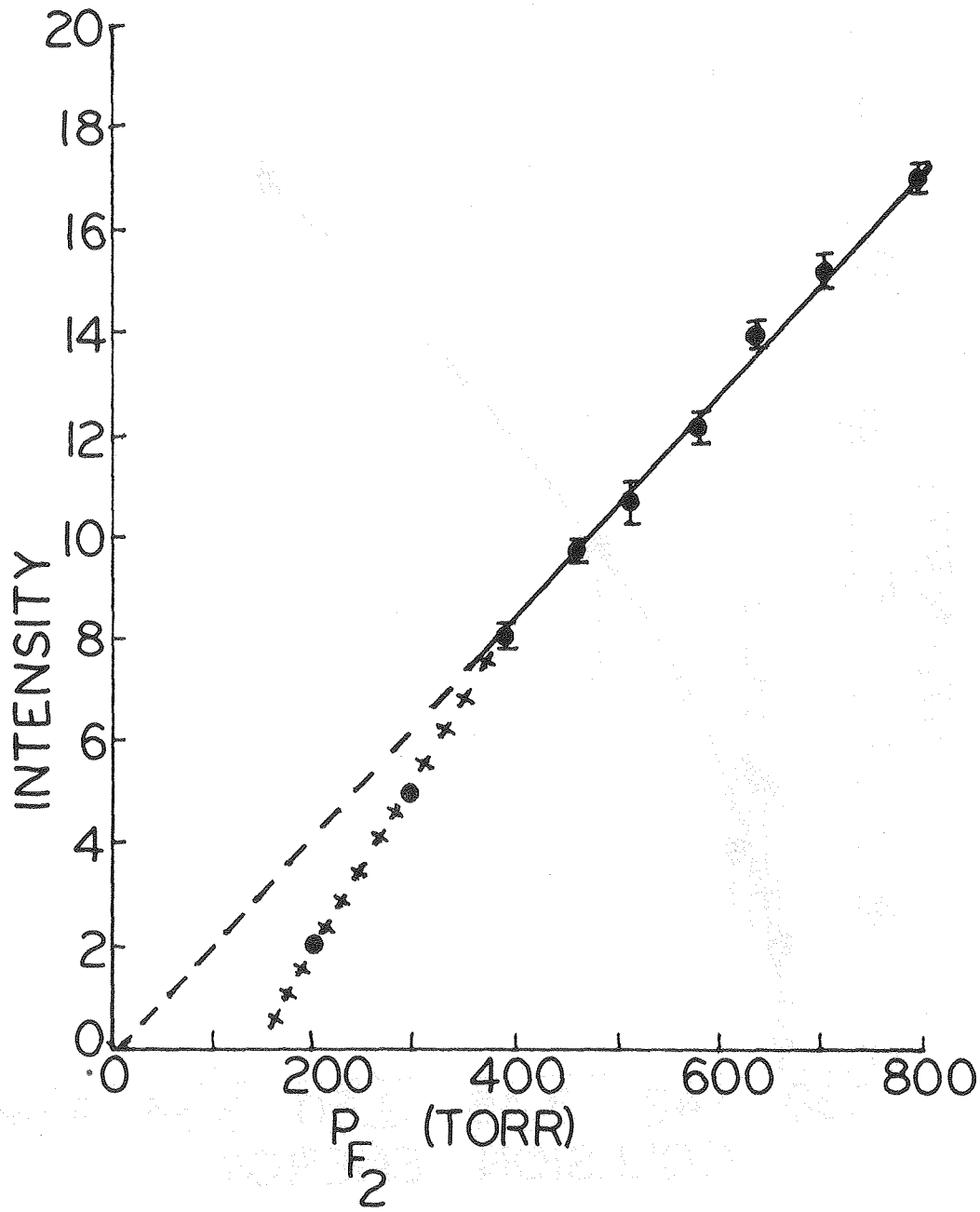

Fig. 4

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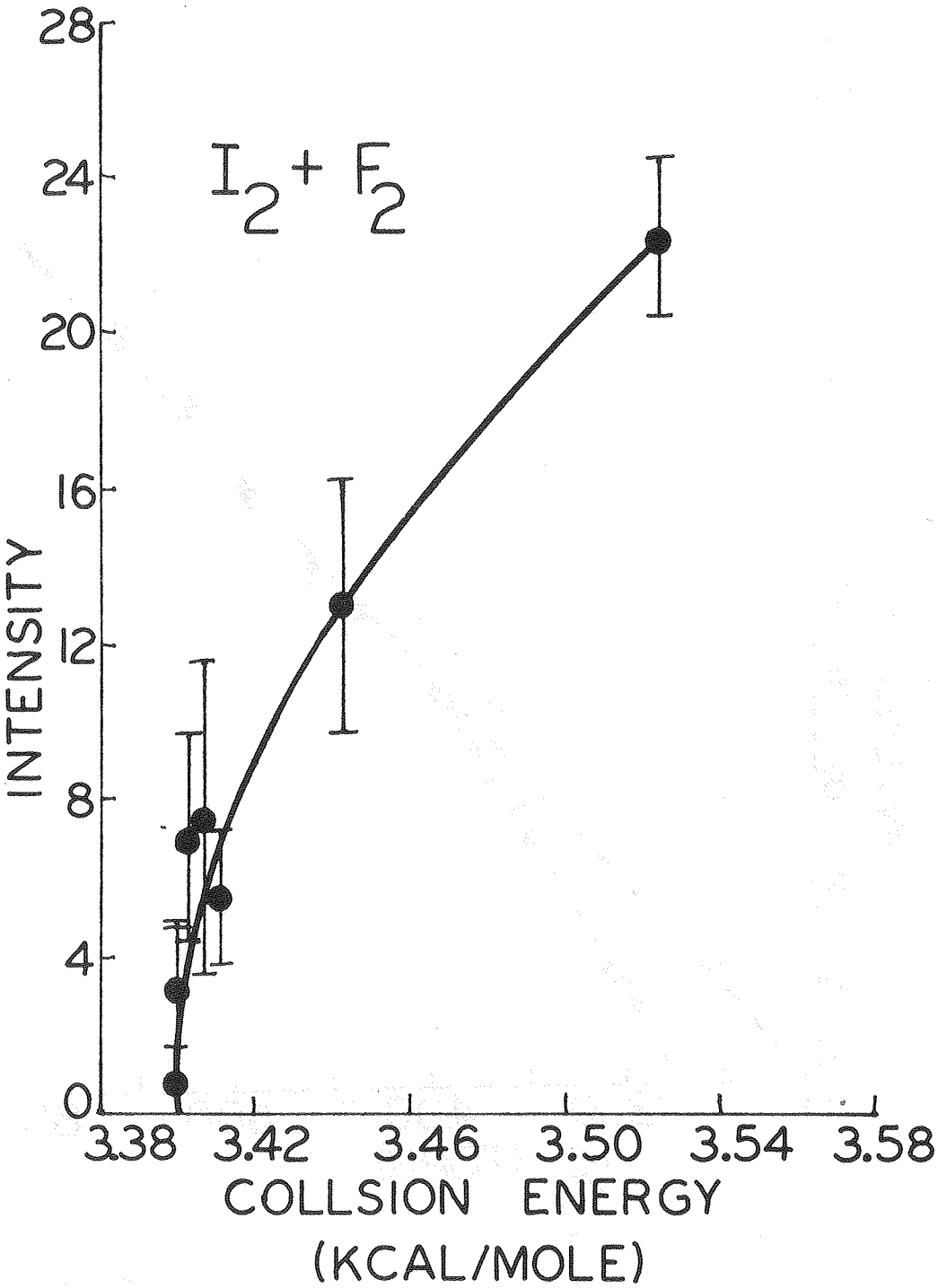

Fig. 5

XBL 805-9627

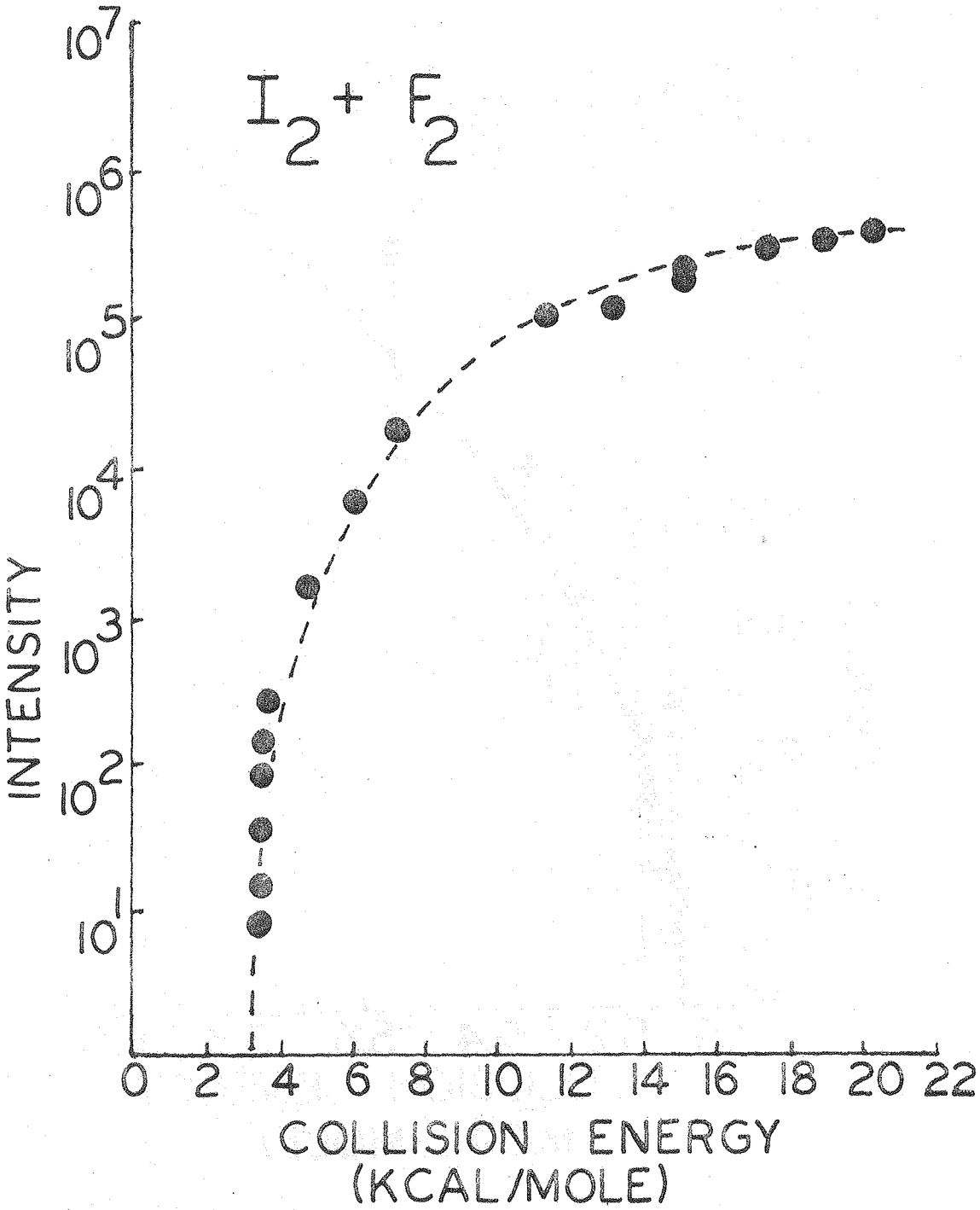

Fig. 6

XBL 805-9628

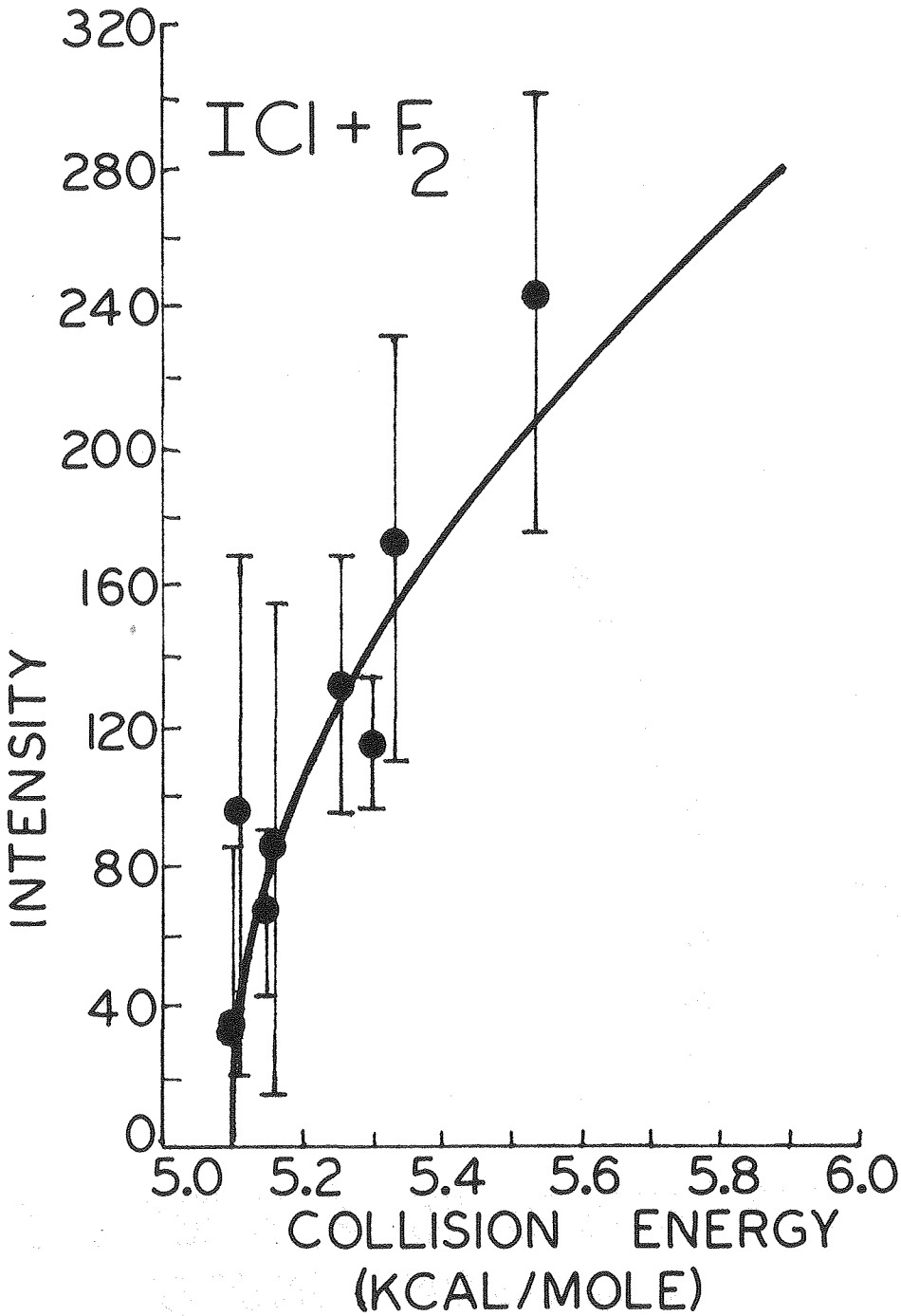

Fig. 7 XBL 805-9625

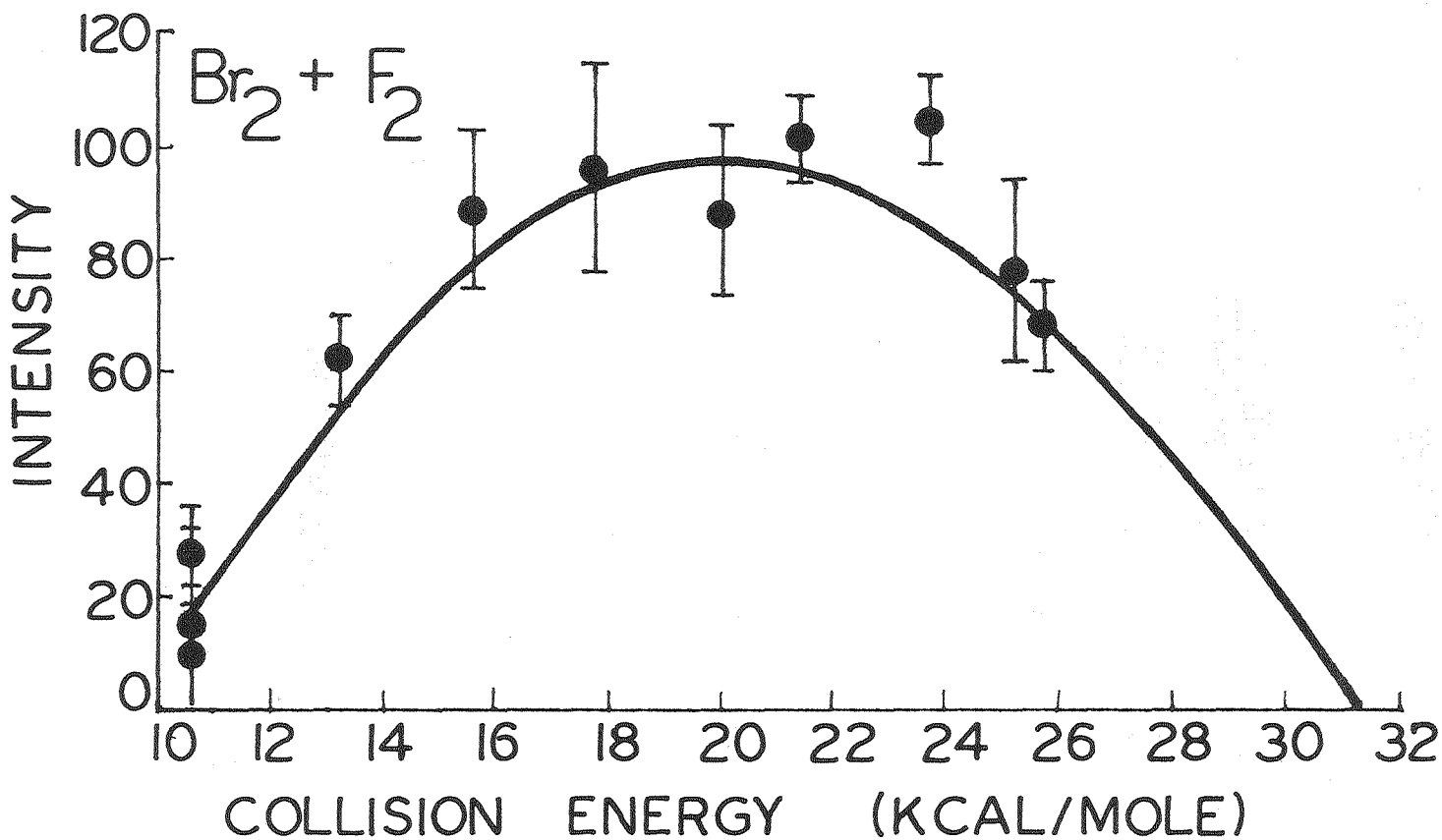

Fig. 8

XBL 805-9621

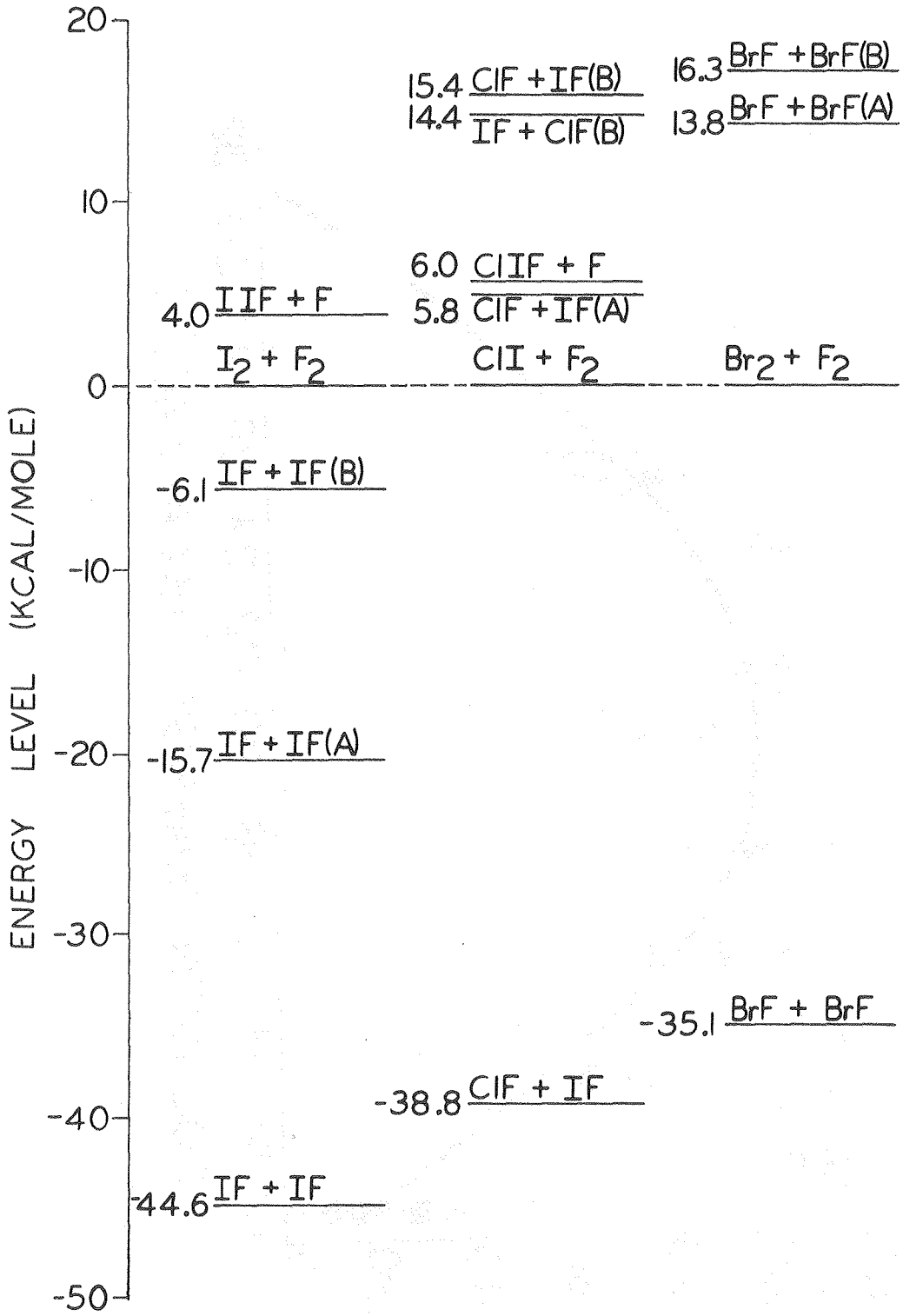

Fig. 9

XBL 805-9619

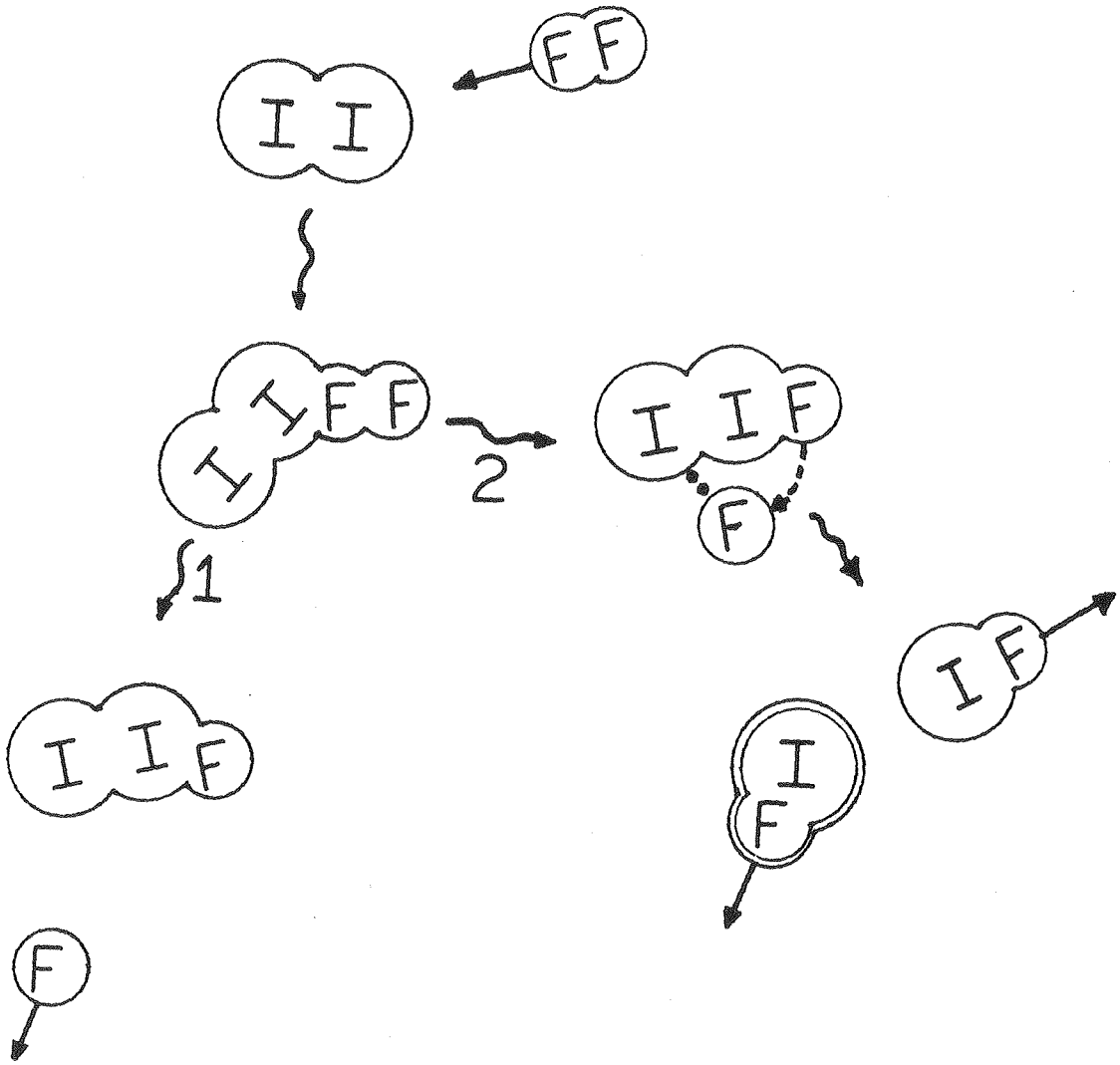

Fig. 10

XBL 805-9626